

Investigation of the Conducting Properties of a Photoswitching Dithienylethene Molecule

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The field of molecular electronics has seen a growing interest among the research community in the past 10 years. It has attracted scientists from physics, chemistry, materials science, electronic engineering, and biology due to its interdisciplinary appeal and the prospect of making innovative devices and sensors. Since the first seminal idea of Aviram and Ratner of a molecular *p-n* junction,¹ functioning molecular rectifiers,² conductance switches,³ and logic gates⁴ have all been made with molecules. Although some reports have raised controversy,⁴ mainly because the underlying mechanism for the observed phenomena was not fully understood, the field is making progress toward functioning devices. Future applications include sensors for biological and medical diagnosis,^{5,6} disposable electronics, optoelectronic devices, and spin-sensitive applications.⁷

One interesting class of molecules is that of photoswitching complexes whose geometry undergoes reversible changes between different states when acted upon by light. In particular, molecules that switch between states with different conducting properties are appealing candidates for use in organic opto-electronics. In this work the energetics and the transport properties of one of these molecules, namely, dithienylethene, are investigated theoretically with a combination of density functional theory (DFT) and the nonequilibrium Green's functions (NEGF) method for electron transport. We find that the low bias conductances of the two accessible dithienylethene geometries differ by a factor of about 20, suggesting that molecular optoelectronic switches with a large on/off ratio can be made with dithienylethene. Away

ABSTRACT Photoswitching molecules are attractive candidates as organic materials for optoelectronics applications because light impulses can switch them between states with different conducting characteristics. Here, we report a fully self-consistent density functional theory calculation of the electron transport properties of photoswitching dithienylethene attached to Au leads in both the open and closed conformations. The molecule is found to be a good conductor in both conformations, with the low-bias current for the closed one being about 20 times larger than that of the open. Importantly, the current–voltage characteristics away from the linear response are largely determined by molecular orbital rehybridization in an electric field, in close analogy to what happens for Mn₁₂ molecules. However, in the case of dithienylethene attached to Au, such a mechanism is effective also in conditions of strong electronic coupling to the electrodes. This makes the dithienylethene family an intriguing materials platform for constructing highly conducting organic optoelectronics switches.

KEYWORDS: density functional theory · nonequilibrium Green's function theory · self-consistent · molecular electronics · opto-electronics · electron transport · molecular conduction · photoswitching · polarization · rehybridization

from the low-bias regime, a detailed analysis of the transmission coefficient as a function of the applied voltage has revealed that the current–voltage characteristics are largely determined by a subtle molecular orbital rehybridization driven by the electric field. As such, a precise evaluation of the nonequilibrium charge density at any given bias becomes necessary and allows us to rationalize our results in comparison to previously published work. In particular, we demonstrate that extrapolations of finite bias currents from the linear response transmission may be largely misleading and provide unrealistic on/off current ratios.

Photoswitching dithienylethene derivatives change their conformation in solution from a closed to an open structure under visible light (400–700 nm) and reverse under UV conditions (<400 nm). Several studies, both experimental^{8–13} and theoretical,^{12–17} have recently appeared, but a consensus over the mechanism of the switching and its effects over the electron transport properties seems to be far from

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reach. For instance, Dulic *et al.* reported the quenching of the closing reaction¹⁷ when the molecule is attached to the electrodes and found, with break-junction experiments, that the conductance of the closed molecule is 3 orders of magnitude larger than that of the open one. On the other hand, several experimental works have demonstrated reversible switching for different variations of dithienylethene molecules connected to one^{8,10,13} and two gold contacts^{9,11} and have reported a ratio between the current for the closed and open conformations of 25,⁹ 16,¹⁰ and 131¹³ for different experimental setups. In these experiments, the molecule experiences both photophysical and mechanical stress, which may influence the switching reaction differently due to the experimental technique used.

A number of theoretical works have dealt with these experimental findings. Li *et al.* calculated non-self-consistent current–voltage characteristics (*I*-*V*) by integrating the zero-bias transmission function over a bias window.¹⁶ They found a low bias conduction ratio between the two configurations ranging between 20 and 40 depending on the anchoring site. The same approach was used by He *et al.* to find a conduction ratio of 91 and 177 for two different anchoring sites.¹³ Zhuang and Ernzerhof¹⁸ used a tight-binding Hamiltonian for the electrodes and a model voltage profile for the electrostatic potential and reported a conduction ratio of about 100 at 1.0 V. Kondo *et al.*¹⁹ calculated the transmission function for the two forms of the molecule and found a large difference at 0 V. Tsuji *et al.*²⁰ performed a NEGF-DFT calculation for the open and closed forms of a diarylethene molecule attached to gold leads and found a switching ratio of about 3 orders of magnitude. To the best of our knowledge, however, there is still no report of a fully self-consistent calculation of the *I*-*V* characteristics of the two different states of dithienylethene.

