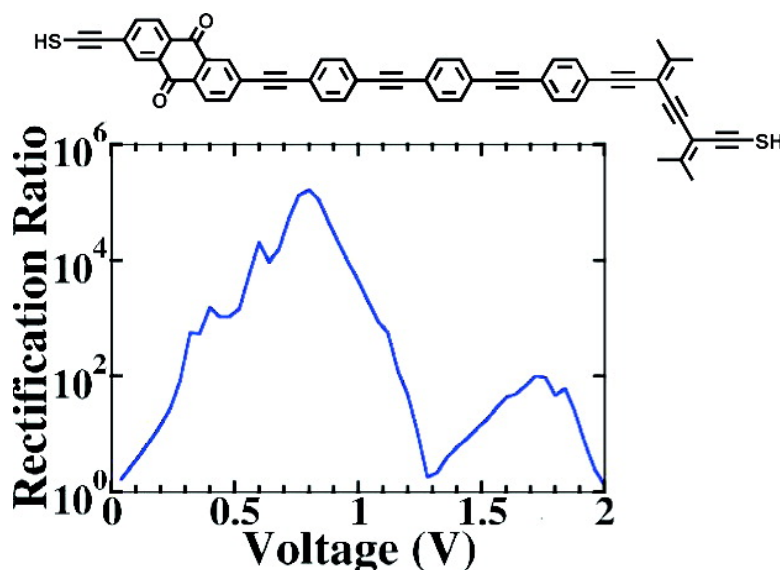


Single Molecule Electronics: Increasing Dynamic Range and Switching Speed Using Cross-Conjugated Species

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Single Molecule Electronics: Increasing Dynamic Range and Switching Speed Using Cross-Conjugated Species

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Abstract: Molecular electronics is partly driven by the goal of producing active electronic elements that rival the performance of their solid-state counterparts, but on a much smaller size scale. We investigate what constitutes an ideal switch or molecular device, and how it can be designed, by analyzing transmission plots. The interference features in cross-conjugated molecules provide a large dynamic range in electron transmission probability, opening a new area for addressing electronic functionality in molecules. This large dynamic range is accessible through changes in electron density alone, enabling fast and stable switching. Using cross-conjugated molecules, we show how the width, depth, and energetic location of the interference features can be controlled. In an example of a single molecule transistor, we calculate a change in conductance of 8 orders of magnitude with an applied gate voltage. Using multiple interference features, we propose and calculate the current/voltage behavior of a molecular rectifier with a rectification ratio of $>150\,000$. We calculate a purely electronic negative differential resistance behavior, suggesting that the large dynamic range in electron transmission probability caused by quantum interference could be exploited in future electronic devices.

1. Introduction

Further miniaturization of electronic devices will require fundamental advances in our approach to building and designing electronic components. Electron transfer^{1–3} is of fundamental importance in broad areas of research encompassing both natural⁴ and artificial systems.⁵ The use of molecules as discrete electronic elements was initiated by the proposal of a single molecule rectifier.⁶ Since this proposal, a number of single molecule electronic devices have been constructed with varied behaviors,⁷ including switching,⁸ rectification,^{9–11} coulomb blockade,¹² Kondo resonance,¹² negative differential resis-

tance,¹³ and memory elements.¹⁴ A number of measurements have established single molecule transistor behavior in ultra-high-vacuum (UHV) conditions,^{15–19} as well as using electrochemical gate control.^{20–24} For single molecule switches, there are a number of theoretical studies on how molecular conformational change can lead to large conductance changes,^{25,26} including measurements using photochromic molecules.²⁷ Many methods for creating molecular switches rely on, or result in,

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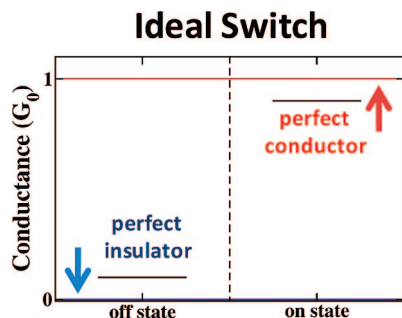


Figure 1. In an ideal switch, the off state would be a perfect insulator (blue line at $0 G_0$), and the on state would be a perfect conductor (red line at $1 G_0$). In a single transport channel, ballistic transport through a perfect conductor representing the on state is $1 G_0$, the quantum of conductance ($\sim 12.91 \text{ k}\Omega$)⁻¹.

conformational change to the molecule of interest.^{28–30} For fast and reproducible switching, and integration in useful devices, switching should not result in conformational change. Recent work has highlighted how this can be accomplished with hydrogen transfer in a naphthalocyanine molecule at low temperature, resulting in an on/off ratio of 2.⁸

All of the molecular devices proposed and measured to date hint at the wide variety of electronic functions that can be completed within a single molecule.³¹ Major drawbacks in comparison with solid-state devices include the low dynamic range in transport through single molecules and in the vibronic mechanisms²⁹ that result in slow switching speed.

In this work, we define the characteristics of an ideal switch, requiring large changes in electronic conductance, and show how its features could appear in a transmission plot. The rich palette of wave function patterns provided by unsaturated organic molecules provides many possibilities for purely electronic functional behavior.^{7,32,33} The interference features in cross-conjugated molecules³⁴ and the breakdown of the simple barrier tunneling model³⁵ provide a system that matches our device design criteria. Specifically, by changes in electron density alone, a wide dynamic range in electron transmission becomes accessible. We calculate how the interference features can be utilized to create molecular switches and transistors, rectifiers, or negative differential resistors.

2. Design Principles

2.1. Switch Design. In designing a single molecule electronic device, it is helpful to ask what transport behavior is necessary for a molecule to function as an ideal transistor (switch), memory element, or chemical sensor. Figure 1 shows the conductance

of a hypothetical single-channel device with well-defined on and off states. To aid in understanding, we have included a blue line to indicate a perfect insulator. The red line at $1 G_0$ indicates a perfect conductor, representing ballistic single-channel transport, where the probability of back electron scattering within the molecule is zero. This limit of $1 G_0$ is a direct result from quantum theory,^{36,37} has been measured in chains of Au atoms^{38,39} at high bias of $\sim 2 \text{ V}$,^{40,41} and has been verified in computational calculations.^{42,43} With the upper and lower bounds of conductance defined by a perfect conductor and a perfect insulator, it seems trivial that a perfect switch would be a perfect insulator in the off state and a perfect conductor in the on state (Figure 1). All molecules have a nonconstant transmission probability as a function of energy and can be considered a switch or transistor (because a change in bias or gate voltage leads to a change in conductance), albeit not necessarily a useful one. We define here the criteria for an ideal switch: (1) an infinite ratio of the on current/off current ($I_{\text{on}}/I_{\text{off}}$); (2) a subthreshold swing⁴⁴ of 0 mV/decade , indicating a switch that abruptly changes from the off state to the on state at a defined threshold voltage; (3) fast switching times that rely not on nuclear motion but only on changes in the relative electron density; (4) reproducibility and stability²⁹ by minimizing charging and geometric organization; and (5) low bias operation, energetically separated from a molecular resonance. While many other factors, including leakage current, threshold voltage, and cost, are extremely important, we focus our discussion on the five criteria listed above, specifically the $I_{\text{on}}/I_{\text{off}}$ ratio and the subthreshold swing.

