Molecular Switches

DOI: 10.1002/ange.201311134

Frontier Orbital Control of Molecular Conductance and its Switching**

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Abstract: *For transmission of electrons through a π system, when the Landauer theory of molecular conductance is viewed from a molecular orbital (MO) perspective, there obtains a simple perturbation theoretic dependence, due to Yoshizawa and Tada, on a) the product of the orbital coefficients at the sites of electrode attachment, and b) the MO energies. The frontier orbitals consistently and simply indicate high or low transmission, even if other orbitals may contribute. This formalism, with its consequent reinforcement and/or interference of conductance, accounts for the (previously explained) difference in direct vs. cross conjugated transmission across an ethylene, as well as the comparative ON/OFF ratios in the experimentally investigated dimethyldihydropyrene and dithienylethene-type single-molecule switches. A strong dependence of the conductance on the site of attachment of the electrodes in a π system is an immediate extrapolation; the theory then predicts that for some specified sites the switching behavior will be inverted; i.e. the "open" molecular form of the switch will be more conductive.*

Dramatic advances in the fabrication of electrode–molecule–electrode junctions, for example mechanically controllable and scanning tunneling microscopy-based break junctions,[1] have opened the door to measurements of the conductance of individual molecules.[2] Switching comes next to mind, thus bistable molecules, whose electronic and geometrical structures can be reversibly changed by external stimuli such as light and heat.[3] In this context, a series of diarylethene molecules have attracted considerable attention, due to their thermal stability and fatigue resistance.[4]

Abruña, Ralph and co-workers measured light-induced conductance switching of dithienylethene derivatives connected to gold electrodes through pyridine anchor units, as schematically shown in Figure 1 a.[5,6] They observed an ON/OFF ratio of at least 30 between the high-conductance closed-ring extended π-system form and low-conductance open-ring form. Complementary density functional theory calculations by the Chan group indicated an ON/OFF ratio of approximately 2 orders of magnitude. These values agree roughly with earlier experimental and theoretical results on diarylethene switches.[7–9]

In a quite independent study Royal, Wandlowski and co-workers measured the transformation between high-conductance closed-ring dimethyldihydropyrene (DHP) and low-conductance open-ring cyclophanediene (CPD) derivatives (Figure 1 b), a change induced by a combination of optical and thermal stimuli.[10] They also employed pyridine anchor units to connect to gold electrodes. A reversible ON/OFF ratio greater than 4 orders of magnitude was measured.

Here, we use simple Hückel molecular orbital (HMO) calculations, combined with the Green's function theory of conductance,[11,12] and the theoretical framework introduced by Yoshizawa and Tada,[13] to understand the higher ON/OFF ratio for the DHP/CPD couple compared to the dithienylethene case. We demonstrate that the phase and amplitude of the frontier molecular orbitals (FMOs)[14] at the sites that are connected to electrodes determine the essential features of the switching behavior. The simple theory further allows some striking predictions of the site specificity of the ON/OFF ratio across π-systems, spanning a range from a large difference, little difference, to even inverted behavior, where we predict the open-ring form to be more conductive.

Before we study the switches, however, let us illustrate our approach with a simple case that rehearses a theoretical result already in the literature,[15,16] seen here in perhaps a new light. This is transmission or conductance 1,2 vs. 1,1 across a double bond, **1** vs. **2** (Figure 2).

The π-electron system of ethylene could not be better known; the MOs are shown in **3**; here a filled circle is one phase of the top of the 2p orbital at a given C, an unfilled circle the opposite phase. When one computes the transmission spectrum (see Figure S1 in the Supporting Information), one obtains substantial transmission for situation **1**, and interference, small transmission (especially for 0 bias) for **2**.

Why is there this difference in transmission for direct and cross-conjugation, much diminished for the latter case? Ratner, Solomon, and co-workers have explained the interference in the cross-conjugated case through an analysis of local atom to atom transmission channels;[15] we find our way to a parallel explanation (which we will extend to the switching systems).