RESULTS AND DISCUSSIONS

Our analysis of the switching reaction between the open and the closed conformations is presented first. This is based on DFT calculations of both the ground state and the first excited state as a function of the reaction coordinates. We then proceed to discuss the results of the electronic transport calculations for both conformations when the molecule is attached to Au electrodes, forming a two-probe junction. In particular and at variance with the previously published literature, we perform fully self-consistent calculations at finite bias with realistic electrodes.

Opening/Closing Reaction. To investigate the switching properties, the total energy of dithienylethene in its gas phase is calculated for a range of values of the reaction coordinate between those of the closed and the open forms of the molecule. We define as reaction coordinate the distance between the two carbon atoms in the central benzene ring of dithienylethene, because

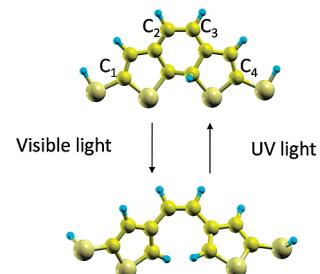


Figure 1. Two geometrical configurations of the dithienylethene molecule investigated in this work. The reaction coordinate is defined as the distance between the two central C atoms involved in the bond breaking during the opening reaction. The values for the reaction coordinate are 3.3 Å for the open molecule (below) and 1.5 Å for the closed one (above). Color code: light gray (light blue) H, dark gray small balls (yellow) C; dark gray large balls (pale yellow) S.

these are involved in the opening and the closing of the molecule (see Figure 1). In the calculations, the two C atoms defining the reaction coordinate are kept fixed, while all the other atoms of the molecule are allowed to relax to their lowest energy configuration. The gas phase is simulated by placing the molecule in a $25 \times 25 \times 25$ Å³ supercell, which is large enough to avoid interactions with its periodic replicas. The atomic positions are then relaxed using the conjugate gradient scheme until the forces are smaller than 0.002 eV/Å.

A challenge when performing atomic relaxation calculations is associated with selecting a good initial configuration. In fact, if the initial atomic positions are far from the lowest energy configuration, the relaxation requires many steps, or it might not even converge. Thus, in absence of experimental data for the two end structures of the opening/closing reaction, we construct the initial condition by starting from known configurations of organic molecules such as benzene and thiophene. Then the initial structure for each intermediate geometry along the reaction path is generated by a linear interpolation between the atomic positions of the open and closed isomer. The interpolation is defined as

$$\vec{R}_{i,k} = \alpha \vec{R}_{i,\text{closed}} + (1 - \alpha) \vec{R}_{i,\text{open}}, \quad \forall \alpha = \frac{k}{N_{\text{step}}} \quad (1)$$

where $\vec{R}_{i,k}$ are the coordinates of the *i*th atom in the *k*th geometry, $k = 0, 1, 2, \dots, N_{\text{step}}$ and N_{step} is the number of geometries explored between those of the open and closed isomers.

The calculated total energy as a function of the reaction coordinate is presented in Figure 2 (solid black line and crosses). Note that there is a robust potential energy barrier of about 1.5 eV (17000 K) separating the open configuration from the closed one, although the total energies of the two configurations at their relative equilibrium positions are rather similar. This demonstrates that both configurations are stable against thermal fluctuations, so that one expects the molecule to re-

