Nanometer-Size Conducting and Insulating Molecular Devices

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Using quantum ab initio techniques—a theoretical "microscope"—we demonstrate that molecules of nanometer sizes can be characterized as low and high impedance devices, needed as building blocks in the field of molecular electronics. Small alkanes and polyynes chains with σ and π bonding, respectively, yield a high-low impedance relation of 2 orders of magnitude at 1-nm length and of 3 orders of magnitude at 1.3-nm length. For these small chains, it is concluded that no simple trends of conductance versus length can be determined. We also successfully test our methods against a recent precise experiment.

Introduction

Molecular electronics, or moletronics for short, is the ultimate frontier in the use of matter for information processing. It is the technology which aims to use small molecules as electronic devices. In the search for smaller electronic devices, we are faced with the task of constructing them using a minimum number of atoms. Present electronic devices require the use of more than one billion atoms. Undoubtedly, the best choice of material is silicon because of its electrical properties and, more importantly, the ability to tailor it using present lithographic technology. Since materials with more than one billion atoms can be considered bulk, the process of miniaturization is practically a process of scaling down, limited only by the ability to address smaller sizes (feature size) of the bulk material. Modern processes of miniaturization cannot be continued to levels where only a few atoms are to be used, since bulk properties are not observed at such dimensions. For instance, feature sizes in the nanometer and subnanometer ranges will require using less than 50 atoms; existing semiconductor materials are definitely not the best choice at such small sizes. Fortunately, carbon-based materials provide an alternative for the construction of electronic devices using very few atoms.[1−19] Organic molecules, for instance, can be made small and can transfer electrons with similar or even better electrical characteristics than those in electronic devices. Although technical difficulties associated with the use of small molecules are similar to those encountered with modern semiconductor devices, for example, the interconnection and addressing problems, the use of small organic molecules allows us to propose other scenarios and architectures where those problems can be overcome.[3,4,19−21] One of the requirements for the use of new materials for electronic devices is that they should be able to provide a large range of impedances with excellent tolerances; families of molecules with precisely determined high and low impedances are needed for the design of complex devices. We focus our study on the current−voltage (I−V) characteristics of small alkane and polyyne chains because of the attractiveness of these

systems in single molecule experiments and because they are typical σ and π systems for which a qualitative high and low impedance, respectively, can be assumed; however, the required quantitative evaluation is a difficult task. We choose to connect these molecules through thio clips to Pd atoms and then to Pd bulk contacts. Pd, among a few other metals, showed the best electrical coupling to S in a study,[22] which is in agreement with a recent experimental report indicating that Pd is a better contact than Au.[23]

Methodology

The quantitative evaluation of molecular impedances to compare with experiments on single molecules requires a precise representation of the molecule and its connection to the metallic atoms. Such calculations are necessary because of the almost practical impossibility of measuring single molecules. The molecules for which experimental I−V characteristics are to be measured need to be connected to macroscopic tips. Although such a connection is not necessary in the actual molecular circuits, since one molecular circuit can be connected to other molecular circuits through chemical bonds, there is a need to compare I−V results to the very few experiments that aim to get single molecule measurements. This necessitates the inclusion of a mesoscopic interface to the macroscopic world into the calculations. The problem still can be separated into two serial problems: the macroscopic−mesoscopic contact, which can be studied by the standard mesoscopic methods, for which the reader is referred to the standard literature,[24] and the molecule augmented with the nearest metal atoms binding to the molecule, which determines the extended molecule and thus the main properties of the system. A careful selection and application of rigorous quantum chemistry techniques is essential for the study of the electrical characteristics of the extended molecule. Several problems related to the calculation of I−V characteristics are the following: (1) Hartree−Fock techniques yield unreliable results because of neglecting the electron correlation. (2) Density functional techniques that use local approximations for the exchange-correlation functional provide results that ignore several chemical features of the molecule.[25] (3) Semiempirical techniques use strong simplifications. (4) The representation of the metal by a jellium model totally ignores the local nature of the molecule−metal interface. (5) The