2.2. Voltage Switch. In this section we discuss how the conductance through a molecule can switch as a function of voltage. In a two-probe single molecule junction, measurements are limited to the current as a function of voltage, along with the derivative and second derivative of the data. In charge transport calculations, we determine the transmission probability of an incident electron as a function of energy. Integration of the transmission probability over the range of chemical potentials of the left and right leads will give the current.³⁷ The transmission plots provide more details on the molecular causes of the I/V characteristics; therefore, we focus our discussion on understanding and controlling the electron transmission probability.

In Figure 2a, the transmission through a perfect conductor is shown in red, a perfect insulator in blue, and a candidate for a molecular switch in green. This hypothetical molecule behaves as a voltage switch where it is a perfect insulator near E_f , with a transmission probability $\cong 0$, and a perfect conductor at all other energies. Figure 2b is the same plot with the shaded area

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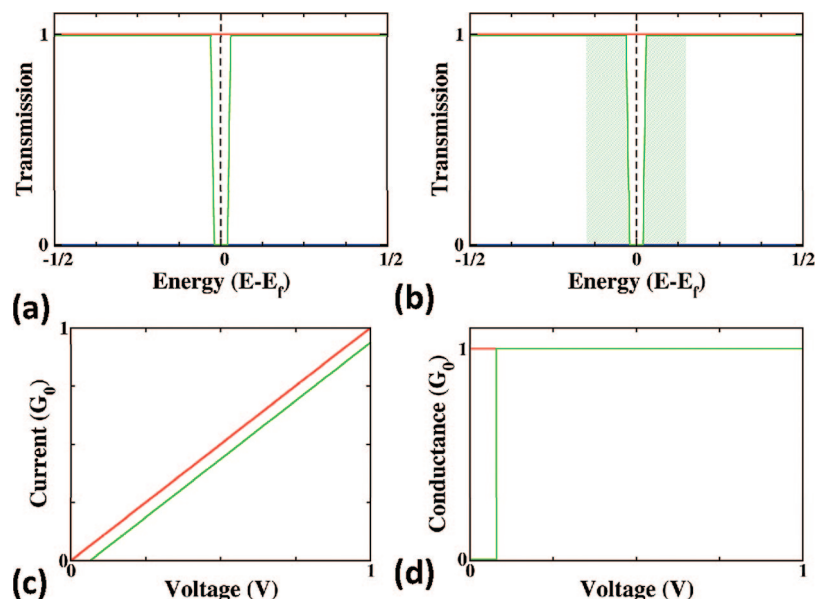


Figure 2. Transmission and current/voltage behavior of a voltage switch, shown schematically, where the conductance goes from 0 to $\sim 1 G_0$ as a function of voltage. The red line represents a Au wire, and the green line represents the molecule of interest. (a) The transmission plot for a potential device is shown in green, having an off state at and near $E = E_f$ and an on state at all other energies. (b) To calculate the current and conductance for panel a, the transmission plot (assuming invariance to applied voltage) is integrated between the chemical potentials of the leads, shown as the shaded region. (c) The current/voltage behavior realized by integrating the transmission plot in panel b. (d) The conductance as a function of voltage.

representing a discrete bias voltage applied across the molecular switch (assuming the bias shifts the chemical potentials symmetrically about E_f). The current is calculated by integrating the area under the transmission and is shown in Figure 2c. In Figure 2d, the conductance as a function of voltage is shown. In Figure 2d, the hypothetical molecule is switching from a low conductance state at low bias voltage to a high conductance state at high bias voltage.

2.3. Switching a Molecule. Having demonstrated what represents an ideal transmission function for a single molecule with on and off states, we now show a few possible scenarios of how this transmission function can be manipulated to achieve switching behavior. In a three-terminal measurement, the maximum $I_{\text{on}}/I_{\text{off}}$ ratio for a specific molecule is defined as the transmission probability at the energetically closest frontier molecular orbital/the transmission probability at the Fermi level.⁴⁴ When the incident electron energy corresponds to a molecular resonance, the elastic transmission probability is $\cong 1$. To get a large dynamic range, we thus need to create molecular systems where the transmission probability also goes to zero. A molecular insulator has a very low conductance state at the Fermi level, and the energetically closest resonance should have a transmission probability of ~ 1 . This would indicate that an imperfect molecular insulator might be an ideal electronic device—for example, a molecule with saturated alkane groups. We use such a molecule as one of our reference points in the following calculations. The energetic separation of the nearest molecular resonance and the Fermi level defines the subthreshold swing. To create functional devices, we would like to combine a transmission probability $\cong 0$ at the Fermi level with an energetically nearby molecular resonance. In Figure 3b, we show how a gate voltage may shift the transmission zero away from the Fermi energy. For a functional transistor, this behavior would be ideal because, at very low source–drain voltage, an applied gate could switch the molecule from an on state to an off state.

Figure 3c,d represents two possible scenarios that can occur in a chemical sensor device. In Figure 3c, a chemical reaction,

photoisomerization, or possibly a change in the number of electrons on the molecule causes a very large change in the transmission function. A large change in the molecule of interest would make reproducible switching more difficult to control in a device. While not ideal for fast, repetitive switching, this method of charging a device may provide a route to creating a functional memory device with distinct on/off states representing bit storage. Figure 3d represents a shift of the molecular orbital energies upon chemical or physical binding of a molecular group, switching the molecule from an off conductance state to an on conductance state. It is also conceivable that smaller shifts in the transmission spectrum would allow sequential detection of multiple molecules. Calculations showing the effects of both gating (b) and the tuning of a transmission feature (d) will be shown in the following sections.