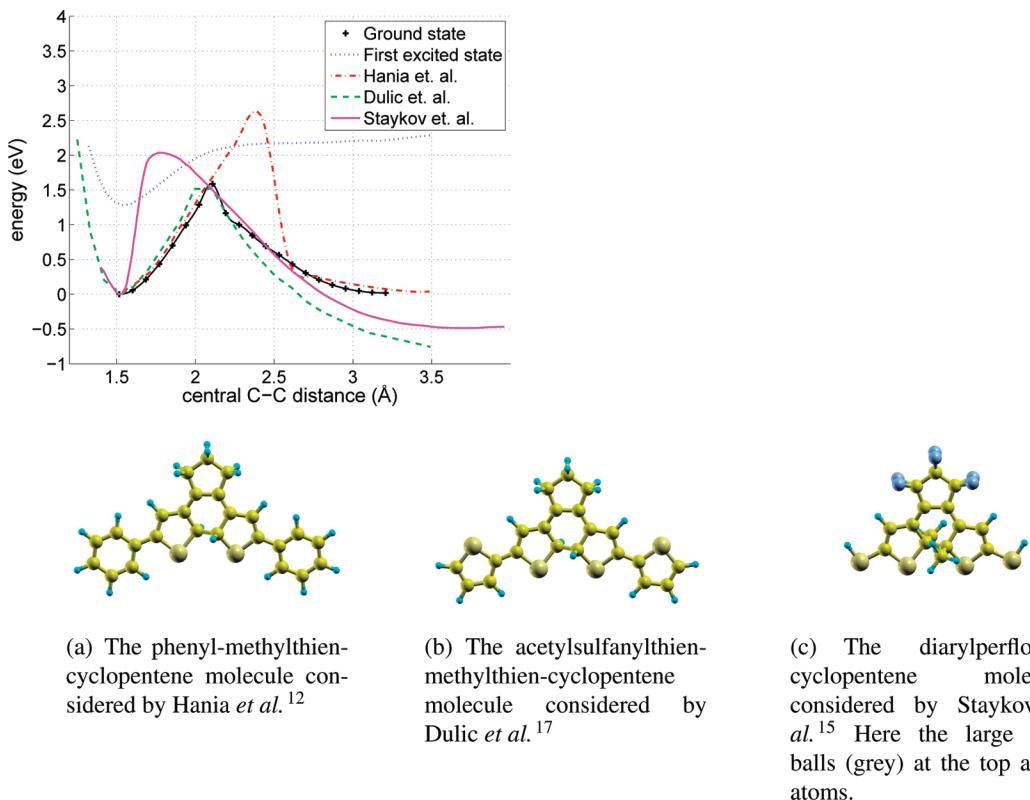


Figure 2. Total energy as a function of reaction coordinate for the dithienylethene molecule investigated in this work (calculated data points are marked with “+”; the black solid line is a guide for the eye) and the first excited state (blue dotted line) along the path defined by the reaction coordinate. The excited state is obtained by promoting an electron from the HOMO to the LUMO. We also show results for three related molecules investigated previously in the literature by Hania *et al.*¹² (red dash-dot curve), Dulic *et al.*¹⁷ (green dashed line), and Staykov *et al.*¹⁵ (magenta solid line). The geometries of these molecules are presented in a, b, and c, respectively.

main in a given configuration unless an electronic excitation is produced.

Also shown in Figure 2 are results extracted from the literature for three alternative photoswitching complexes. The first is the molecule investigated both experimentally and theoretically by Hania *et al.*¹² (Figure 2a). This has two phenyl groups at each end of the molecule, and the two central C atoms opposite to the atoms involved in the opening/closing reaction are replaced by a cyclopentene unit. The second is the molecule investigated by Dulic *et al.*¹⁷ (Figure 2b) and differs from the previous one by having terminating thiophene instead of the phenyl groups. The third is a diarylperfluorocyclopentene investigated by Staykov and Yoshizawa¹⁵ (Figure 2c) that has methyl groups attached to the carbon atoms involved in the opening/closing reaction. In all three cases the authors concluded that the opening/closing reaction is driven by the occupation of excited states during the irradiation.

Although slightly different molecules were investigated in these previous works compared to the present one, the obtained potential energy profiles are rather similar, indicating that the switching reaction is mostly driven by the central part of the molecule.

To obtain deeper insight into the mechanisms of the reaction, it is useful to investigate the energy pro-

file along the reaction path for some excited states. This is not an easy task in standard DFT. However, as a first approximation, we calculate the total energy as a function of the reaction coordinates for an electronic configuration, where one electron is promoted from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).²¹

The calculated energy profile for such an excited state is also presented in Figure 2, and it indicates that the open molecule should be able to relax into the closed one when excited with a single photon excitation. This is because the total energy of the excited state is larger than that of the ground state along the entire reaction path and, furthermore, the energy of the closed molecule in the excited state is lower than that of the closed isomer.