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geometric parameters of the extended system are unknown even for those systems treated experimentally; since the $I-V$ characteristics strongly depend on the geometry of the systems, a consistent method is needed to also determine the correct geometric parameters of the molecules and their contacts. In view of all these problems, we have developed a combined density functional theory–Green function (DFT-GF) approach that overcomes all these problems and obtains the current–voltage characteristics of single molecules attached to two metal contacts using two interactive steps. First, density functional theory (DFT) is used to obtain geometrical and electronic information of an extended molecule consisting of the molecule under study (isolated molecule) attached to few metallic atoms of the same kind as those of the bulk metal contacts (two Pd atoms per molecule are used in this study). This combination of bulk and discrete atoms defines the contact. Notice that the discrete atoms are not representing the continuum. Then, the Hamiltonian describing the extended system is used within a scattering formalism, on the basis of Green function theory, to obtain electron transport properties.[2,7,24,26–28] Our approach, which has been strongly improved from its earlier version in ref 7, is fully explained in refs 17 and 29. The effect of several substituents on π-conjugated oligomer systems and their properties as memory devices were also studied,[2] yielding results in good agreement with experimental findings.[5] More recently, a study of the conduction through a phenyl ring with two different clips and six different metals was performed[22] and was also found to be in agreement with the available experimental findings.[30] Other problems related to electron conduction in mesoscopic systems are of less importance in molecular systems like, for instance, (1) inelastic scattering processes at molecular vibrations (including electron relaxation during the transport) since at the molecular level, electronic-vibrational coupling is negligible in single molecules as indicated by recent experiments.[31] However, low-energy torsional motion, which practically modifies the geometry of the molecule, can be considered exactly by performing the calculation at the corresponding geometries. (2) The interaction with the electron gas of the electrodes (mirror charge effects) is considered at the molecular level with the atomistic nature of the interface, where the molecule is assumed to be bonded to the metallic contacts. (3) The simultaneous conduction of two or more electrons through the molecule is considered with the multichannel approach to calculating the transmission function. In addition, care must be taken when calculating electron transport in molecules; not to confuse them with solid-state devices where electron transport is considered a continuum process; the electron transfer in a molecule is a discrete process. Thus, we modified our procedure to consider that only one electron can be transmitted at a time through a molecule by considering that all molecular orbitals make a single conduction channel.

Kohn–Sham Hamiltonians, H_{KS}, and overlap matrixes, S, are obtained from DFT geometry optimizations at the B3PW91/LANL2DZ level of theory, as implemented in the Gaussian 98[32] and Gaussian 2003[33] programs which allow the self-consistent application of an external electrical field to the extended molecule, thereby permitting us to represent the external bias voltage. The B3PW91/LANL2DZ level of theory uses the Becke-3 hybrid exchange fully nonlocal functional and the generalized-gradient approximation (GGA) Perdew–Wang 91 correlation functional[34–36] with the LANL2DZ effective core potential and basis set.[37–39] The extended-molecule Hamiltonian described in atomic orbital (AO) basis is partitioned into isolated molecule, isolated metal atoms, and the coupling

TABLE 1: Molecular Lengths of Polyyne and Alkane Systems[a]

n	length (Å) Pd–S–C_n–S–Pd	length (Å) Pd–S–$(CH_2)_n$–S–Pd
1		6.684
2	9.254	8.284
3		9.310
4	11.839	10.480
5		11.883
6	14.434	12.852

[a] Lengths are measured as the Pd–Pd distance.

between them; this partitioning is extended to the Green function.[24] Notice that the Pd atoms added to the molecule forming the extended molecule are not representing the continuum but they are the discrete part of the metal contact that is directly attached to the molecule. In our approach, the bulk contact is represented by the contributions from the s, p, and d electrons to the local density of states (DOS) in the metal, which is treated separately.[2,7,22,40] The transmission function (T) probability is calculated as the sum of the contributions from all the spin–orbitals available for conduction, and the current is obtained by integrating T within the energy gap created by the bias voltage on the two contacts. The external voltage or bias potential is explicitly considered in the calculation affecting the electronic structure of the molecule; however, as already found with systems that do not contain strong electron-withdrawing groups such as NO_2,[41] this effect is minimal. A full description of the methods can be found in refs 17 and 42.