Details of the method we use, basically Landauer's theory of conductance in a Green's function formalism,[11,12] as implemented by the Yoshizawa group,[13] are described in the Supporting Information. The electrodes are assumed to be metallic gold. We defined the midpoint in energy between the energy of the highest occupied molecular orbital (HOMO) and that of the lowest unoccupied molecular orbital (LUMO) of the isolated molecule as the Fermi energy (E_F). This placement of the Fermi level may be problematic when there is significant charge transfer between electrode and mole-

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[**] We are grateful to Kazunari Yoshizawa and Mark Ratner, and to an anonymous reviewer of an earlier version of this manuscript for their comments. Y.T. thanks The Japan Society for the Promotion of Science for a JSPS Research Fellowship for Young Scientists. Our work at Cornell was supported by the National Science Foundation through Grant CHE-1305872.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201311134.

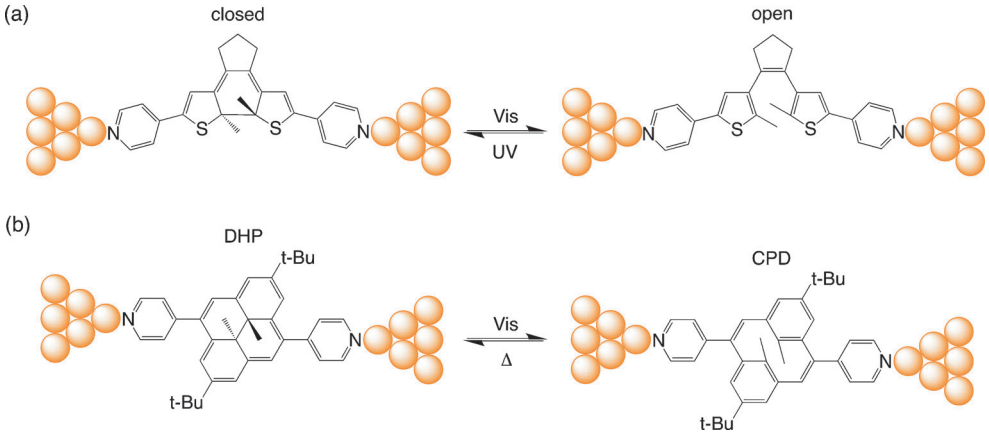

Figure 1. Schematic representation of isomerization reactions of pyridine-terminated a) dithienylethene and b) the DHP/CPD system, both between Au electrodes.

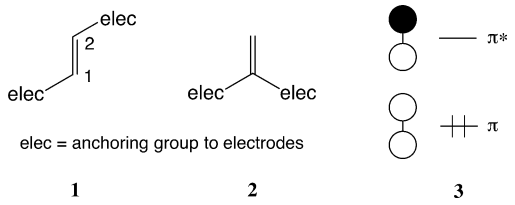

Figure 2.

cule,[17] but since the 6s atomic orbital (AO) in the gold electrode (−10.9 eV) is close in energy to a 2p AO in carbon (−11.4 eV), it is reasonable to assume that the Fermi energy lies between the HOMO and LUMO of most conjugated hydrocarbons.[18]

When gold electrodes are connected at sites r and s of a molecule, the conductance is proportional to the square of the absolute value of the matrix element of Green's function at the Fermi energy, $G_{rs}(E_F)$.[12] The Green's function is approximately proportional to the zeroth order Green's function, which has the following form:[19,20]

$$G_{rs}^{(0)}(E_F) = \sum_k \frac{C_{rk}C_{sk}^*}{E_F - \varepsilon_k + i\eta}, \quad (1)$$

where C_{rk} is the coefficient of the rth AO in the kth MO in an orthogonal basis, ε_k is the kth MO energy, and η is an infinitesimal positive number. Since the Fermi level is assumed to lie in-between the FMO energy levels, the zeroth order Green's function for low bias is likely to be dominated by the contributions from the FMOs, though other levels may contribute.