3. Cross-Conjugation

Quantum interference provides a new opportunity to reinvestigate molecular electronic elements. The sparse density of electronic states in organic molecules stands in sharp contrast to traditional metals or semiconductors and is promising for controllable interference. In recent work, we have shown that cross-conjugated molecules can have a large dip in the electron transmission probability due to interference between electron transport pathways in energetic space.^{45,46} Cross-conjugation dictates the directionality of the coupling across a double bond. According to Phelin and Orchin, “A cross-conjugated compound may be defined as a compound possessing three unsaturated groups, two of which although conjugated to a third unsaturated center are not conjugated to each other.”³⁴

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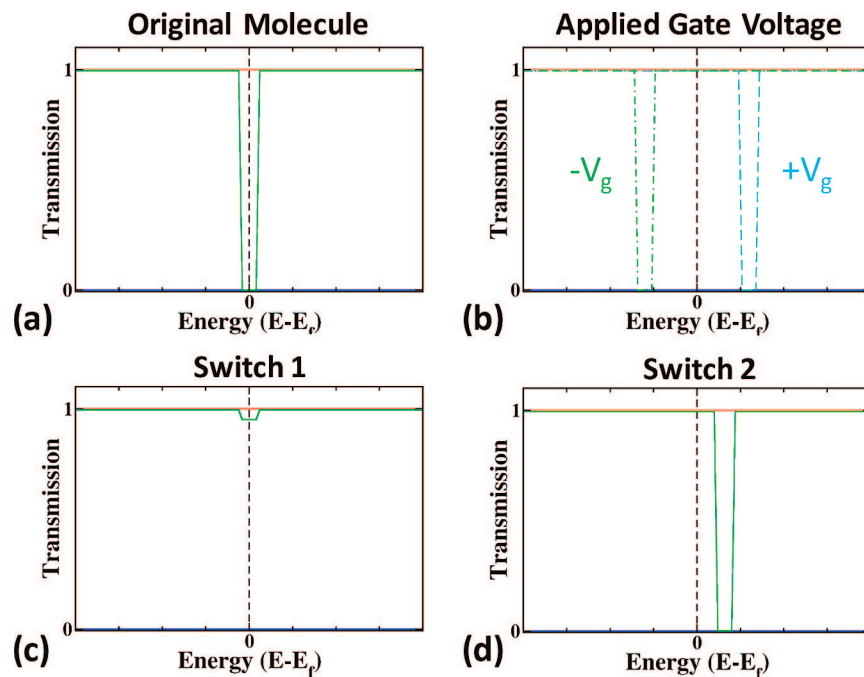


Figure 3. (a) Transmission of our hypothetical molecule with distinct on and off states, shown again as the green line. The molecule is subsequently switched in three different ways from a low conductance state to a high conductance state at low bias voltage. (b) A situation where an applied gate voltage might shift the dip in the transmission spectrum away from the Fermi energy, shown as the green and blue dashed lines. (c) A large change in the molecule occurs, causing the transmission to drastically change. (d) A molecular interaction event or change in electron density in the molecule could shift the transmission spectrum.

We have shown, using model systems, that any site energy not directly between the source and drain will cause interference features in the transmission.⁴⁷ Most of these interference features occur at energies outside the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap. What makes cross-conjugated molecules intriguing from a molecular electronics point of view is the location of the interference feature at or near the Fermi energy in an experimentally relevant location.^{45,47} There is a large synthetic knowledge base regarding cross-conjugated molecules,⁴⁸ indicating that this molecular motif may provide a unique new area for designing electronic devices.

In previous work, we calculated the dynamic range in transmission probability accessible near the Fermi level to be ~ 9 orders of magnitude.⁴⁵ This large variation in transmission probability is attributed to interference canceling transport through the π system.⁴⁵ This interference behavior opens the possibility of having a molecule that acts like an insulator (alkane) at low bias and a π -conjugated molecule at slightly higher bias. The HOMO and LUMO energy levels are unrelated to the presence of an interference feature; thus, it is conceivable to design a conjugated molecule with a small HOMO–LUMO gap and extremely low midgap conductance. This behavior matches well with the specifications that we showed earlier in Figures 2 and 3.

4. Methods

Our work focuses on calculating transport through single molecules in the Landauer–Imry low-bias tunneling regime.^{49–52} In the low-bias tunneling limit, we assume that the electron does not spend a significant amount of time on the molecule in the junction, leaving the molecule in the neutral state. In the molecules that we analyze here, the interference generally occurs within the HOMO–LUMO gap, energetically separated from molecular resonances.

All molecular structures were geometry optimized in the absence of gold electrodes using density functional theory (DFT), using B3LYP^{53,54} and 6-311G** in QCHEM 3.0.⁵⁵ The gas-phase molecules were chemisorbed (terminal hydrogens removed) to the face-centered cubic hollow site of a Au(111) surface with the Au–S bond length taken from the literature.⁵⁶ All transport calculations were initially done using Hückel-IV 3.0^{43,44,57} due to the speed of the calculation. The results from Hückel-IV 3.0 have been shown to be quite consistent⁴⁵ with those obtained using the more computationally intensive density functional transport codes such

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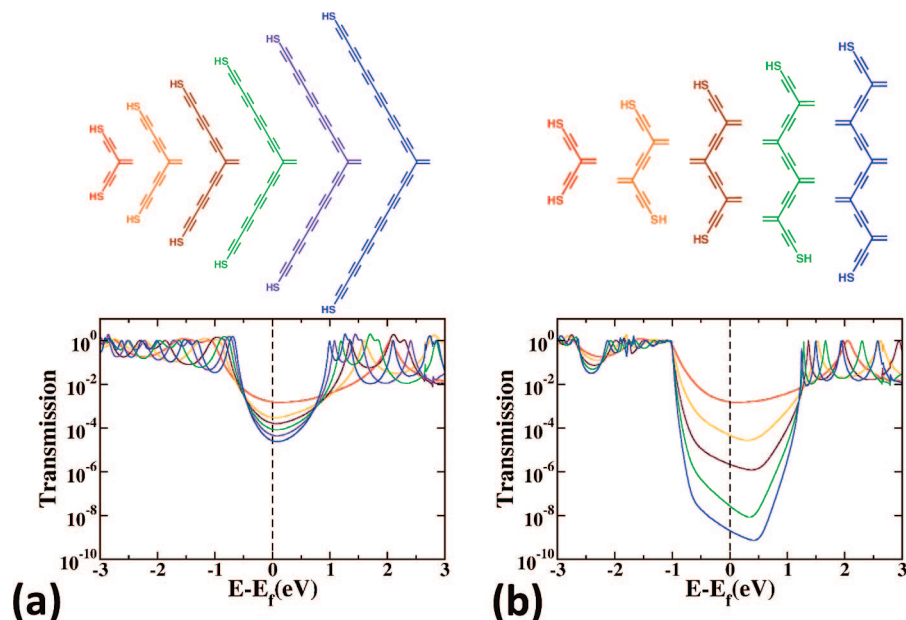


Figure 4. Behavior of the HOMO and LUMO energies and the interference minimum with increasing molecular length. (a) In the series of molecules shown, one triple bond is added to both ends of the molecule. This increased conjugation length leads to a smaller HOMO–LUMO gap and a small decrease in the transmission minimum. (b) A cross-conjugated unit and a triple bond are added, leading to little change in the HOMO–LUMO gap but a large decrease in the transmission minimum.

