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Molecular Diodes Enabled by Quantum Interference

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Abstract

We use scanning tunneling microscope break-junction (STM-BJ) measurements to study the low-bias conductance and high-bias current-voltage (IV) characteristics of a series of asymmetric para-meta connected diphenyl-oligoenes. From tight-binding calculations, we determine that the quantum interference features inherent in our molecular design result in a ‘through-bond’ coupling on the para side, and through-space coupling on the meta-side. We show that these molecular junctions form single molecule diodes, and show that the rectification results from a difference in the voltage dependence of the coupling strength on the through-bond and the through-space side. The interplay between the applied voltage and the molecule-metal coupling results from the asymmetric polarizability of the conducting orbital under an external field.
Understanding charge transport across single molecule junctions as well as transfer at metal-organic interfaces is of critical importance in the field of molecular/organic electronics, such as light emitting devices (OLEDs) and photovoltaics (OPVs). Organic materials as alternates to standard silicon based semiconductors are fast becoming commercially viable especially in applied areas including flexible electronics, sensors and photovoltaics. However, the physical mechanism by which charge transport and transfer occur in relation to the chemical structure in these systems is poorly understood. One route to understand and fully characterize such physical processes in organic electronics is to focus on nanoscale single-molecule devices where one can probe structure-function relations directly. The proposal to create molecular analogs of circuit components dates back to the work of Aviram and Ratner. In their seminal work from 1974, they proposed using a single molecule as a diode circuit element in giving birth to the field of molecular electronics, and research in this field has advanced tremendously since then. For example, highly conductive molecular junctions have been realized, and recent scientific developments have demonstrated molecular analogues of several conventional circuit components, such as transistors, potentiometers, diodes and switches. Furthermore, devices that utilize purely quantum mechanical aspects of charge transport – interference effects arising due to the wave nature of electrons – have been demonstrated; such behavior has no counterpart in conventional electronic circuits.

Molecular diodes are of great interest in the nanoscale electronics community because they are the simplest example of non-trivial electronic behavior in a molecular system, and because they form the basis for more complicated device architectures.
Despite the long-standing interest in the production of these devices, their experimental realization has been difficult, with only a handful of studies showing rectification at the single molecule level.\textsuperscript{20, 21, 23} This is because most theoretical designs, such as the Aviram-Ratner model of rectification\textsuperscript{11}, rely on the complex interplay between many variables, such as the level alignments of the molecular components and the Fermi level of the metal electrodes.\textsuperscript{33} For example, in the pioneering work of Elbing et al.,\textsuperscript{20} the molecule studied consisted of two weakly coupled conjugated segments that were energetically shifted relative to the electrode Fermi level by using electron withdrawing and electron donating substituents. They showed experimentally that the current-voltage across molecular device was asymmetric with respect to the applied voltage, however, it was hard to quantitatively assess the effects of the substituents on the rectification ratio determined experimentally making the behavior of such diodes difficult to predict\textsuperscript{34, 35}. Simpler ‘unimolecular’ rectifier designs had been proposed\textsuperscript{36-38}, but have been demonstrated primarily on thin-films, or many molecule junctions\textsuperscript{39-42}. Theoretical work has also focused on the role of the electronic contact\textsuperscript{43} in defining rectification behavior, and recent experimental evidence\textsuperscript{23} has shown the efficacy of such an approach in developing tunable rectifiers. Here, we show that quantum interference effects\textsuperscript{29, 44, 45} can be used to create asymmetrically coupled molecular junctions\textsuperscript{46} and attribute the rectification to a novel mechanism that can in principle be applied to a variety of other molecular structures.

In this work, we measure conductance and current-voltage characteristics in a series of conjugated molecules of increasing length with linkers at the \textit{para} position on one side and at the \textit{meta} position on the other, and find that these molecular junctions
rectify current. From our experimental and theoretical results, we conclude that the quantum interference inherent in our molecular design effectively ensures that the molecular orbital dominating transport across the junction is strongly coupled to one electrode while allowing only weak electronic coupling to the other electrode. We show further that rectification results from a difference in the voltage dependence of the coupling strength between two sides of the molecule, an effect that depends on the molecular backbone length. The interplay between the applied voltage and the molecule-metal coupling results from the asymmetric polarizability of the conducting orbital under an external field.