Returning to the ethylene case, the contributions from the HOMO (π) and LUMO (π*) can be written schematically as

$$\frac{C_{1,\pi}C_{2,\pi}^*}{E_F - \varepsilon_\pi + i\eta} + \frac{C_{1,\pi^*}C_{2,\pi^*}^*}{E_F - \varepsilon_{\pi^*} + i\eta} \approx \frac{(+)(+)}{(+)} + \frac{(+)(-)}{(-)} \quad (2)$$

for the 1,2 case, and

$$\frac{C_{1,\pi}C_{1,\pi}^*}{E_F - \varepsilon_\pi + i\eta} + \frac{C_{1,\pi^*}C_{1,\pi^*}^*}{E_F - \varepsilon_{\pi^*} + i\eta} \approx \frac{(+)(+)}{(+)} + \frac{(+)(+)}{(-)} \quad (3)$$

for the 1,1 case. In the estimation of the sums (+) means a positive contribution, (−) a negative one.

The contributions of HOMO and LUMO reinforce for the 1,2-case and interfere in the 1,1-case.

As mentioned, Ratner, Solomon and their co-workers, and Tada and co-workers, as well as others have already analyzed this system in detail;[15,16] we present it here only as an illustration of the frontier orbital approach. Site-specific quantum interference across another simple molecule, benzene, in particular a dramatic differential between *meta* and *para* linkages, has been studied experimentally by the Venkataraman group[21] using a conductive atomic force microscope, and the van der Zant group using a mechanically controlled break-junction technique.[22] Interference in the benzene system has been the subject of many theoretical calculations;[23] Yoshizawa and co-workers have applied to this case (and to a variety of other differentially transmittive molecules) the same simple frontier orbital analysis we use.[13]

We now turn to the case of the diarylethylene switches, first DHP/CPD.[24] The Landauer model of conductance[11,12] implies that the conductance of a metal–molecule–metal junction in the limit of zero temperature and zero bias voltage is proportional to the transmission probability at the Fermi energy. Figure S2 shows that DHP is calculated to have high transmission probability at the Fermi energy ($E = 0$), whereas the CPD transmission probability is low. These computational results are qualitatively consistent with the experimental data of Royal, Wandlowski and co-workers.[10] We will soon make the estimate of the ON/OFF ratio more quantitative, but let's quickly see how the FMO analysis explains the qualitative difference in transmission probability.

The Hückel π MOs of DHP and CPD are shown in Figure 3. Both open and closed forms are alternant hydrocarbons, so filled and unfilled orbitals are paired in energy and have complementary orbital coefficients.[25] In the Hückel model, DHP is a cyclic polyene, so there are degeneracies in the MOs; these would be lifted (slightly) in a better calculation.

In the experiment of Royal, Wandlowski and co-workers,[10] sites 3 and 8 are connected to gold electrodes through pyridine anchor units. The FMO coefficients at these sites then play a crucial role in determining the conductance. The analysis (shown in detail in the Supporting Information) is no more complicated than for the ethylene case—the contributions from the FMOs of DHP reinforce, while those of CPD interfere. A positive (and large) ON/OFF ratio results.

So far we have rehearsed what is known. But what if connection is made at sites other than the one studied experimentally? We will next show that the selection of