Our findings are, thus, in qualitative agreement with experiments,¹² although the computed photon energy for the transition is underestimated. We trace this disagreement back to the inability of the GGA to position correctly the empty molecular orbitals with respect to the occupied ones, that is, to the DFT gap problem. Improvements may be expected after self-interaction removal,^{22,23} for instance, by using hybrid exchange-correlation functionals such as B3LYP,²⁴ which has been shown to give excitation energies in closer agreement

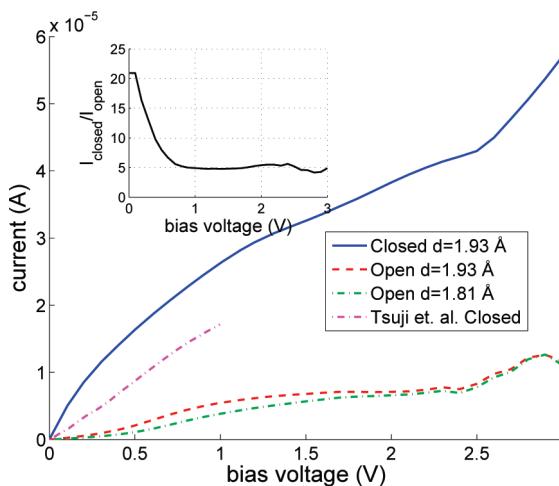


Figure 3. Self-consistent I - V characteristics for the closed and open molecules sandwiched between two Au electrodes. In the figure, we also present the calculation of Tsuji *et al.*²⁰ for a diarylethene molecule attached to gold leads in the closed conformation. For the open molecule, the current is evaluated for two different anchoring distances, as discussed in the text. The ratio between the current for the closed and the open molecule at the large anchoring distance is shown in the inset.

with experiments in most cases. Our calculated energy difference between the ground state and the first excited state is 2.18 eV for the open isomer and corresponds to an optical excitation in the visible part of the spectrum (568 nm), whereas the closing reaction occurs only under UV light.

Another piece of information we extract from Figure 2 is that the opening reaction does not seem to be accessible with a single optical excitation of the type investigated here. This suggests that further excitations are necessary to move the molecule into an electronic state with minimum at the open coordinates. Our results are then consistent with the idea that the ring-opening reaction involves a multiphoton process, in agreement with earlier work.^{12,16,14}

Transport Properties. The I - V characteristics, up to 3 V, for both the closed and the open molecules and for the two different anchoring distances of the open configuration (see section Computational Methods for explanation) are presented in Figure 3. Also shown in the inset is the ratio between the current for the closed and the open isomer $I_{\text{closed}}/I_{\text{open}}$. We calculate the current only for positive bias, because the molecule is anchored approximately symmetrically to the leads and, therefore, the current at negative bias is almost identical (except for the sign).

In Figure 3 a recent NEGF-DFT calculation by Tsuji *et al.*²⁰ for a diarylethene molecule attached to gold leads in the closed conformation is also shown.

The most striking feature emerging from the figure is the large $I_{\text{closed}}/I_{\text{open}}$ ratio. This is quite pronounced ($I_{\text{closed}}/I_{\text{open}} \sim 20$) at low bias, but it still persists as the bias increases up to 3 V. In fact, we note that, for bias voltages exceeding 0.8 V, the $I_{\text{closed}}/I_{\text{open}}$ ratio saturates

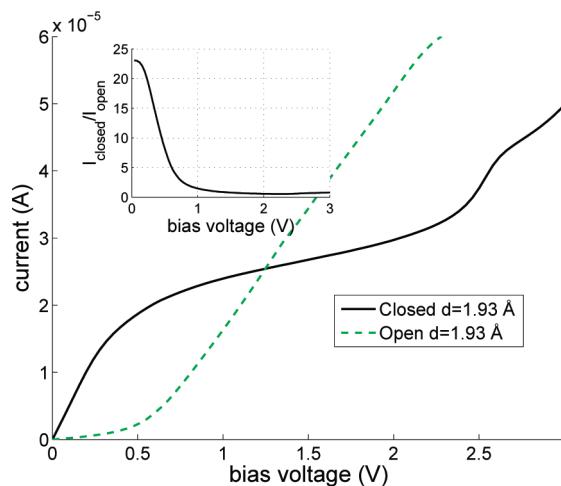


Figure 4. Non-self-consistent I - V characteristics for the closed and open molecules sandwiched between two Au electrodes. This is obtained by integrating the zero-bias transmission function over an increasingly large bias window. The inset shows the ratio between the calculated current for the closed and open molecule.