The molecules used in this work are based on diphenyl-oligoene backbones (Figure 1A, molecules 1-5) of lengths ranging from 1.2 nm to 2.3 nm. The backbones are functionalized with two methylsulfide (SMe) linkers, in the para position on one phenyl ring and in the meta position on the other (see SI for synthesis details). To first understand what conductance we can expect to measure in this system, we carry out a simple tight-binding based theoretical model calculation for molecular junctions formed using such para-meta linked molecules. We focus on the stilbene molecule (1) and consider only the $p_z$ orbitals on each carbon atom in our model. In this model, we assume an on-site energy of $\varepsilon=0$ eV and a coupling strength to the nearest neighbor orbital, $\tau=1$ eV. The molecule is coupled to electrodes through $\Gamma_L$ and $\Gamma_R$ at the carbon atom at the 4 position on one benzene ring (para) and at the 3’ (meta) or 4’ (para) position on the other benzene ring. For the purpose of this calculation we set $\Gamma_L = \Gamma_R = 0.04$. Transmission probability $T(E)$ calculated by first determining the Hamiltonian matrix $H$ (which in this case is an 14×14 matrix). The retarded Green’s function for the model junction is then
\[ G(E) = [E\mathbb{1} - H]^{-1} \]

and the transmission is given by

\[ T(E) = \Gamma^2 |G_{LR}|^2 \]

where \( G_{LR} \) denotes the component of the Green’s function matrix that describes the propagation between the left and right electrodes\(^{49}\). Figure 1B compares the tight-binding transmission functions for the \textit{para-para} connected stilbene (dashed curve) and the \textit{para-meta} connected version (solid curve). We see a clear non-zero transmission probability at zero energy for the \textit{para-para} system while the \textit{para-meta} curve shows close to zero transmission probability. The negligible transmission seen in the \textit{para-meta} system is due to an anti-resonance which results from destructive interference\(^{29, 45, 50}\) at the Fermi energy.\(^{29, 45, 50}\)

To determine the conductance from these transmission probabilities, we use the Landauer formalism\(^{51}\), which is perhaps the most well accepted theoretical framework for describing ballistic transport in one dimension. This method converts the electron transport problem into a scattering problem. In this formalism, the conductance \( G \) of a metal-molecule-metal junction is related to the probability of an electron from one electrode, emerging at the Fermi energy (modulo any applied bias), being transmitted across the molecular junction. The conductance \( G \) at zero applied bias is given by

\[ G = G_0 T(E_F) = \frac{2e^2}{h} \sum_i T_i(E_F) \quad \text{Eq. 1} \]

where \( e \) is the charge of an electron, \( h \) is Planck’s constant, \( i \) is the index associated with a conducting channel, and \( G_0 = \frac{2e^2}{h} \) is the quantum of conductance. Applying the Landauer equation to the transmission function shown in Figure 1B, we would expect a close to zero conductance for these \textit{para-meta} coupled molecules at zero bias.

We measure the conductance and current-voltage characteristics of this series of molecules in ambient, room-temperature conditions with a scanning tunneling...
microscope (STM) in break-junction mode. Conductance measurements under low-bias ($V_{\text{bias}} \sim 250 \text{ mV}$) conditions are carried out first using 1 mM solutions of the compounds in 1,2,4-trichlorobenzene (Sigma-Aldrich, >99% purity). A gold STM tip is brought into contact with a solution-covered gold-on-mica substrate until a junction conductance greater than $5 \, G_0$ ($G_0 = 2e^2/h = 77.6 \, \mu\text{S}$) is measured. The tip is then withdrawn at a rate of 15 nm/s while the current is measured at a constant bias. The inset of Figure 1C shows sample conductance traces showing a prominent molecular conductance feature for molecules 1, 3 and 5, in contrast with the negligible conductance predicted by tight-binding.

Figure 1C shows a two-dimensional conductance histogram for molecule 3 which is created by overlaying thousands of conductance traces after first aligning them to have zero displacement at a conductance of 0.5 $G_0$. The conductance feature seen in this 2D histogram starts at $10^{-3} \, G_0$ at zero relative displacements and goes down to $\sim 3 \times 10^{-5} \, G_0$ by 1 nm relative displacement. The sloped nature of this feature indicates that the molecular conductances decrease as electrode separation is increased. Previous measurements with similar molecules have shown that such a sloped feature results from a non-specific $\pi$-Au molecule-electrode interaction. This is in contrast to symmetric $para$-connected versions of the same molecules studied previously, which show a flatter conductance feature typically seen when molecules are coupled through donor-acceptor bonds on both ends. We conclude that the asymmetric functionalization allows for one side ($para$) to be electronically coupled ‘through-bond’, and other side ($meta$) to be coupled ‘through-space’. Figure 1D show logarithmically binned one-dimensional histograms of thousands of such traces for each molecule without data selection, which
allows a characteristic conductance value to be statistically determined. On going from the shortest molecule, \(1\), through the series to the longest molecule, \(5\), the conductance decays exponentially (inset Figure 1D), with a decay parameter \(\beta = 0.25 \pm 0.03/\text{Å}\). This is a similar decay constant to previous studies on the oligoene molecular system\(^{45, 46}\), and suggests that the \(\pi\)-Au interaction occurs at end carbons on the phenyl ring near the meta-linker, rather than on the backbone.