Results and Discussion

As shown in Table 1, polyynes (linear) systems are longer than alkanes (zigzag) for the same number of C atoms despite the longer C–C bond in alkanes. Polyynes chains tend to form double bonds rather than alternate single–triple bonds. The bond lengths fluctuate between 1.32 and 1.26 Å, which are closer to each other and also closer to the typical double-bond length of 1.339 Å for ethene[43] than to the typical single and triple bonds of 1.531 and 1.203 Å for ethane and ethyne, respectively.[43]

Figure 1a shows the molecular orbitals (MOs) for the polyynes with 2, 4, and 6 carbon atoms. Only α MOs are shown. The π nature of these orbitals is reflected in their delocalized shape at each side of the C–C bonds. The presence of Pd atoms yields two effects: the mixture of Pd AOs with polyynes MOs and the intercalation of almost pure Pd AOs. The highest occupied MO (HOMO) α and the lowest unoccupied MO (LUMO) β in the three systems are combinations of molecular and Pd orbitals, leading to fully delocalized orbitals (not shown). In all cases, the HOMO is the first orbital below the Fermi level of Pd while the LUMO is the first above. The HOMO α and the LUMO β are the closest MOs to the Fermi level for the corresponding spin state. They are fully delocalized; thus, a high conductivity is expected.

The spin-α HOMO-2, LUMO, and LUMO+1, as well as the spin-β HOMO, HOMO-1, HOMO-2, and LUMO+2, are mostly of Pd character, without contribution of the isolated molecule MOs. HOMO-1 α and LUMO+1 β are of similar shape, and they yield π orbitals localized in the molecule, with slight contribution from the Pd AOs. The LUMO+2 is also delocalized over the whole molecule, with π characteristics, except for the 2-C chain.

The α HOMO–LUMO gap (HLG) for the extended molecule decreases with the length of the chain, 3.46, 3.37, and 3.20 eV for the 2-, 4-, and 6-C chain, respectively. The β HLG is smaller than the α HLG and also decreases with the length of the chain,

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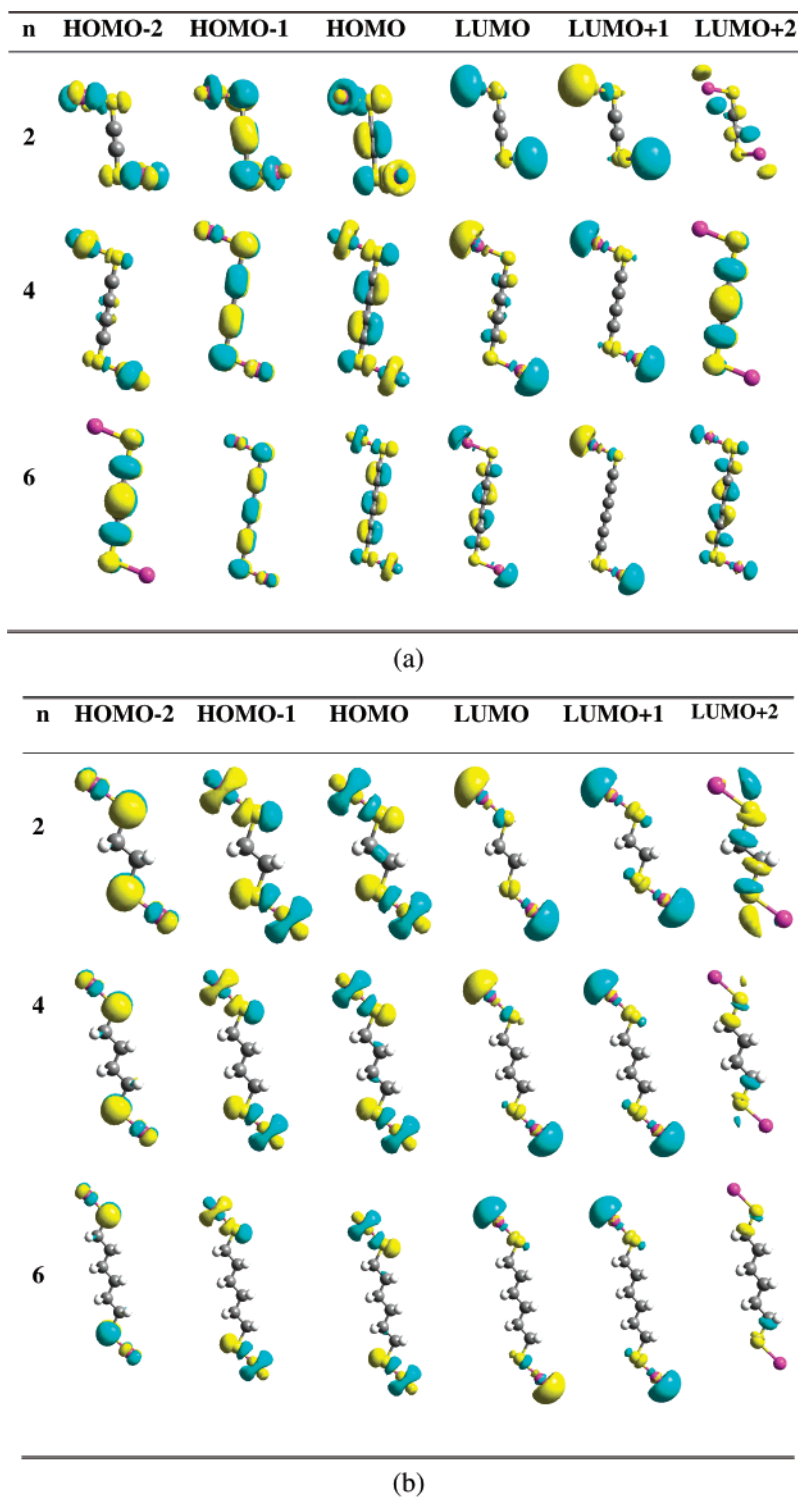