to around a value of 5. It is also important to observe that little differences are found in the I - V for the two anchoring distances of the open geometry, demonstrating that our result is rather independent from the anchoring distance. To compare our calculations with existing literature,^{13,16} we also perform a non-self-consistent evaluation of the I - V , where the current is simply obtained by integrating the zero-bias transmission function over an increasingly large bias window. This is shown in Figure 4. We note that the I - V of the closed molecule is rather similar to its self-consistent counterpart (see Figure 3). In contrast, that for the open isomer is remarkably different for voltages above 0.5 V. As a consequence, the non-self-consistent $I_{\text{closed}}/I_{\text{open}}$ ratio is similar to the self-consistent one at small bias (up to about 0.5 V), but differs substantially in the high bias region. In particular, in the non-self-consistent calculations, there is a crossover between the I - V curves of the open and closed molecules at around 1.2 V, so that the high bias $I_{\text{closed}}/I_{\text{open}}$ ratio becomes smaller than 1 beyond such a voltage. We then have to conclude that $T(E, V)$ of the open molecule must display a rather severe bias-dependence, which is not taken into account in the non-self-consistent calculation. This dependence is examined next.

The transmission functions as a function of energy and for different bias voltages are presented in Figures 5 and 6, respectively, for the closed and open isomer. In general and for both the molecular configurations we find that the peaks in $T(E, V)$ associated to the various molecular levels are rather broad, indicating a strong electronic coupling between the molecule and the electrodes. This strong coupling limit is the one where the NEGF-DFT formalism is expected to perform better.²⁵

Going into more details and starting from the closed molecule (Figure 5), we observe that $T(E, V = 0)$ has a

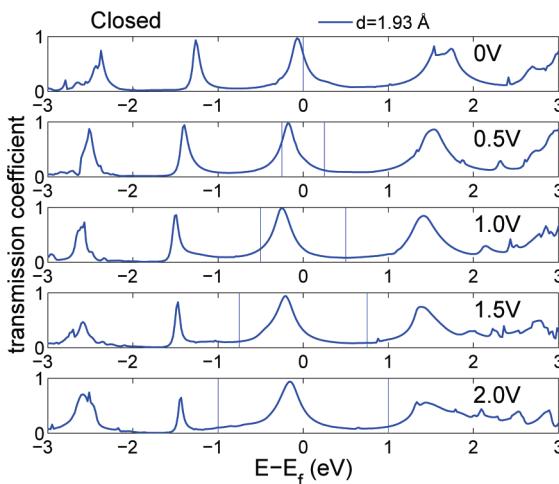


Figure 5. Transmission coefficient as a function of energy for the open isomer and two different anchoring distances at different bias voltages. The vertical lines denote the bias window.

large peak centered just below the Fermi level (E_F) of the electrodes. This means that the zero-bias transmission and, therefore, the conductivity are rather large. Such a peak has only a modest shift when the bias is applied, and already for $V = 1$ V it is completely positioned within the bias window. As the bias is further increased, no new peaks enter the bias window, so that one expects the current to increase only moderately. This explains the I - V curve of Figure 3. Furthermore, because in this case $T(E, V)$ is dominated by a single peak, whose position and width change only marginally with bias, we expect that the non-self-consistent I - V is a good approximation for the self-consistent one, as it is indeed confirmed by our calculated curves.

Note that the exact position of the first transmission peak, corresponding to the molecule HOMO, can be affected in DFT by the self-interaction error, intrinsic to the local and semilocal approximations of the ex-

change and correlation functional.²⁶ This shortfall can be corrected by subtracting the spurious self-interaction, a procedure that usually improves the agreement between the calculated I - V and experiments. The main effect of self-interaction removal is that of downshifting in energy the occupied part of the molecular spectrum. This is somehow equivalent to applying a gate to the entire system. Because the same corrections apply to both the open and closed molecules, we expect that our main result will remain unchanged, except for a shift of the current onset from zero to larger biases.

In contrast, the situation for the open molecule appears rather different. At $V = 0$ the transmission coefficient shows a broad peak, approximately 1 eV wide, positioned at about 0.3 eV below E_F . Only the far tail of this peak crosses E_F and therefore the zero-bias conductance is small, approximately 20 times smaller than the same for the closed isomer (see the inset of Figure 3). Our results are therefore in close agreement with the non-self-consistent calculations of Li *et al.*, who obtained an $I_{\text{closed}}/I_{\text{open}}$ ratio of 31 for the same molecules as those considered here.¹⁶ In contrast, the current calculated by Zhuang and Ernzerhof with a tight-binding model Hamiltonian for the leads is ≈ 10 μA at 1 V for the closed molecule (this is similar to ours), but that for the open molecule is much smaller for voltages up to 1.5 V.¹⁸ As a consequence, the $I_{\text{closed}}/I_{\text{open}}$ ratio calculated by Zhuang and Ernzerhof is much larger and peaks to 400 for $V = 0.5$ V.