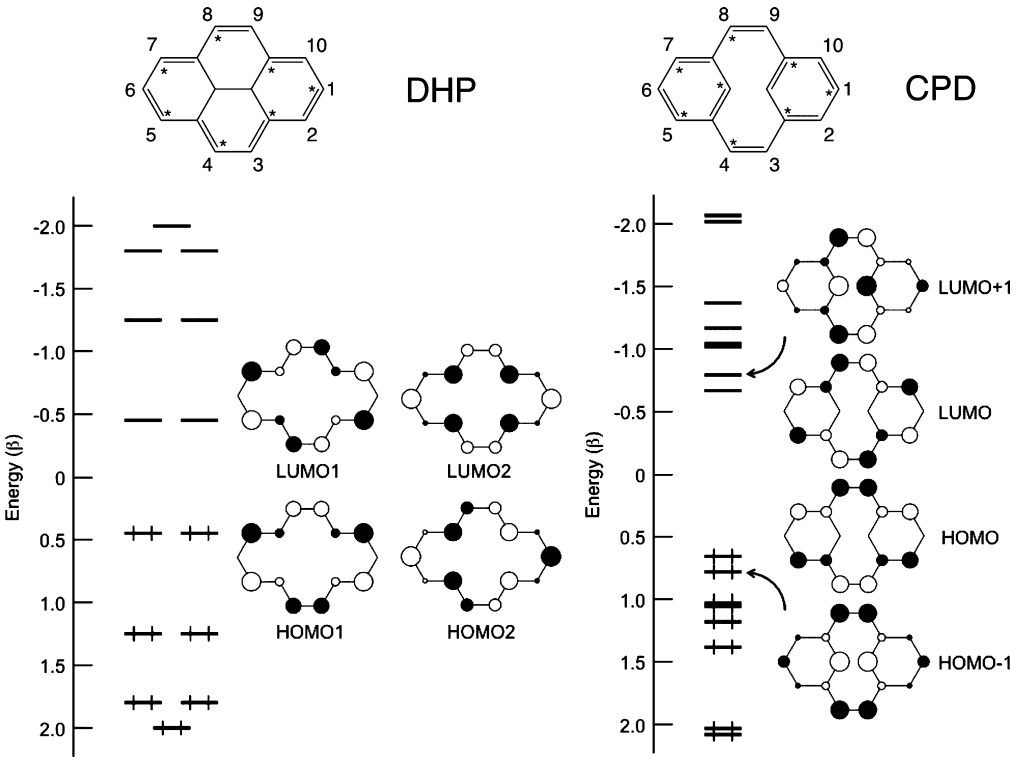

Figure 3. The Hückel MOs of DHP (left) and CPD (right). The shape of the FMOs is indicated qualitatively; the black and white circles indicate orbital phases of the tops of the 2pπ orbitals at a given C; the circle areas are proportional to the respective coefficient sizes.

electrode connection sites in a molecule should significantly affect the ON/OFF ratio of a molecular switch. Attachment site selectivity in molecular conductance is, of course, not new;[2,13] a particularly striking observation is in the naphthalene system.[26]

Figure 4 shows the calculated connection-site specificity of the ON/OFF ratio of the DHP/CPD system as a function of bias voltage.[27] Here the ON/OFF ratio is defined as $I_{DHP}(V)/I_{CPD}(V)$, where $I_{DHP}(V)$ and $I_{CPD}(V)$ are bias-dependent currents through DHP and CPD, respectively (see the Supporting Information for the way the currents are calculated; in each case we estimated the nonplanarity of the open form of the conducting system).

To be a good switch, not only does one need a good ON/OFF ratio, but also good transmission in the ON form. For this reason we do not include in the graph (though as a check we have calculated them, see Supporting Information) connections with low conductance in both open and closed forms—those between starred and starred atoms (the language is that of alternant hydrocarbons), and unstarred with unstarred. Such connections, for example, 1–4, 1–5, 2–3, 2–6, 2–9, 2–10, 3–9 are automatically subject to cancelling interference due to the coefficient/energy pairing of alternant hydrocarbons.[25,26,28]

Looking at the connections where at least one of molecular forms has a high calculated transmission, we find that where the electrodes are attached 1–6, 1–3, and 3–8, we expect high ON/OFF ratios, decreasing with increasing bias. The predicted 3—8 ratio of our model is substantially higher than that observed. The predicted ON/OFF ratios for the switches form an upper limit in the cases where interference is evident in the OFF state. This is because non-nearest neighbor coupling terms and interactions beyond mean-field can shift interference features away from the mid-gap position,[15] i.e. the assumed Fermi level in our simple model, resulting in the increase in transmission probability of the OFF state. Connections 2–7, 2–5, 2–4, and 2–8 are expected to show a low ON/OFF ratio. In these cases, transmission probabilities around the Fermi energy for both DHP and CPD are high, paralleling each other, although the transmission probability for DHP in each case is slightly larger than that for CPD. For 1–2 connection the transmission probabilities are nearly the same. And connection 3–4, quite surprisingly, is predicted to show moderate "inverted" switching behavior, with the ring-opened CPD slightly more conductive than the ring-closed DHP.