(a)

(b)

Figure 1. α MOs of the 2, 4, and 6-C polyynes (a) and alkanes (b). Notice the delocalized nature of the polyynes HOMO, main conducting channel, and those in its neighborhood. However, the HOMO and its neighbors for the alkanes show a highly localized nature, not showing any clear path for electron transport through the molecule.

1.27, 1.26, and 0.91 eV, respectively. However, because of the intercalation of Pd AOs, the first α unoccupied MO with contribution from the molecule is the LUMO+2. Considering this orbital as the LUMO α, the α HLGs are 5.69, 4.63, and 3.69 eV, that is, still decreasing with the size of the system. This is not the case for the β MOs, for which the LUMO is localized in the molecule. Pd and S atoms are slightly positive, with Mulliken charges of 0.1 au, while the C atoms bonded directly to the S atoms are negative in the three cases, that is, −0.2, −0.4, and −0.4 au for the chain with 2-, 4-, and 6-C

atoms, respectively. C atoms bonded to the C atoms attached to the S atoms are positive, 0.2 au for the $n = 4$ and $n = 6$ systems, and the two central C atoms in the chain with $n = 6$ are neutral.

Figure 1b shows the α frontier orbitals of three of the six alkanes. A strong localization on the Pd and S atoms is observed. There is almost no participation from CH_2 MOs, except for a small contribution to the α LUMO+2, where a σ antibonding orbital links the last C at each side of the chain to the S clips. The HOMO α and β also show a σ bonding between consecutive
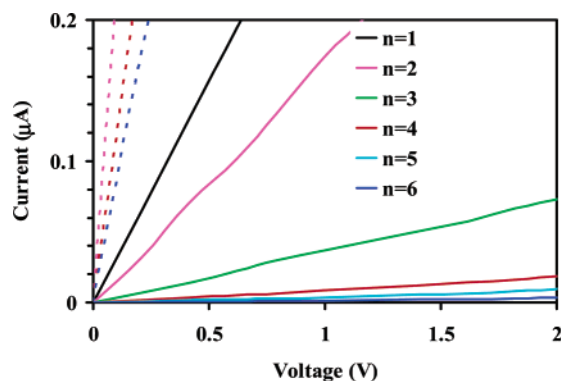
Figure 2. Current−voltage characteristics of the polyynes and alkanes. Notice the high conductance (slope) of the polyynes (dashed lines) with respect to the alkanes of similar lengths (continuous lines).
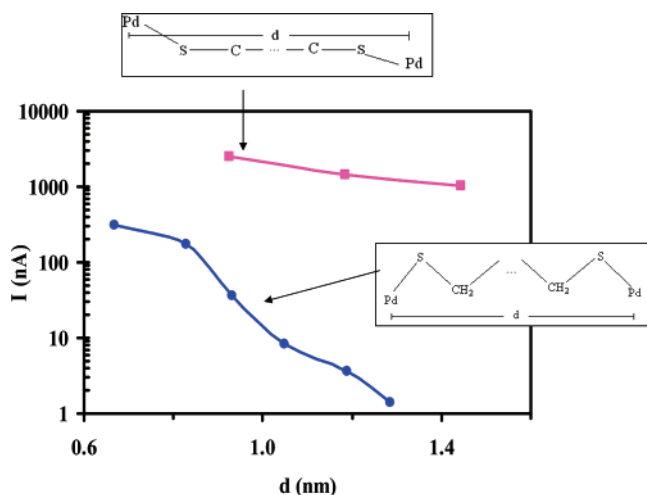

Figure 3. Current versus length, *d*, of the molecules for a bias voltage of 1 V. The upper curve corresponds to the polyyenes, and the lower one to the alkanes. Notice the large decrease in current for larger alkanes. Both curves hardly follow an exponential decay. When they are fitted to exponentials, a barrier 3 times larger can be predicted for the alkanes than for the polyynes. The behavior of molecular systems for these short distances does not follow any of the standard models for electron conduction.