as gDFTB^{58–63} and ATK.^{42,64–67} We used gDFTB to analyze the symmetry components of the transport, and we used ATK to simulate an applied gate voltage. In both cases, the Hückel-IV calculation is shown for comparison. In situations where we calculate interesting transport behavior, it is verified using density functional calculations as indicated in the text. In the work described in this article, all of our calculations were completed on the geometry-optimized structure; however, using molecular dynamics coupled to transport calculations,⁶⁸ the interference features have been shown to be stable to geometric fluctuations and the breaking of symmetry.^{45,47}

The use of three transport codes allows for verification of results over a range of methods. Common among the three methods are the use of one-electron Hamiltonians and nonequilibrium Green's function methods for the transport. Both Hückel-IV and ATK calculate the full 3D self-consistent potential under voltage bias. Hückel-IV 3.0 uses extended Hückel molecular orbitals and a relatively small Au electrode pad of three atoms on each end of the molecule. It is also the fastest computationally. gDFTB is a tight-binding DFT program. Due to the computational benefits of

self-consistent parametrization, this code allows for analysis of very large systems, including large physical electrodes. The gDFTB program has symmetry implemented, allowing a detailed analysis of the results. ATK is currently the state-of-the-art DFT commercial transport package. ATK is run using a DZP (SZP for Au) basis set using the LDA functional.

The gate voltage is calculated within the ATK code by shifting the part of the Hamiltonian that remains when the electrode and surface atoms are removed, which assumes an external electrostatic potential localized to the molecular region and not a physical electrode.⁶⁷ In this calculation, the gate is not included as a physical electrode, but solely as a shift in the energy levels. The actual gating effect may deviate substantially from this idealized model. Experimental methods of gating a molecule could utilize previous techniques or a third electrode in UHV^{12,15–19} or with electrochemical control.^{20–24}

5. Controlling Interference Features

In Figure 4, we show two series of molecules with increasing carbon backbone length. In Figure 4a, we add a pair of triple bonds symmetrically to a cross-conjugated molecule. Shown in Figure 4b is a series of molecules where the cross-conjugated backbone has been synthesized,^{48,69} made with an increasing number of cross-conjugated units separated by triple bonds. Comparing the position of the HOMO and LUMO for the molecules shown in panels a and b, there is a noticeable difference in the energy shift of the resonances near -1 and 1 eV. In Figure 4a, the addition of two triple bonds to the molecule increases the length of electron delocalization and decreases the HOMO–LUMO gap. In Figure 4b, with the addition of a cross-conjugated bond and a triple bond, the HOMO level remains unchanged and the LUMO orbital shifts slightly, lowering the energetic gap. This behavior is indicative of the cross-conjugated unit breaking electron delocalization.^{70–73}

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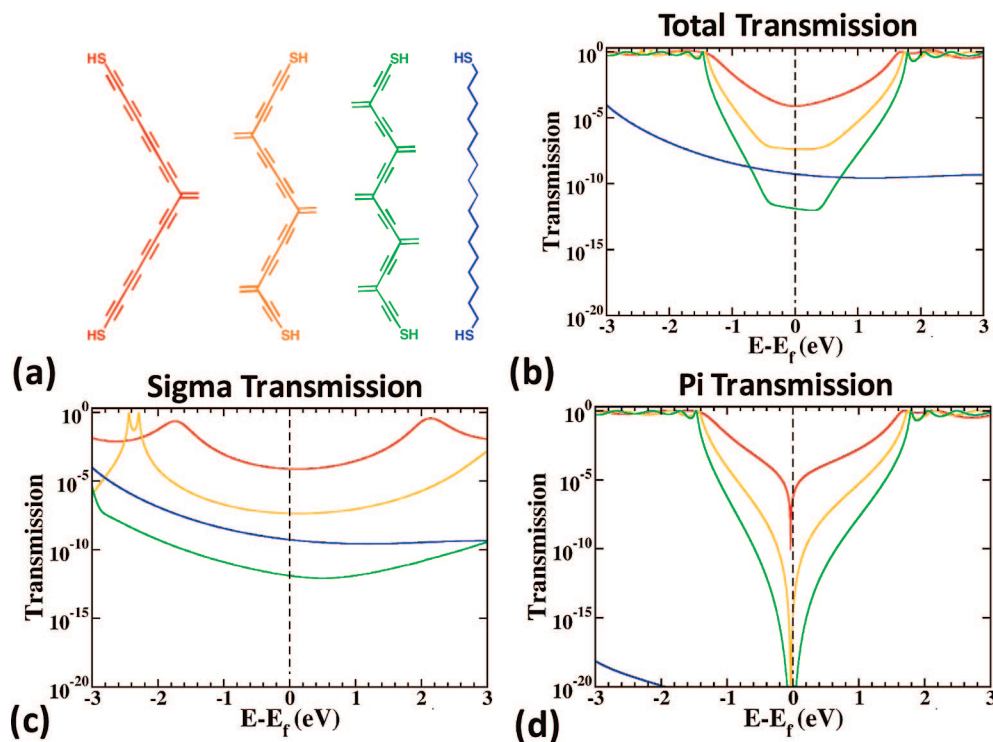


Figure 5. All calculations in these plots were done using gDFTB to differentiate between the σ and π transport. (a) Four molecules with a 17-carbon-atom backbone are shown: three conjugated molecules with one, three, and five cross-conjugated units, and one saturated carbon chain. (b) The total transmission through the four molecules is shown with ~ 8 orders of magnitude variation in transmission at E_f . (c) The σ transmission at E_f decreases ~ 2 orders of magnitude for each added cross-conjugated bond. The kinks in the carbon backbone in the cross-conjugated molecule decrease the σ coupling. (d) The π component of the transmission: both the depth and the width of the interference feature increase sharply with added cross-conjugated units.

As the transmission near π -electron-dominated interference features in cross-conjugated molecules is determined by the σ transport, we need only lower the σ coupling across the molecule to lower the transmittance minimum. In Figure 4a, the increased electrode separation caused by the additional triple bonds results in a relatively small reduction in the interference minimum. In Figure 4b, the transmission minimum decreases ~ 1.5 orders of magnitude for each three-carbon-atom repeat unit added. This is a much greater sensitivity to length than in Figure 4a, where each pair of triple bonds decreases the transmission ~ 0.3 order of magnitude for each repeat unit.

To address the different behavior of these two classes of molecules, we calculated the transmission for a series of molecules with 17 carbon atoms in the backbone, shown in Figure 5a. All plots in Figure 5 are calculated in the gDFTB code so that a symmetry analysis⁷⁴ could be completed (details and calculations using Hückel-IV are given in the Supporting Information). From the plot shown in Figure 5a, it seems that increasing the number of cross-conjugated units increases both the width and the depth of the interference feature. To separate the contributions from decreasing σ coupling across the molecule and the increasing number of cross-conjugated units, we have included a plot of the σ transport through all four molecules in Figure 5c. This plot indicates that it is the σ transport and not

the number of cross-conjugated units that defines transmission near the minimum. Thus, at low bias, it is possible to directly measure the σ transport in conjugated molecules. Cross-conjugated molecules may thus provide a template for studying σ transport through bridged molecules, including alkene, alkyne, and aryl systems.