Comparing our results with Tsuji *et al.*,²⁰ we obtain a similar current for the closed conformation (Figure 3), while their result for the open conformation is considerably smaller (not shown). One should keep in mind, however, that the molecule they investigated is not identical to ours.

Because the peak in $T(E, V = 0)$ for the open molecule of Figure 6 is much broader than that for the closed isomer, one might expect that at sufficiently large biases the dominant current will be that associated to the open isomer. This is precisely what happens if the calculation is carried out non-self-consistently (see Figure 4). However, when the nonequilibrium charge density is recalculated at every bias step, the situation changes dramatically. In fact, the broad transmission peak narrows considerably as the bias grows and it remains almost pinned at the lower boundary of the bias window (*i.e.*, at the lowest of the chemical potentials of the two electrodes). Therefore, for all the values of the bias voltage considered, the current receives contributions only from the tail of the transmission coefficient, so that the current does not grow much with bias.

The sharpening of the peak in $T(E, V)$ of the open isomer with bias is investigated by calculating the projected density of states (PDOS) of the two isomers. This is obtained from the non-Hermitian part of the Green's

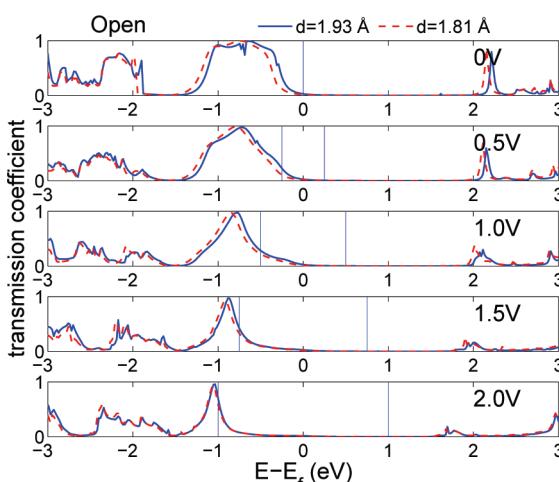


Figure 6. Transmission coefficient as a function of energy for the open isomer and two different anchoring distances at different bias voltages. The vertical lines denote the bias window.

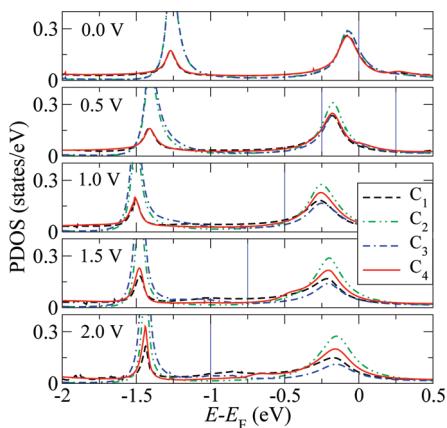


Figure 7. Projected density of states for four C atoms of the closed isomer at different applied bias. The atom labels C_1 , C_2 , C_3 , and C_4 are defined in Figure 1. The vertical lines define the bias window.

function, so that it corresponds to the nonequilibrium charge density at a given bias, and it is presented in Figures 7 and 8, respectively, for the closed and open molecules. As a matter of notation, we denote with C_1 the left-most carbon atom of the molecule, with C_4 the right-most carbon atom, and with C_2 and C_3 the two central carbon atoms not involved in the opening/closing reaction (see Figure 1 for illustration). For both the closed and the open isomers, one can clearly identify a one to one correspondence between peaks in the PDOS and those in $T(E, V = 0)$. Importantly, the transmission peak heights are directly related to the electronic coupling between the given molecular orbital and the electrodes.^{27,28} In particular, if there is an identical electronic coupling with both the leads, one expects $T = 1$ at the maximum of each peak.