Figure 4. DOS versus energy for the polyynes (a) and alkanes (b). The electron energy reference is the vacuum level. The vertical line represents the Fermi energy of bulk Pd. Despite the similar values of the DOS at the Fermi energy, the conductance is much higher for the polyynes, because of their delocalized MOs as shown in Figure 1.

C atoms in the chains of up to $n = 3$, and no MO delocalization allows connection to the S or Pd.

The alkanes HLGs are larger than those for polyynes with the same number of C atoms; however, the HLGs for alkanes do not change significantly with the number of C atoms in the chain, because of a major contribution from Pd to these MOs, and thus, they are not strongly affected by the number of CH_2 in the chain.

The current through β MOs for alkanes is larger than the current through the α MOs because of the contribution from two unoccupied β orbitals with energies just slightly above the Fermi level (E_f). These two unoccupied MOs are fully localized on the Pd and S atoms; thus, electrons should overcome an increasingly large barrier to go from one contact to the other. Their effect on the current vanishes as the number of C atoms in the chain increases; thus, the larger the chain, the smaller the difference between α and β currents.

Pd and S are almost neutral as in the polyynes; however, C atoms are strongly negative, and H strongly positive, so the CH_2 group Mulliken charges oscillate, as in the polyynes, along the chain. However, the most external CH_2 charges are negative for all the systems, and the larger negative charge is accumulated in the C atoms bonded to S atoms.
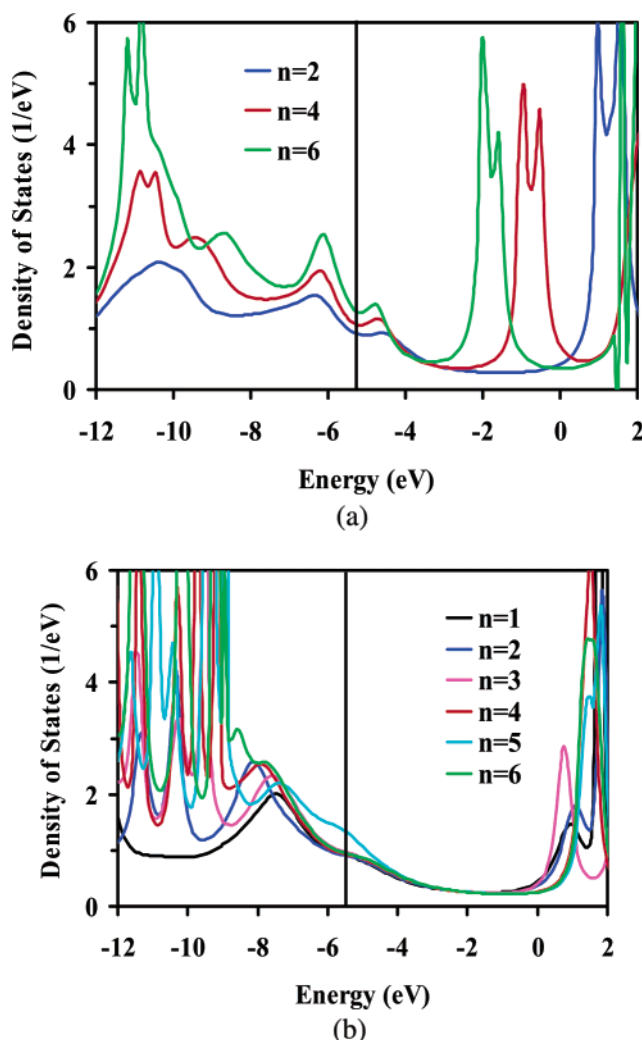
The current in the alkanes is relatively small compared to the current in the polyynes. The current in the polyynes linearly increases with the voltage as shown in Figure 2, but it does not change drastically with the size of the polyyne. On the other hand, the current through the alkanes is smaller, and it decreases very rapidly with the number of C atoms in the chain.