6. Tuning the Interference Location: Simulation of Gate Control or a Molecular Switch

To investigate the sensitivity to changes in electron density, we investigate the effects of attaching electron-withdrawing and electron-donating groups. These calculations were all completed using Hückel-IV (the corresponding calculations using ATK are shown in the Supporting Information). Using a known molecular scaffold⁷⁵ with a single cross-conjugated unit, we calculated the change in transmission upon binding a series of electron-donating and electron-withdrawing groups to the cross-conjugated unit.

Figure 6a shows the effect of increasing the electron-withdrawing strength of groups bonded to the cross-conjugated unit. The electron-withdrawing groups have two major effects on the transmission near the Fermi level. The first effect is the movement of the LUMO resonance from ~ 1.5 eV for the hydrogen-terminated cross-conjugated molecules to ~ 0.4 eV for the NO_2 -substituted molecule. This correlates with a similar shift in the interference feature to lower energy. In the CHO- and NO_2 -substituted molecules, the interference feature is seen at an energy below the HOMO level. The low-bias conductance for these molecules changes by $\sim 10^3$ with increasing electron-withdrawing strength.

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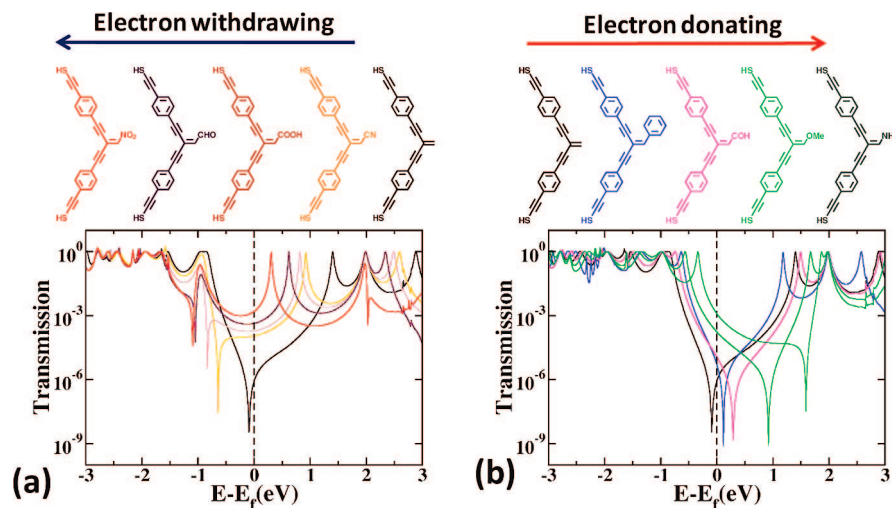


Figure 6. Effect of (a) electron-withdrawing and (b) electron-donating groups attached to the cross-conjugated unit. The interference feature is shown to be tuned ± 1.5 eV from the Fermi level by changing the electron density on the cross-conjugated bond. Qualitatively similar results calculated using ATK are given in the Supporting Information.

In Figure 6b, the electron-donating groups have an effect similar to that observed with the electron-withdrawing groups, but in the opposite energy direction. In most cases both the HOMO and LUMO shift to higher energy. The one exception to this is the phenyl-substituted group shown in blue, where the increased electron delocalization provided by the aryl ring narrows the HOMO–LUMO gap. In all of the molecules with electron-donating substituents, the interference features shift to higher energy and toward the LUMO. These calculations suggest that the interference feature is broadly tunable across the HOMO–LUMO gap region. In designing molecular devices, this broad tunability should allow alignment of the Fermi level with the interference minimum, providing an effective off state at zero voltage bias. To aid in experimental studies, we have included a section in the Supporting Information showing calculations of the transmission through cross-conjugated molecules with a variety of substituent groups used in the synthetic literature for cross-conjugated compounds.⁴⁸

7. A Molecular Transistor

We described above the ideal transistor as a molecule with a high conductance state provided by a molecular resonance in close proximity to a low conductance state at the Fermi energy. There have been a number of experimental measurements on single molecule transistors.^{19,76,77} To illustrate a potential molecular transistor, we use a cross-conjugated oligo(phenylene–enynylene) molecule with three repeat units.⁷⁵ In Figure 7, we compare the cross-conjugated molecule to a molecule where the conjugation is broken and to the full conjugated oligo(phenylene–ethynylene). In Figure 7b, the transmission curves for these three molecules are calculated using two different transport codes: ATK, shown with solid lines, and Hückel-IV, shown as a dotted line. For transmission factors that span ~ 16 orders of magnitude, the two transport codes agree very well. The differences between the two codes lie in the exact position of the resonances and the minima between them. Experimental results are required to calibrate the performance of these

methods; however, the trends are consistent. We can see from Figure 7b that the cross-conjugated molecule shown in black has a change in transmission probability of ~ 16 orders of magnitude over a 0.88 eV range in incident electron energy. In comparison, for the molecule shown in green, with CH_2 groups breaking the conjugation, the electron transmission changes ~ 8 orders of magnitude over 1.2 eV. In Figure 7c, the transmission probability is shown for a fully conjugated species with a 5 V applied gate voltage, calculated in ATK. To compare the gate voltage effect, conductance for a cross-conjugated molecule is plotted in Figure 7d. As the bias voltage approaches 0, the conductance is proportional to the transmission at the Fermi level. In Figure 7f, we have defined the off state as no perturbation to the system and the on state as 5 V gate voltage.

The conductance through the cross-conjugated molecule changes by 8 orders of magnitude with an applied gate voltage of 5 V. When the cross-conjugated units are replaced by saturated carbons, the conductance changes by 3 orders of magnitude, and for the fully conjugated molecule, shown in red, the conductance changes by 1.5 orders of magnitude. These results could be optimized by engineering the interference minimum to occur directly at the Fermi level. The on state could possibly be increased 5 orders of magnitude in the case of the cross-conjugated molecule by increasing the gate voltage, shifting the HOMO closer to the Fermi level; however, approaching resonance increases the probability of electron charging and molecular rearrangement. The cross-conjugated molecule has a subthreshold swing of ~ 625 mV/decade (calculated by using the transmission difference between 0 and 5 V gate voltage), which is ~ 2.5 and ~ 5.25 times lower than in the conjugated and saturated molecules, respectively. The comparison between these rates is important because the conversion between the gate voltage used in the calculations and the gate electrode in the experiment is nontrivial⁶⁷ and will have a large effect on the absolute value of the subthreshold swing. The large dynamic range, sensitivity to incident electron energy, and switching based on changes in electron density make cross-conjugated molecules promising candidates for molecular transistors.