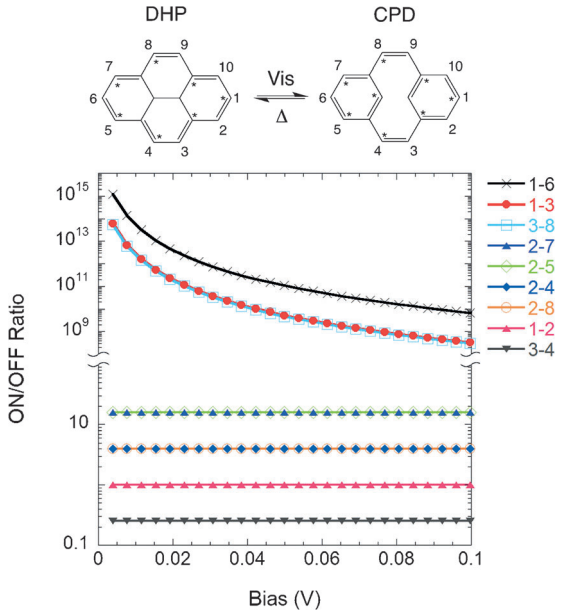

Figure 4. Connection-site specificity of the ON/OFF ratio of the DHP/CPD system as a function of bias voltage. The colored legend numbers refer to the site of electrode attachment.

In each case, we can carry out a qualitative, HOMO/LUMO-based analysis of the transmission—the outcome is that the frontier orbitals (HOMO/LUMO nearby HOMO+1/LUMO−1) are a guidepost to the overall ON/OFF ratio. For instance, for the interesting case of the inverted conductance for a 3–4 junction, the contributions to the conductance in the open CPD form from the HOMO and HOMO−1 reinforce (as do those from the corresponding LUMOs), while for the closed DHP isomer, the contributions of HOMO1 and HOMO2 are of opposite phase.

The analysis we carry through is simplified. There are some cases with small LUMO/HOMO coefficients where the contributions of lower lying occupied/higher lying unoccupied orbitals are important, and lower the transmission at the Fermi level in the CPD form to zero. Conversely, there are also cases where the contributions of lower lying occupied/higher lying unoccupied orbitals increase the transmission at the Fermi level and may obscure interference features.[29,30] But in general the frontier orbitals are a good guide to what happens.

The experimentally studied dithienylethene system may be analyzed in a similar manner. Figure 5 shows the computed connection-site specificity of the ON/OFF ratio, $I_{closed}(V)/I_{open}(V)$, of a dithienylethene molecule as a function of bias voltage. In the experiment by Abruña, Ralph and co-workers,[5] sites 1 and 6 are connected to gold electrodes. Although this connection has a relatively high ON/OFF ratio among alternatives in the dithienylethene molecule, this ON/OFF ratio is much smaller than that of connection 3–8 in the DHP/CPD system. This is qualitatively consistent with experiment. Since the dithienylethene molecule includes hetero atoms and five-membered rings, the pairing theorem[25] with respect to the MO energies and MO coefficients does not apply. As a consequence, the extensive reinforcement and cancellation of the zeroth Green's function that occurs for DHP/CPD (see discussion in the Supporting Information) cannot occur in the dithienylethene molecule, resulting in smaller ON/OFF ratios.

For this system, connections 3–4, 2–4, and 1–4 are predicted to show inverted switching behavior, where the open-ring isomer is calculated to be more conductive than the closed-ring isomer. The large inverted ON/OFF ratio of 4 orders of magnitude for the 3–4 connection begs for an explanation. Let us concentrate on the HOMO and LUMO here (see Figure 6 for energy levels and sketches of FMOs; the calculations took account of the nonplanarity of the molecules).