In contrast, if a molecular state is coupled unevenly, then the height of the corresponding transmission peak is reduced, until it reaches zero when the electronic coupling with one of the leads vanishes. From Figures 5 and 6 one can immediately deduce that at $V = 0$ all the molecular levels involved are essentially equally

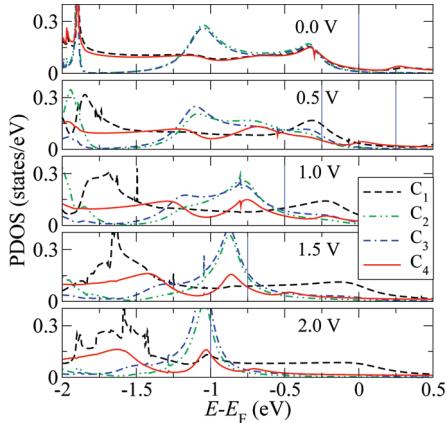


Figure 8. Projected density of states for four C atoms of the open isomer at different applied bias. The atom labels C_1 , C_2 , C_3 , and C_4 are defined in Figure 1. The vertical lines define the bias window.

coupled to the leads. For the closed molecule such a situation is maintained even after the bias is applied, mainly because the relevant molecular level receives orbital contribution from all C_1 , C_2 , C_3 and C_4 , that is, it is delocalized over the entire molecule. Note also that the relative contribution of atoms symmetrically placed with respect to the molecule axis (for instance C_1 and C_4) is different at finite bias, reflecting the potential drop within the molecule. In contrast, the broad peak in transmission of the open isomer originates from the overlap of a number of molecular orbitals. As the bias increases, the PDOS shows that different atoms contribute differently to the various peaks. This indicates that the molecular levels involved in the transport develop a different spatial localization, that is, that they localize in space and polarize. As such, the initially broad peak under bias fragments in a number of more narrow peaks, whose spectral contributions to $T(E)$ overall decrease.

We then conclude that the reduction in height of the transmission peak of the open isomer is due to the localization of the molecular orbitals responsible for the transport under bias, with the consequent development of a progressively more uneven electronic coupling with the leads. This is analogous to what has already been found for Mn_{12} attached to Au surfaces.²⁸ In the case of Mn_{12} , however, the molecule is only weakly coupled to the electrodes. As a consequence, the rehybridization is abrupt at certain critical voltages and generates negative differential resistance (NDR). Note that orbital rehybridization is by no means a sufficient condition for NDR. Here, in fact, we demonstrate that, although the same mechanism for rehybridization is possible also in the strong coupling regime, no NDRs are found. The main difference between the present case and that of the Mn_{12} molecule, is that here the HOMO always remains at the edge of the scattering region. As a consequence, the current is associated to the transmission of the tail of the HOMO resonance only. This changes little with bias because a reduction of the HOMO width is compensated by a relative shift of its center toward the edge of the bias window. For Mn_{12} at the NDR, the HOMO is already completely within the bias window, so that a reduction of its width results in a reduction of the current.

Before concluding this section, we briefly analyze the electrostatic potential across the scattering region at finite bias. This is reported in Figure 9 where we plot the planar average ΔV of the difference in the electrostatic potential calculated at 0.5 and 0.0 V (the planar average is taken along the plane perpendicular to the transport direction). The figure demonstrates that the potential drop occurs entirely across the molecule, while it is constant in the metallic electrodes. This reassures us that the scattering region is large enough for the electron screening to be correctly described.

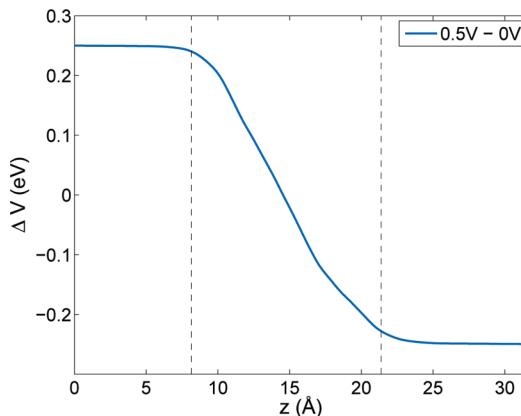


Figure 9. Planar average of the difference between the potential profiles calculated at 0.5 and 0 V. The black dashed vertical lines indicate the positions of the electrode surfaces.

CONCLUSIONS

In conclusion, we have performed a fully self-consistent calculation of the electronic transport properties of the two forms of dithienylethene attached to Au leads and analyzed the mechanisms of conduction, polarization, and switching. The switching reaction for a photoswitching dithienylethene molecule was simulated with potential energy calculations along the switching path in both the ground state and in an approximation to the first excited state. Our results indicate that the switching between the open and the closed form of the molecule can only be triggered by photonic excitations due to a high potential energy barrier separating the states. We conclude that the switching from the open to the closed isomer can be initiated with a single photon excitation, while the reverse reaction requires excitations to higher states. We next move our attention to the transport and find a conductance ratio of about 20 for the two configurations for small applied bias voltages. A marked difference in the currents persists up to high voltages, although the ratio reduces to about 5. We attribute this difference in conductance to changes in the alignment of the transmission peaks with respect to the Fermi level in the two forms of the molecule at zero bias. The difference remains at applied bias due to the polarization of the molecular orbitals in the open form of the molecule, and the resulting suppression of the corresponding peaks in the transmission function. From this analysis we conclude that the polarization of the molecular orbitals is of paramount importance. Therefore in order to get even qualitatively correct results for the conductance under finite bias a self-consistent approach is necessary. Although this paper deals with only one specific system, it is reasonable to expect that our conclusion is generally valid for calculations of molecular conductance at finite bias.