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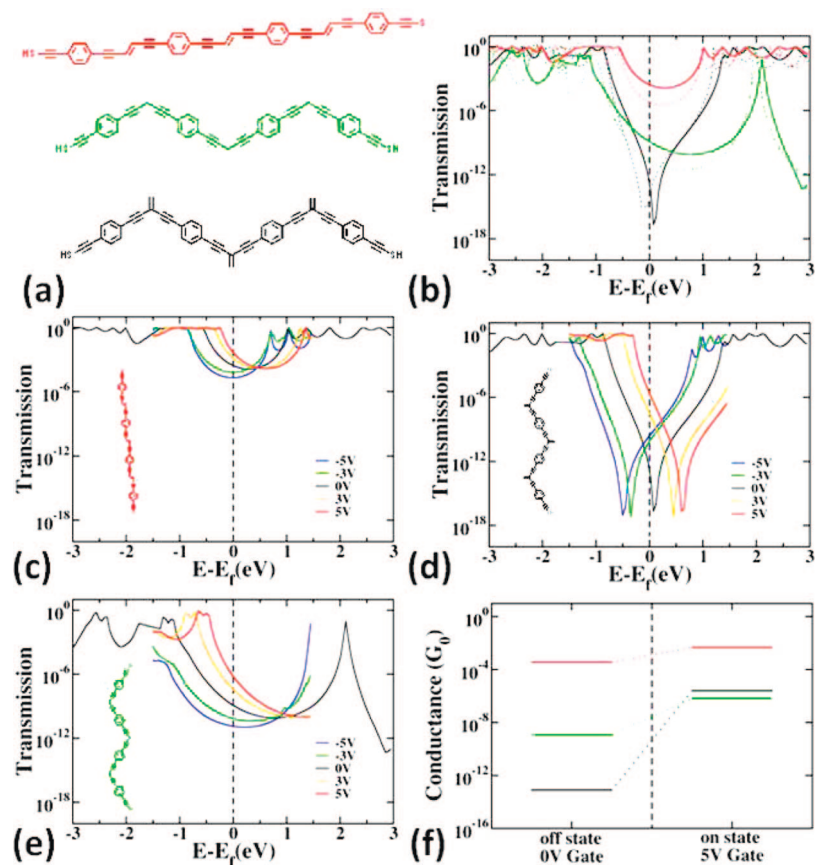


Figure 7. Calculations of conductance change with applied gate voltage in three test molecules. In panel b, the transmission spectrum calculated for the molecules shown in panel a includes a promising potential molecular transistor, the cross-conjugated molecule in black. The solid lines are calculated using ATK and the dashed lines using Hückel-IV. (c–e) Effect of gate voltage on the conductance plot. (f) Calculated change in conductance between on and off state of ~ 8 orders of magnitude in the cross-conjugated molecule.

8. A Molecular Rectifier

Our analyses of cross-conjugation and interference effects in transmission have dealt with the case of a single (sometimes degenerate) interference peak in symmetric molecules. In asymmetric molecules, we calculate a splitting of the interference peaks and more complex transmission features. By engineering the interference locations and using asymmetric molecules, more complex devices can be designed. The field of single molecule electronics is rooted in the proposal of a single molecule rectifier.⁶ This proposal was based on having a donor group and an acceptor group in a single molecule, with a saturated molecular spacer separating the groups. The saturated linkage between the functional parts of the molecule reduces communication between these distinctly separate groups.⁶ In the intervening years, many experimental attempts have been made⁷⁸ to measure a rectification ratio in single molecule transport, with marginal success in comparison with solid state devices.

It has been noted that having asymmetric coupling to the electrode also leads to an increased rectification ratio.^{79–83} The rectification ratio as a function of voltage is defined as the

current in one bias direction divided by the current in the other bias direction. Measurements of rectification in thin films have been completed for over 40 years.^{84,85} Recent experimental measurements on thin films of molecules have measured rectification ratios of up to 3000.⁸⁶ While molecules in a thin film can behave differently than at the single molecule level, experimental advances have been made toward understanding systems at both limits.⁸⁶

A number of published experimental and theoretical investigations show molecular rectifiers with rectification ratios typically $\ll 100$.^{78,80,81,87} Very recent work using the barrier tunneling model for transport suggests that the rectification ratio for single molecules will never be greater than 100.⁸⁸ All of these results are a far cry from typical solid-state rectification ratios that can be $> 10^5$.

In this section we focus on the electronic responses that can occur when multiple non-degenerate interference features are

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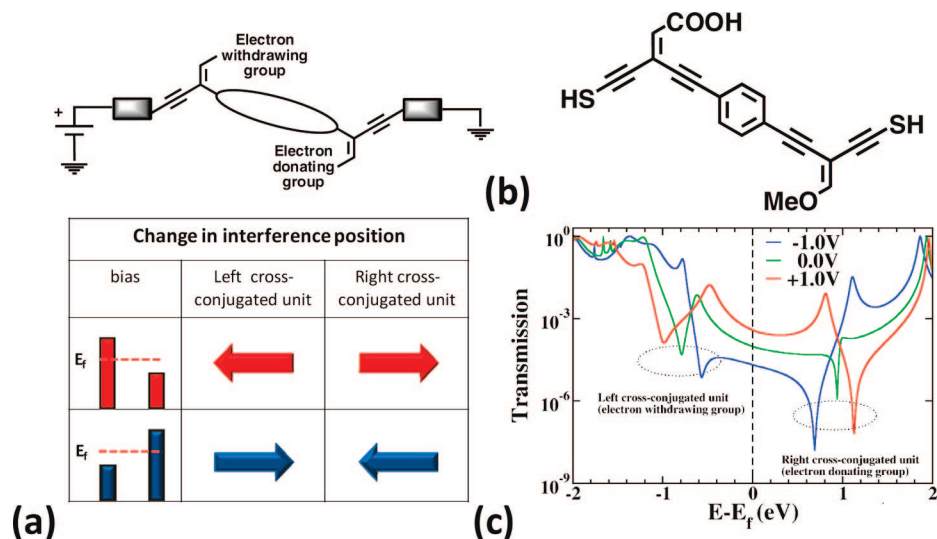


Figure 8. In molecules with multiple cross-conjugated units, an applied bias voltage will split the interference features. This splitting occurs because an applied bias has an electron-donating or -withdrawing effect that moves the interference position, as shown in Figure 6. (a) The more positive an electrode is, the more it moves the interference feature of the closest cross-conjugated group to lower energy, and conversely, the more negative an electrode, the more it moves the interference feature to higher energy. (b) An asymmetric molecule and (c) the corresponding transmission plots. The asymmetry causes two antiresonance features at different energies. At negative bias these antiresonance features move together, and at positive applied bias they move apart.

found in a single molecule. Essentially, most of the desired electrical elements can be redesigned in molecules with interference features to take advantage of the increased dynamic range. To illustrate these effects, we show model calculations on candidate molecules. It should be cautioned that, in molecules that are very sensitive to Fermi level placement (band lineup), the accuracy of the calculation is limited. While the molecules presented here show extremely interesting behavior, small changes in the relative position of the Fermi level and the molecular resonances could have large consequences in the measured response. The extreme sensitivity to these features will surely test the computational codes but will also provide a direct way to improve their accuracy by comparison with future experimental measurements. Much of the uncertainty lies in the location of the Fermi level. It would be ideal if the Fermi level could be varied and tuned to test the behavior of the molecule (perhaps using an alloyed or coated tip).