Since the product of the MO coefficients on the two electrode connection in the HOMO is different in sign from that in the LUMO for both closed- and open-ring isomers, the HOMO and LUMO terms of the zeroth Green's function have the same sign. Although this leads to the enhancement

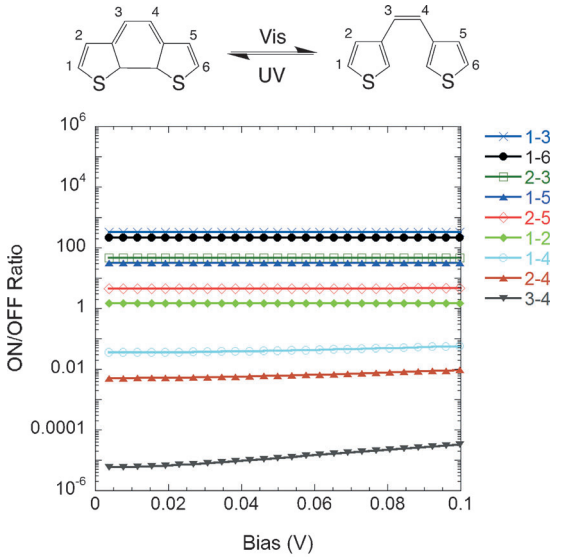

Figure 5. Connection-site specificity of the ON/OFF ratio of the dithienylethene system as a function of bias voltage. The numbers in the color legend refer to sites of attachment of electrodes to the molecule.

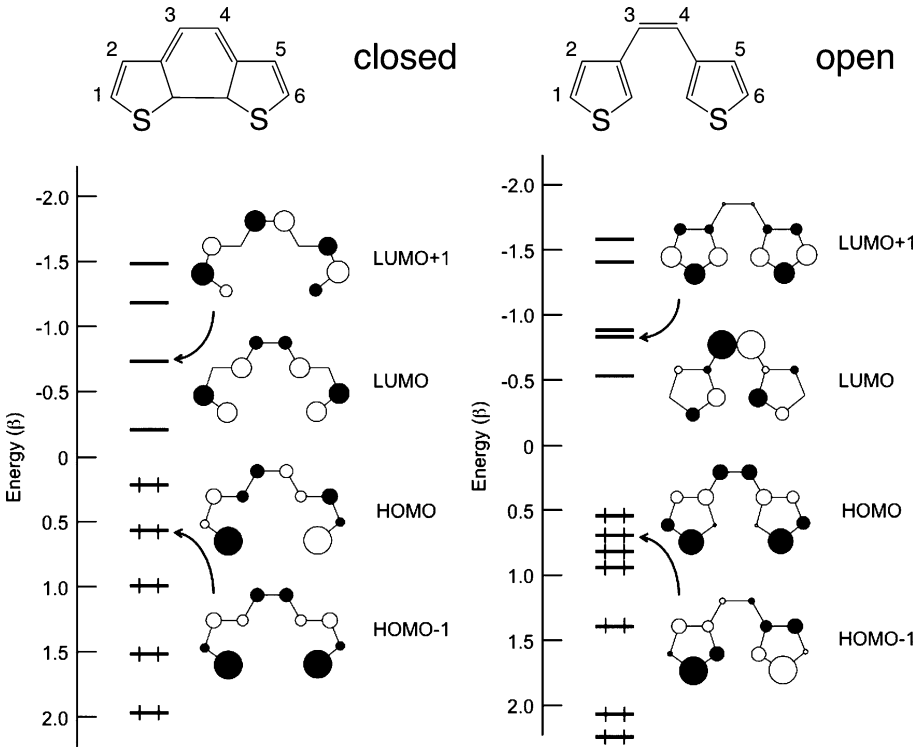

Figure 6. The Hückel MOs of the closed-ring form (left) and open-ring form (right) of dithienylethene. The shape of the FMOs is indicated qualitatively; the black and white circles indicate orbital phases; the circle areas are proportional to the respective coefficient sizes.

of the contributions from the HOMO and LUMO to the Green's function for both closed- and open-ring isomers, the amplitudes of the LUMO of the open-ring isomer on the connection sites are so large (see Figure 6 right) that the zeroth order Green's function for the open-ring isomer is much greater than the closed-ring isomer.

In summary, the phase and amplitude of the frontier molecular orbitals at the sites that are connected to electrodes[8,13] play an essential role in determining transmission through a π system. When applied to two diarylethene switches, a risky prediction of site-dependent inversion of conductance ensues.

Received: December 22, 2013
Revised: January 27, 2014
Published online: March 12, 2014

Keywords: frontier orbital control · interference effects · molecular conductance · molecular switches

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