We next measure the current-voltage (IV) characteristics of these molecules using procedures published previously.\(^5\) Briefly, a gold STM tip is brought into contact with a gold-on-mica substrate. The tip is first withdrawn at a rate of 15 nm/s for 125 ms, and held at this displacement for 150 ms before being withdrawn for an additional 75 ms. During the ‘hold’ section when the tip/substrate distance is not changed, the voltage is ramped between ±1V, while the current is measured (Figure 2A). The IV procedure is repeated tens of thousands of times. Each measured trace is first analyzed to determine if a molecule was trapped during the hold section by comparing the conductance at the start and end of this section with the range determined from the conductance histogram shown in Figure 1D. If the conductance corresponds to that of a molecular junction, we select the trace to analyze the IV data. We typically find that ~1-10% of all measured junctions showing a stable, unbroken, molecular conductance signature during the IV measurement. Due to the instability of molecular junctions at higher biases at room temperature, measurements beyond ±1V do not yield sufficient numbers of traces to analyze statistically. We then sort all selected IV traces into two sets based on the magnitude of current in a range of positive biases (+0.75 to +0.80V) and corresponding negative voltages (-0.75V to -0.80V).\(^2\) Traces that show larger current at positive than negative
voltages correspond to molecular junctions in the forward orientation; traces that show smaller current at positive than negative voltages correspond to molecular junctions in the reverse orientation. For each molecule, the IV portion of the selected traces from each set are binned logarithmically on the current axis, and added together to create two two-dimensional histograms of absolute current against voltage.

As an illustration, sorted 2D histograms from 4 are shown in Figure 2B (reverse bias, top panel and forward bias, bottom panel). To make a quantitative comparison of the histograms, we fit each vertical slice of the histograms to a Gaussian distribution and extract the most frequently measured current at each voltage. These values are plotted as the red and black IV curves overlaid in the top and bottom panels of Figure 2B respectively and are also shown on a linear scale in Figure 2C. The resulting curves represent the averaged IV curves for this molecule. The forward bias average IV (black curve, Figure 2C) overlays the reverse bias IV (red curve), which has been mirrored in the voltage axis. The near-identical shape of these curves indicates that sorting recovers the inherent structure in the IV curves without biasing the data. A similar sorting algorithm applied to fully symmetric molecules further confirms this conclusion: the separated 2D histograms for these control molecules are identical and do not show rectification. Figure 2D compares statistically averaged IV curves for molecules 1-5. We find that the absolute current decreases with length. The rectification ratio for each molecule is determined from the ratio of the current at +0.85V and -0.85V. We see that the rectifying behavior increases slightly with increasing molecular length as will be discussed further below.
To understand the origin of rectification and its length dependence, we conduct density functional theory (DFT) calculations of molecules 1-5 in which we include an electric field applied parallel to the molecular axis. Molecules are structurally relaxed by performing spin-unrestricted calculations using the B3LYP exchange-correlation functional and 6-31G* basis set using the Q-Chem software suite. Default grids and convergence thresholds were used for relaxation. Subsequently, single-point calculations were carried out using B3LYP/6-311G** either without field, or with a monopole field applied along the long axis of the molecule. We apply the field along the long axis of the molecule to simulate the field due to the applied bias on a molecular trapped between the tip and substrate.

Generally, the factors affecting rectification are voltage dependence in energy level alignment (Stark shifts), or a voltage dependent coupling term $\Gamma$. For an applied voltage of ±1V, the HOMOs of molecules 1-5 show negligible Stark shifts as shown in Figure 3A, where we see that the energies of the HOMO orbitals do not differ by more than 0.1 eV under positive or negative voltage. This small Stark shift is not enough to explain the rectification effects observed experimentally. We therefore concentrate on the voltage dependence of the coupling terms on the para and meta side $\Gamma_{para}$ and $\Gamma_{meta}$.

Figure 3B shows representative isosurface plots of the HOMO of molecule 5 under an applied voltage of +1V (upper panel) and -1V (lower panel). The weight of the HOMO on the carbon atoms adjacent to the para and meta linkers (arrows, Figure 3B) changes significantly with field polarity. We can quantify this change in HOMO distribution using the projection of HOMO onto the $p_z$ orbital of the para carbon of the ‘through-bond’ coupled side (Figure 3C), and the projection of the $p_z$ orbitals of all carbons on the phenyl
ring of the ‘through-space’ meta connected side of the molecule (Figure 3D). We show in Figures 3C and 3D these projections for the entire series at 0V and ±1V.