In Figure 6, electron-donating and -withdrawing groups were shown to move the interference peak over ± 1.5 eV from the Fermi energy. Using the effects of the electron-donating and -withdrawing groups on the position of the molecular resonance, we propose a class of single molecule rectifiers as shown in Figure 8. This molecule consists of two cross-conjugated units (or other groups that produce interference features, e.g., *meta*-substituted benzene) with split interference features, separated by a conjugated spacer. With an applied bias across the molecule, the interference positions are expected to move toward each other or away from each other, as shown in Figure 8a. This is a result of the interference response in cross-conjugated molecules to electron donation and withdrawal.

We calculate this response with Hückel-IV as shown in Figure 8. This molecule has a cross-conjugated unit with a methyl ether and a cross-conjugated unit carboxyl termination. In this context, the carboxyl-terminated cross-conjugated unit is the more “electron-withdrawing” group, and the ether-terminated unit is the more “electron-donating” group. In Figure 8c, the transmission through this molecule is shown at three different voltage points: -1 , 0 , and $+1$ V. The interference dips come toward each other at negative bias and split farther apart at positive

bias. Using Hückel-IV, we calculated a rectification ratio of 249 at 1.2 V, as shown in Figure 9b. Also shown in Figure 9 is the variation calculated in the rectification ratio among three transport programs. The maximum rectification ratios are calculated to be 18.6 at 1.0 V in gDFTB and 17.6 at 0.6 V in ATK. The behavior of the molecules under applied bias is nearly consistent between the codes, with the interference features moving ~ 0.25 eV per 1 V bias.

In all of our transport calculations, increasing the conjugated spacer length in the center of the molecule leads to a corresponding increase in the rectification ratio. One other limiting factor is the relatively small change in transmission probability between the dip in the interference features and the highest transmission point between the interference dips. This region between the split interference features has a large effect on the maximum rectification ratio. The magnitude of the transmission between the split interference features can be increased dramatically by having a molecular resonance near the Fermi level with interference features separated equally energetically above and below this resonance.

Oxygen-containing molecules can have molecular resonances near the Fermi level. A molecule that has been experimentally measured⁸⁹ and calculated³ contains the anthraquinone functional group, a cyclic cross-conjugated group. This group has the characteristics of interest: an interference feature below the Fermi energy and a localized resonance just above the Fermi energy.⁸⁹ To create a molecule with a resonance split by two antiresonance peaks, we have asymmetrically added a cross-conjugated unit. As shown in Figure 10, we have taken the anthraquinone functional group and added a large conjugated spacer and two methyl-terminated cross-conjugated groups (the second cross-conjugated unit orients the sulfur termination toward the Au electrodes).

In Figure 10, we show the current/voltage behavior and the rectification ratio for our proposed rectifier. As the interference features come together with negative bias (shown in the

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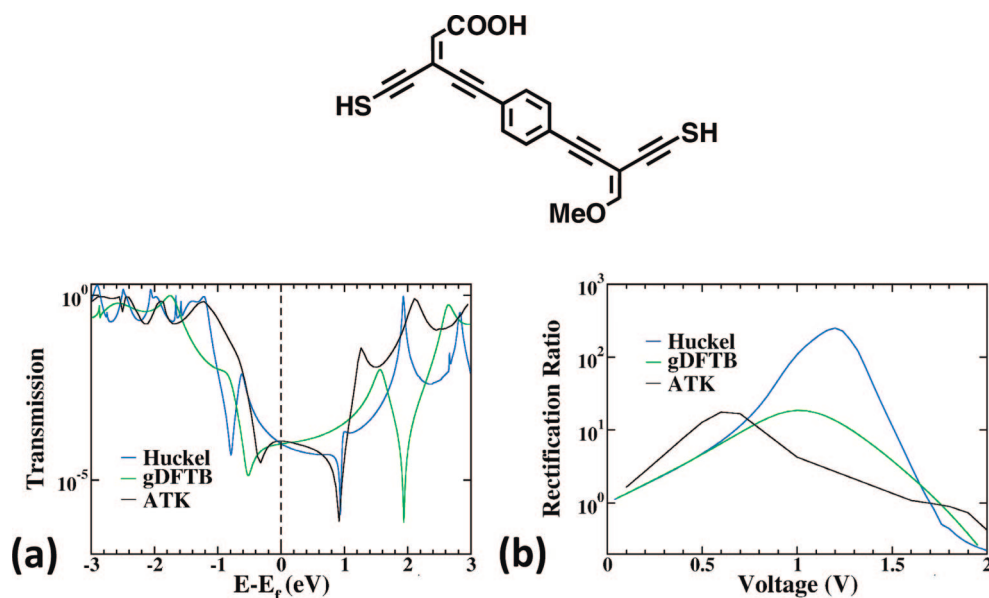


Figure 9. (a) Transmission spectra calculated using gDFTB, ATK, and Hückel-IV, and (b) the rectification ratio as a function of voltage calculated using these programs. Differences in the location of the resonance and interference features between the codes lead to a change in the voltage and magnitude of the maximum rectification ratio. More importantly, the behavior of the antiresonances is consistent between codes.

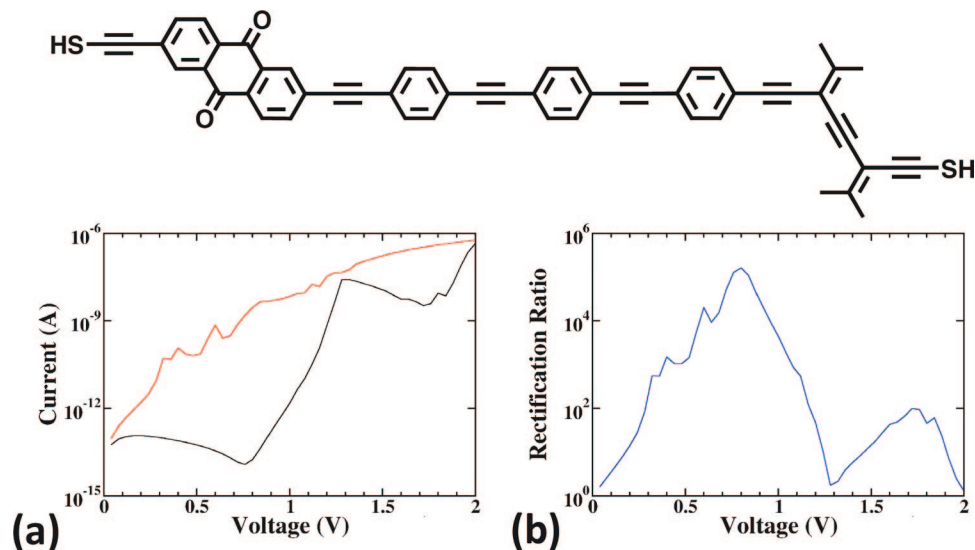


Figure 10. Rectifier behavior maximized in the Hückel IV transport code. (a) Positive bias current/voltage behavior is shown in red, and negative bias current/voltage behavior is shown in black. The rectification ratio is calculated by dividing the positive voltage bias by the negative voltage bias. (b) The rectification ratio as a function of voltage, showing a peak of $>150\,000$ at 0.8 V applied voltage.