Figure 3 shows, in logarithmic scale, the current at 1 V for all the cases. While polyynes do not show a significant change with the size of the chain, the current through alkanes decreases rapidly and almost exponentially for the larger alkanes. At 1 nm, the target size for nanodevices, the relation between high and low impedance systems can be of about 2 orders of magnitude. This relation grows exponentially with the feature size; at 1.3 nm for instance, it is of 3 orders of magnitude.

Figure 4a shows the DOS for the polyynes. The first peak below the Fermi level in the DOS has contributions from α HOMO and β LUMO, while the first peak above E_f is purely from β LUMO+1 contributions. The T and DOS plots for the polyynes show two peaks at high energy that changes their position toward Fermi level as the polyyne size increases.

The T yielded by the β MOs, and thus the current of β electrons, is larger than that of the α's. The LUMO and LUMO+1 β have similar characteristics as the HOMO-1 α and HOMO α, respectively. These two lowest unoccupied β states

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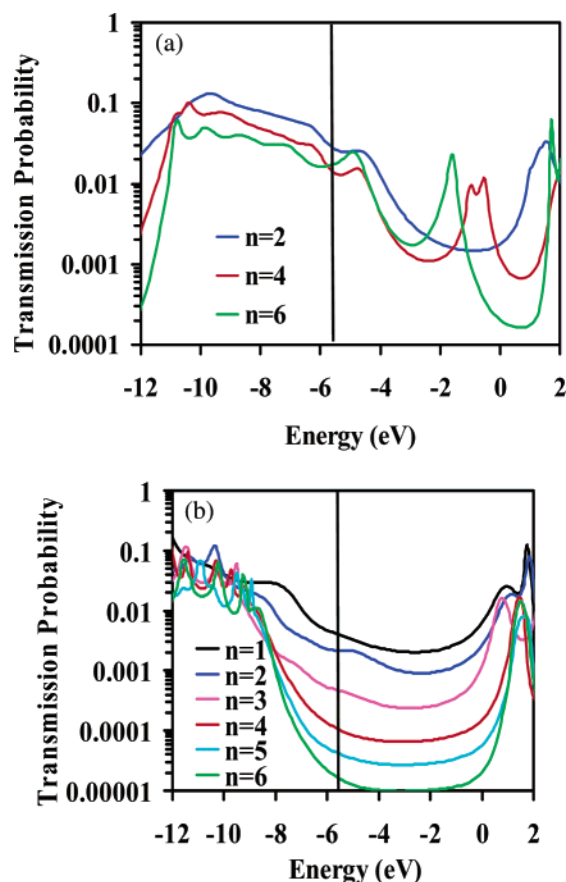*J. Phys. Chem. B, Vol. 108, No. 46, 2004* **17883**