The coupling $\Gamma$ of the HOMO to each electrode is proportional to the square of the projections shown in Figures 3C and 3D\(^{35,36}\). To determine the voltage dependence of the coupling terms $\Gamma_{\text{meta}}$ and $\Gamma_{\text{para}}$, we square the projections shown in Figure 3C and 3D and fit a line to the result to determine the change in the $\Gamma$ values as a function of voltage. The voltage dependence on $\Gamma$ is thus incorporated as:

$$\Gamma_{\text{meta/para}}(V) = \Gamma_{0,\text{meta/para}} \cdot (1 + \nu_{\text{meta/para}} \times V)$$  \hspace{1cm} \text{Eq. 2}$$

where $\Gamma_{0,\text{meta/para}}$ is the zero-field $\Gamma_{\text{meta/para}}$ and $\nu_{\text{meta/para}}$ is calculated from the slope of the voltage dependence of $\Gamma_{\text{meta/para}}$. In Figure 4A we plot the difference between the -1V and +1V $\Gamma_{\text{meta/para}}$ normalized by the 0V $\Gamma_{\text{meta/para}} (\Delta \Gamma_{\text{meta/para}}/ \Gamma_{0,\text{meta/para}})$ for all five molecules. We see first that longer molecules have a larger fractional change in $\Gamma_{\text{meta/para}}$ due to a higher molecular polarizability. More importantly, we see that this trend is more pronounced for $\Gamma_{\text{meta}}$ than for $\Gamma_{\text{para}}$. This indicates that the coupling on the meta-side of the molecule changes much more with applied bias than that on the para-side. In other words, a positive or negative bias applied to the para side has a much smaller effect on the charge density than the same voltage applied to the meta side. We therefore attribute the rectification observed in these molecular junctions to the asymmetric polarizability of the conducting orbital in this system.

We now extend the tight binding model developed earlier to obtain current/voltage curves based on model transmission functions to understand if this change in coupling does indeed result in rectification for this system. To simplify the
modeling, we use a single molecular orbital (the HOMO) coupled to the left and right electrode through coupling terms $\Gamma_{\text{para}}$ and $\Gamma_{\text{meta}}$ (Figure 4B, inset). This reduces the tight binding Hamiltonian to a $1 \times 1$ matrix rather than the atomistic $14 \times 14$ Hamiltonian used to illustrate the interference effect above,\textsuperscript{60, 61} yielding a transmission function that has a single-Lorenzian form.\textsuperscript{62} Including a voltage dependent $\Gamma_{\text{para}}$ and $\Gamma_{\text{meta}}$ given in Equation 2, the single-level model described results in a transmission function of the form:

$$T(E, V) = \frac{\Gamma_{\text{para}} \Gamma_{\text{meta}} (1 + v_{\text{para}} V) (1 + v_{\text{meta}} V)}{(E - E_0)^2 + \frac{1}{4}(\Gamma_{\text{para}} (1 + v_{\text{para}} V) + (\Gamma_{\text{meta}} (1 + v_{\text{meta}} V))^2} \quad \text{Eq. 3}$$

IV curves are generated from the transmission function using the voltage dependent Landauer formula

$$I(V) = \frac{2e}{h} \int dE \ T(E, V) \ [f\left(E + \frac{eV}{2}\right) - f\left(E - \frac{eV}{2}\right)] \quad \text{Eq. 4}$$

where $f$ is the Fermi distribution function. For simplicity, we take the temperature to be 0K, although results from using $T=300K$ are not very different.

The calculated model IV curves determined from Eq. 4 above while varying voltage dependences of $\Gamma_{\text{para}}$ and $\Gamma_{\text{meta}}$ are shown in Figure 4B. We see that rectification increases with difference in $\Delta \Gamma_{\text{para}}$ and $\Delta \Gamma_{\text{meta}}$, and when $\Delta \Gamma_{\text{para}}$ and $\Delta \Gamma_{\text{meta}}$ are equal, no rectification occurs (dashed IV curve). For each IV curve, we determine a rectification from the ratio of the current at 0.85 V to –0.85 V. These are plotted in Figure 4C along with the experimentally determined rectifications. Our model explains the length dependence of our data, and suggests that rectification occurs due not to a difference between $\Gamma_{\text{para}}$ and $\Gamma_{\text{meta}}$, but due to a difference in $\Delta \Gamma_{\text{meta/para}}$ which we attribute to the different nature of electronic coupling on the para (through-bond) and meta (through-
space) sides. Further, our model shows that increasing the length of the molecule can enhance rectification by increasing the asymmetric polarizability of the conducting orbital (in this case, HOMO).