Supporting Information), the current decreases from 0.2 to 0.8 V, while in the positive bias, the current increases as the interference dips move apart. The rectification ratio increases steadily from 0 to 0.8 V, where it quickly falls off. At 0.8 V, the rectification ratio of $>150\,000$ is orders of magnitude higher than other published single molecule rectifier calculations or experiments, without relying on asymmetric binding to the electrodes. This result indicates that molecular devices may function as coherent (fast) electronic devices.

The choice of molecule was dictated by the location of the resonances and the interference features within one transport code. Any candidate molecular rectifier would show slightly different behavior using the three transport programs that we have chosen. While we are calculating the rectification behavior for one code, we believe that this behavior can be seen in

experimental measurements with different functional groups chosen to control the position of the resonances and interference locations.

In Figure 11, the zero voltage transmission is shown using the three different transport codes. These changes in the transmission features, specifically the lack of split antiresonance features in ATK, have a noticeable effect on the calculated maximum rectification ratio. In gDFTB, the maximum rectification ratio is 501 at 0.52 V, and in ATK the maximum rectification is 83.5 at 1.5 V. While these rectification ratios are very high for calculations on single molecule rectifiers, they are much lower than the value calculated in Hückel-IV. This is not surprising and is a direct consequence of the variations between transport codes. All three of these results will likely vary from experimental measurements because of the sensitivity

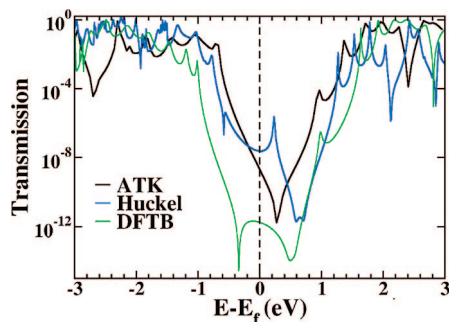


Figure 11. Transmission plots for the molecule shown in Figure 10, calculated using gDFTB, Hückel-IV 3.0, and ATK. The differences in the transmission spectra are largely due to the energetic positioning of the antiresonance features and the localized oxygen resonance. The changes in the transmission spectra lead to large changes in the maximum rectification ratios calculated, from >150 000 in Hückel-IV, to 501 in gDFTB, and to 83.5 in ATK.

to interference and resonance peaks. This sensitivity is a direct result of having a large dynamic range in transmission probability, where small changes in the energy have large effects on the transport behavior.

9. Negative Differential Resistance

One other feature observed in the current/voltage behavior of some of these cross-conjugated molecules is a rapid decrease in current with increasing voltage, or negative differential resistance (NDR). An NDR-like behavior is most strikingly seen in Figure 10a, where the current in the negative voltage direction decreases by 1 order of magnitude between 0.2 and 0.7 V. This is a result of interference features moving together with increasing voltage.

In reported NDR in molecules on silicon surfaces, the conductance dip is attributed to the conduction band edge passing a molecular resonance.^{13,90} Interference features in a transmission spectrum are equivalent to resonant peaks but with an opposite sign in transmission plots. If the transport is dominated by the band edge, this indicates that interference dips should provide NDR behavior similar to that reported in the literature for the case of sweeping through molecular resonances. The advantage of observing NDR features caused by interferences (or by resonance without charging) is that these can occur without geometry change in the low-bias tunneling regime. This could lead to a much faster response, enhanced stability, and longevity of potential devices.

10. Conclusion

Cross-conjugated molecules and their extreme sensitivity to incident electron energy open up new possibilities in single molecule electronics. Most switching and nonlinear behavior in molecules has relied on tuning the incident electron energy past a molecular resonance or conformation change. This can lead to charging of the molecule and possible device instability.^{29,91} With cross-conjugated molecules, we calculate a large dynamic range in electron transmission probability to occur in a chemically tunable coherent tunneling range between the frontier

molecular orbitals. This allows complex electronic behavior such as switching, negative differential resistance, and rectification to occur in the low-bias electron tunneling regime without charging the molecule.

The depth of the interference feature is tunable by minimizing the σ transport. The location of the interference feature is shown to be tunable across the HOMO–LUMO gap. This tunability should allow for manipulation of the interference feature by chemical means so that it occurs near the Fermi level. To minimize the off-state current, having the interference minimum at the Fermi level is important and also results in the maximum dynamic range. To study molecules with such sensitivity to the band lineup,^{37,44} it would be ideal if the Fermi level could be experimentally tuned, as this might prove easier than chemical modification. These molecules and their sensitivity to the location of the Fermi level should provide a useful means of calibrating experimental results and theoretical methods.

Cross-conjugated molecules could be useful in chemical sensors where an extremely small change in electron density must be measured.⁹² We have calculated that changing the electron-donating or -withdrawing ability of a side group attached to the cross-conjugated unit can produce a 3 orders of magnitude change in the conductance. This sensitivity of the cross-conjugated unit to electron density also indicates that a third terminal could be attached to the cross-conjugated double bond to gate the molecule. Experimental realization of three terminal devices with single molecules is exceedingly difficult, but these cross-conjugated molecules seem to be promising candidates for initial tests. Using a calculated electrostatic potential to gate cross-conjugated molecules, our calculations suggest that the large dynamic range in electron transmission probability could be used to tune the Fermi level along the 16 orders of magnitude change in electron transmission probability.

If the interference features could be generated in all symmetry components of the transmission, it would be conceivable to have a near-perfect insulator in close proximity to a molecular resonance, increasing the dynamic range of the system. Cross-conjugated molecules serve as an interesting case where quantum interference effects dominate the transmission spectrum near the Fermi level and the correlation of molecular conductance and energetic proximity to a frontier molecular orbital breaks down. These molecules serve as a reminder that the vast dimension of chemical space should yield many more interesting candidates for functional electronic devices.

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Supporting Information Available: Calculation details, figures showing the comparison between transport codes for Figures 5 and 7, the interference position for a variety of synthetically terminated cross-conjugated molecules, and complete ref 55. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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