COMPUTATIONAL METHODS

We performed electronic structure and geometry optimization calculations with the DFT code SIESTA.²⁹ SIESTA utilizes norm-conserving, nonlocal Troullier-Martins pseudopotentials³⁰ for the core electrons, together with an efficient numerical atomic orbital basis set³¹ for the valence electrons. The exchange-correlation energy functional is approximated with the PBE³² form of the generalized gradient approximation (GGA). The electronic transport calculations were carried out with the SMEAGOL code,^{33–35} that interfaces the NEGF scheme for transport,^{27,33–36} with the DFT numerical implementation contained in SIESTA.

In a transport calculation, the system is divided into three parts: a left lead, a scattering region, or a scattering center (SC) and a right lead. The SC is defined as the region of space where scattering takes place, that is, where the electrostatic potential deviates from that of the electrodes (periodic). This typically contains the molecule of interest and a number of atomic layers of the leads large enough for the electron screening to be effective. SMEAGOL then calculates the SC Green's function

$$G(E, V) = [E + i0^+ - H(V) - \Sigma_L(E, V) - \Sigma_R(E, V)]^{-1} \quad (2)$$

that enters into a self-consistent procedure leading to the non-equilibrium charge density in the scattering region and the electrostatic potential drop.^{33–35} In eq 2, $H(V)$ is the Hamiltonian of the SC (a functional of the charge density), V is the applied potential (bias), E is the energy, and Σ_α ($\alpha = L, R$) are the energy- and bias-dependent self-energies of the electrodes.³⁵ The latter describe the interaction of the SC with the electrodes and establish the appropriate boundary conditions to the problem. Once the self-consistent procedure is converged, the transmission function can be evaluated from the Landauer-Büttiker formula as

$T(E, V) = \text{Tr}[\Gamma_L(E, V)G(E, V)\Gamma_R(E, V)G^\dagger(E, V)] \quad (3)$

where $\Gamma_\alpha(E, V) = i(\Sigma_\alpha - \Sigma_\alpha^\dagger)$ is the broadening matrix for lead α . The transmission function of eq 3 can be integrated over the bias window to yield the current $I(V)$

$$I(V) = \frac{2e}{h} \int_{-\infty}^{\infty} T(E, V)[f(E - \mu_L) - f(E - \mu_R)]dE \quad (4)$$

Our calculations then proceed as follows. First, the equilibrium structures of the two molecular configurations in vacuum are found by coordinate optimization. The molecule is subsequently inserted into the scattering region, which consists of five layers of Au[100] (3×3 atoms per layer) on each side of the molecule. For the electrodes, we assumed the experimental value of the Au bulk lattice parameter. Further, we chose to anchor the molecule to the leads at the hollow site of the (100) surface, since this is the energetically preferred site. The distance between the Au surface and the S end atom, the anchoring distance, was also calculated by relaxation and found to be 1.93 Å for the closed molecule, in agreement with earlier results.^{13,16,18} In regard to the open molecule, the relaxed anchoring distance was found to be somewhat smaller, 1.81 Å. We performed conduction calculations for the open molecule with both anchoring distances in order to facilitate comparison. We used a double ζ plus polarization orbital basis set for all the atoms in the molecule. In contrast, the Au atoms in the leads were treated at the level of single ζ orbitals for the 5d electrons and double ζ orbitals for the 6s electrons plus a 6p polarization orbital. Because the scattering region is quite large (110 atoms), the conduction calculations become rather time consuming. Therefore, we also employed a smaller basis for the Au atoms, consisting of only double ζ 6s orbitals. Previous calculations show that such a reduced basis can indeed reproduce

reasonably well the *I*-*V* characteristics calculated with a full Au *spd* basis set up to about 2 V,³⁷ and we come to a similar conclusion (see Supporting Information).

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Supporting Information Available: Results for the minimal Au 6s basis set. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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