In summary, we have used the unique properties of quantum interference to create a series of asymmetrically coupled molecular diodes. We find that rectification ratios increase with molecular length, and model this trend using a tight-binding model taking into account the asymmetric coupling in these molecular junctions. We show that the increase in rectification is due to differences in the voltage-dependence of ‘through-space’ and ‘through-bond’ coupling terms with molecular length.

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References:


Figure Captions

**Figure 1:** A. Molecular structures for molecules with n = 1-5. B. Tight-binding transmission functions for molecular junctions with molecule 1 (black); this *para-meta* system shows negligible transmission probability near E\textsubscript{Fermi} (0 eV). A *para-para* (dashed black) connected version of molecule 1 shows higher transmission. C. Inset: Sample conductance traces for molecules 1, 3 and 5 showing molecular plateaus. Two dimensional (2D) conductance histogram for molecule 3, showing characteristic downward slope in conductance with increasing relative displacement. D. Conductance histograms for *para-meta* connected molecules 1-5 showing measurable conductance. 

**Inset:** Logarithm of conductance versus molecule length obtained using S-S distances from DFT optimized structures of molecules 1-5 fit with a line. The decay constant determined from this least-squares fit is \( \beta = 0.25 \pm 0.03 \text{ Å}^{-1} \).

**Figure 2:** A. Representative current, voltage and displacement (piezo z-position) traces for a single break junction measurement for molecule 4. The IV ramp is applied when z is held constant. B. Two-dimensional histograms created from thousands of IV curves for molecule 4 that are either in reverse bias (top panel) or forward bias (bottom panel). Average IV curves are overlaid in red and black respectively. The counts in this 2D histogram range from 0 (black) to 1000 (yellow). C. Average IV curves from B shown on a linear scale with reverse-bias (red) reflected about the x-axis. D. Averaged IV curves for molecules 1-5 analyzed following the same procedure detailed in panel B and C.

**Figure 3:** A. Stark shifts for HOMO as a function of constant field (voltage scaled with molecular length, with ± 1V applied to molecule 5). Molecules 2-5 (purple, yellow, blue,
red, and green respectively) show quadratic dependence on field, as expected for molecules without significant dipoles. Molecule 1 shows a slight stark shift due to a dipole moment along the length of the molecule. **B.** DFT calculated HOMO for molecule 5 with an applied potential of +1V (upper panel) and -1V (lower panel). The red arrows point to the para carbon on the strongly coupled side. The black arrows point to the para carbon on the weakly coupled side. Isosurface value = 0.05/A³. **C.** Projection of HOMO on the pₓ orbitals of six ring carbons on the meta side of the molecule for constant voltage of ±1V (for 1-5). **D.** Projection of HOMO on the pₓ orbitals of the carbon attached to the sulfur on the para side of the molecule for constant voltage of ±1V (for 1-5). Molecules 2-5 all show a linear dependence of projection on voltage. Molecule 1 shows nonlinearities associated with a dipole moment along the length of the backbone.

**Figure 4:** **A.** Fractional change in coupling Γ_{meta} (black) and Γ_{para} (red), estimated as the square of projection of HOMO on the pₓ atomic basis of the para atom (Γ_{para}) or the meta-connected phenyl ring (Γ_{meta}). Fractional change shown is an average of change for V=+1V and V=-1V. **B.** Calculated IV curves for a single-level model (Inset) with ε=−0.8 eV, Ω_{para} = 0.04, Ω_{meta} = 0.004, with Ω_{meta} and Ω_{para} set to vary linearly with voltage (see main text). Yellow, red, and green curves are calculated using voltage dependent Ω_{meta} and Ω_{para} with ν_{meta} = 0.19, 0.39, 0.43 and ν_{para} = 0.22, 0.47, 0.60 for molecules 2, 4, and 5 respectively (panel A). These curves show the effect of increasing differences in ΔΩ_{para} and ΔΩ_{meta} on IV line shape. Dashed line shows a non-rectifying case where Ω_{meta} and Ω_{para} have the same voltage dependence. **C.** Rectification ratio calculated (solid markers) from the ratios shown in A, compared with experimental data (open circles). Both ratios
are calculated by taking the ratio of the current at 0.85 V and -0.85 V. Rectification increases with increase in molecular length.
76x23mm (300 x 300 DPI)