Figure 5. Transmission probability, T, versus energy for the polyynes (a) and alkanes (b). The electron energy is taken with respect to the vacuum level. The vertical line represents the Fermi energy of bulk Pd. The polyynes show higher transmission probabilities because of the delocalized nature of their MOs. Notice the strong difference in the T's of the alkanes; however, it is within the same order of magnitude for the polyynes at the Fermi energy. A slight increase of conduction probably for $n = 6$ takes place around the Fermi energy.

are less stable than their occupied α counterparts. They are located one above and one below the Fermi level. The LUMO and LUMO+1 β show values of T similar to the HOMO and HOMO-1 α, but the former are closer to the E_f, yielding a larger β current at low bias voltages.

The alkanes DOS (Figure 4b) show low values in the neighborhood of E_f, which is consistent with the low contribution from the molecule's atoms to the frontier orbitals shown in Figure 1b. The T (Figure 5b) shows a sharp decrease in the transmission of electrons as the chain grows. For all alkanes, the T is higher for the occupied channels than for the unoccupied as the occupied MO have their energies closer to the Fermi level.

To evaluate the quality of our calculations, we have extended our analysis to longer σ systems (alkanes) C8, C12, and C16 attached to Au contacts; thus, direct comparison can be made to recently reported experiments in a nanopore structure.[44] Three of the most relevant factors causing discrepancies between theory and experiment are (1) theory has to guess the characterization of the system and assume an equivalent one that closely represents the goal of the experiment, which is to obtain the current−voltage characteristics of single molecules. (2) The number of conducting molecules in the experiment is unknown; however, the area where the molecules are deposited to one of the contacts is known. The maximum number of molecules (N_o) that this area can hold can be determined by geometrical considerations (calculated in a few thousands). A realistic number $N < N_o$ of self-assembled molecules in the
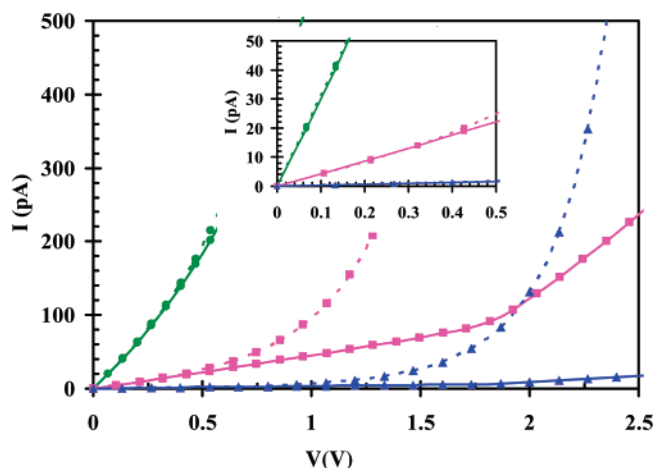

Figure 6. Comparisons of theoretical $I-V$ (solid line) with precise experimental results (dashed line)[44] for C8 (green, circles), C12 (purple, squares), and C16 (blue, triangles) alkanethiol monolayers, assuming that 100, 250, and 1100 molecules contributed to the conduction process, respectively. The inset shows an excellent match within the range of 0−0.5 V.

metallic surface would depend on the assembly conditions and environment. The problem is when the second gold contact is vapor-deposited in the nanopore device. Only M out of the N molecules are attached to the second terminal, thus only M molecules are responsible for the electron conduction. This number M may range from 0 to N, and (3) the geometry of the vapor-deposited attachment is also unknown experimentally and does not have to be similar for the M molecules and its geometry also has to be assumed by the theory.

To deal with 1 and 3, we have performed the calculations to obtain the best geometry out of several possible conformations and checked them to choose a stable one by performing second derivatives of the energy. To deal with 2, it is necessary to scale the current reported in the experiment to the one for a single molecule; M necessarily needs to be estimated. Notice that we scale the current to fit only one point of our curve. The fact that all other points within the range 0−0.5 V fit perfectly well actually corroborates that the equivalent estimated of the number of molecules making contact to the two terminals is correct. Thus, the fact that we only need to fit the only parameter that is actually unknown experimentally should be viewed as a success of the theory that allows us to determine the number of molecules in the experiment.

A direct comparison to the C8, C12, and C16 molecules is shown in Figure 6. The best fit to one of the smallest theoretical values is obtained for 1100, 250, and 100 molecules for the C8, C12, and C16, respectively. Using these values, the extrapolation of currents for the range 0−1 V is acceptable. C8, C12, and C16 have degrees of freedom following a relation of approximately 2, 3, and 4, respectively; thus, we can expect that the C16 molecules do not form a better array than the C8 molecules and therefore the number of contacting molecules has to be strongly different and decreasing as the size of the alkanes increases. The excellent agreement in the inset of Figure 6 would be enough to show the agreement of the method for small voltages. Strong differences can be observed for large bias voltages; however, they are still within the same order of magnitude. A detailed explanation of these differences is in progress but it does not affect the conclusions of the present work, which focuses on the study of high- and low-conducting molecules. This is the case of the vapor-deposited end on the nanopore where the exact connection of the ending CH_3 to the vapor-deposited Au is unknown. We have assumed a

connection similar to the self-assembled end for our theoretical calculations, although not identical to the real case, its effect in these large and highly resistive alkanes is insignificant. Recent indirect measurements using second-harmonic inelastic tunneling spectroscopy seems to confirm the presence of the alkanes in this type of nanopore setting;[45] thus, this group of measurements is one of the best to test our theoretical procedures. The fact that the theoretical results are not only of the same order of magnitude as the experimental results but also very close in agreement is very encouraging. As expected, the agreement is better for the longer alkanes.

The excellent fit in the region from 0 to 0.5 V supports the validity of our calculations. Actually, the value of the barrier from the Fermi energy of gold (-5.31 eV) to the first channel in the molecule (the HOMO at -6.20 eV) is 0.89 eV, which has to compete with a more conducting one from an orbital located at -8.20 eV yielding a barrier of 2.89 eV. The effect of these two barriers when forced to one simple exponential yields a barrier of 1.4 eV. The drastic differences for higher voltages are because a higher barrier and strongly conducting channels $\sim 4-5$ eV cannot be followed experimentally because of the high bias voltages, which might trigger irreversible changes in the nanopore (like electromigration of gold or other atoms for instance or other still unknown causes) when reaching such high bias voltages.

Conclusions

We have used our recently implemented method to study in a reliable way two groups of molecules that can be used as components of molecular electronic circuits. The difference in conductance between the two groups of molecules is due entirely to the difference in their frontier molecular orbitals. In addition, the decay of the current as a function of the length of the molecule hardly follows an exponential decay or any of the typical models of scattering for a barrier. When the current-versus-length curve is fitted to an exponential decay, it yields a barrier 3 times larger for the alkane chain than for the polyynes. It is concluded that the difference between these two types of molecules, and in general, the difference between each of the molecules, is strictly determined by their electronic structure (including the contact atoms), and it cannot be fitted to simple models of electron transport. However, the exponential dependence is correct for longer devices as reported in several other experiments in different environments and for larger systems (see, for instance, refs 12, 44, and 46−50); at 1 nm, there is no longer a pure exponential dependence. Also, for such short molecules, distances are discrete rather than continuum; adding a $-CH_2-$ or $-C-$ group to the molecules may yield changes in the orbital energies and shifts in Fermi levels not necessarily following the same trend as when another $-CH_2-$ or $-C-$ unit is added. We have also carried out calculations using gold contacts instead of palladium and the exponential dependence is not found for systems of $\sim$1-nm size; however, the strong differences in conductance found when using the phenyl ring[22] are not found when using the alkanes and polyynes. The models for bulk systems, using a single barrier, can be viewed as a truncation of a more complete model for molecules. Assuming that the experiment uses a function $F = F_1(E_1)$ where E_1 is the barrier from the Fermi energy of the metal to the first nearest molecular orbital, thus a more complete description of the conduction through the molecule can be written as $F = \Sigma_i F_i(E_i)$ where E_i is the barrier from the Fermi level to the ith nearest MO level. Thus, a satisfactory complete model would consider not one but all barriers because of the discrete nature of the molecule.

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