Rectification and Stability of a Single Molecular Diode with Controlled Orientation

Ismael Díez-Pérez¹, Joshua Hihath¹, Youngu Lee², Luping Yu², Lyudmyla Adamska³, Mortko A. Kozhushner³, Ivan I. Oleynik³ and Nongjian Tao*¹

¹Center for Biosensors and Bioelectronics, Biodesign Institute, Arizona State University, Tempe, Arizona 85287

²Department of Chemistry and The Frank Institute, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

³Department of Physics, University of South Florida, Tampa, Florida 33620.

⁴Institute of Chemical Physics, Russian Academy of Sciences, 4 Kosygin St., Moscow 119991, Russia

#Current address: Samsung Electronics, San #24 Nongseo-Dong, Giheung-Gu, Yongin-City, Gyeonggi-Do, Korea 446-711

AC-modulation assisted method for I-V measurements

As described in the main text, the AC-modulation method provides an unambiguous way to determine the I-V curves of single molecule junctions. Here we provide a more detailed description of the method. We denote the tip-substrate modulated distance, \( z \), as \(^1\):

\[
z = z_0 + A \cos(2\pi ft) \tag{1}
\]
where $z_0$ is the tip-substrate distance without the AC modulation, and $A$ and $f$ are the amplitude and frequency of the $z$-modulation respectively. Then, the corresponding current response yield:

$$I = I_{DC} + I_{AC} \cos(2\pi ft + \theta)$$  \hspace{1cm} (2)$$

where $I_{DC}$ is the DC current, and $I_{AC}$ and $\theta$ are the amplitude and phase of the current response. Note that the $\theta$ found in our experiments is $\sim 180^\circ$, which is expected because an increase in the distance leads to a decrease in the current. A useful way to measure the AC current response is to normalize $I_{AC}$ by $I_{DC}$ and $A$ (in nm) as:

$$\alpha = \frac{I_{AC}}{A \cdot I_{DC}}$$  \hspace{1cm} (3)$$

yielding units of nm$^{-1}$. For a simple tunnelling process either via space or via a molecule, we have $I = I_0 e^{-\beta z}$ where $\beta$ is the tunnelling decay constant given by

$$\beta = \sqrt{\frac{2m^*}{h^2}} (\phi_B - eV_{bias})$$  \hspace{1cm} (4)$$

**S1:** Total current (blue) and AC current component (black) vs. bias for a Au-Au tunnelling junction (no molecule present). The red line is the best fit of the data by Equation 4 with $c = 0.5$.  

---

© 2009 Macmillan Publishers Limited. All rights reserved.
where \( m^* \) is the effective mass of electron, \( \phi_B \) is the local tunnelling barrier height and \( c \) is a barrier symmetry factor. In this case, \( \alpha = \beta \) so that the AC current response also measures the decay constant and the dependence of the decay constant on bias, \( V_{bias} \). Figure S1 shows the total (DC+AC) signal and the pure AC current component versus bias voltage taken for a Au-Au tunnelling junction (no molecules bridged between the tip and substrate). The DC current component in the total current versus bias (blue curve) displays the typical tunnelling characteristic, namely a linear dependence at small biases and then large increase at high biases. Superimposed on the total current is the large AC component, which can be easily extracted with a band-pass filter (black). The amplitude of the AC response, \( \alpha \), in this simple tunnelling process measures how the decay constant, \( \beta \), decreases with the bias. The AC amplitude can be roughly fit using Equation 4 (red line), with fitting parameter, \( c \), close to 0.5 in agreement with a Simmons model\(^2\). Although the discrepancy between the measurement and the simple tunnelling theory demonstrates the need for a more sophisticated model, we can qualitatively state that the AC response constitutes a highly sensitive parameter to small changes in the local tunnelling barrier, \( \phi_B \), at the junction and so it can be directly used to detect the formation of molecular bridges.

The effectiveness of the AC-modulation method is illustrated using a well-studied alkanedithiol (1,8’octanethiol). Figure S2 shows the AC current response at different tip-substrate distances for the 1,8’octanethiol molecule. When the distance is larger than the molecular length (setpoint current \( \leq 0.5 \) nA\(^3\)), the AC response is large with a normalized value close to 10 nm\(^{-1}\) (Figs. S2a and b). When the tip-sample distance approaches the molecular length (setpoint currents \( > 0.5 \) nA), abrupt switching of the AC amplitude to a lower level is observed (Figs. S2c). Each switching event in the AC amplitude is always accompanied by an
abrupt increase in the DC current as it is shown in Fig. 3 (manuscript), which is ascribed to the formation of a single-molecule bridge. The amplitude often switches back to the original value (Figs. S2c). At a smaller tip-substrate distance, the probability of switching events increases and the duration that the AC amplitude at the lower lever also increases (Fig. S2d). The combination of both DC and AC current components allows us to unequivocally identify the formation of a single molecule bridge and then perform electrical measurements avoiding any mechanical artefacts and providing an electrical signature for the formation of a single molecule junction.

**S2**: AC-current response (nm$^{-1}$) at different tip-sample distances for a 1,8’octanedithiol. The frequency and amplitude of the AC-modulation are 2 kHz and 0.03 nm, respectively. Blinking in the AC amplitude is observed when the tip-sample distance approaches the molecular length range (estimated from the tunnelling as 0.5 nA). Bias is -50 mV, and a small feedback gain is maintained to correct slow drift but not the fast tip-substrate distance modulation.
Additional control experiments

The control experiment that examines if rectification can be observed when one end of a molecular junction is broken (referring to regime A in Fig. 3 of the manuscript) has already been discussed in the main text. In that case, the I-Vs are symmetric regardless of whether the molecule is the symmetric tetraphenyl or the asymmetric dipyrimidinyl-diphenyl moiety. Another observation is that in each case the current is much smaller than that of the junction with a formed molecular bridge. Here we provide statistical averaged I-V curves from repeatedly measured open junctions (Au-molecule-gap-Au), which further confirms the result discussed in the main text (Figure S3).

S3: I-V curves of open molecular junctions (tunnelling through space). (a) Tetraphenyl block. (b) Dipyrimidinyl-diphenyl diblock. Error bars correspond to standard deviation.
conductive than the tetraphenyl junction. We have also performed direct control experiments without removing the trimethylsilylethyl protection group (second deprotection stage not performed). The individual conductance traces are simple exponential decays with no sign of formation of molecular junctions (Fig. S4). A conductance histogram constructed from over 1000 traces is featureless. The measurement shows that either the molecular block cannot form a bridge in the presence of the trimethylsilylethyl group or its conductance is below the noise level. These experiments rule out the possibility of observed rectification behaviour as a result of asymmetry in the anchoring groups.

S4: Conductance analysis of the dipyrimidinyl-diphenyl block in the presence of the trimethylsilylethyl protection group (see inset in (b)); (a) Individual current traces. (b) Corresponding histogram constructed from 1000 individual traces. Applied bias is -50 mV.
Measurements at low temperature

In order to obtain additional information on the formation of Au point contacts at large forward bias, we have performed I-V measurements with the asymmetric block at low temperature (~10 K) in a vacuum STM system (Fig. S5). Similar to the results obtained at room temperature, the I-V curves at low temperatures also display pronounced rectification behaviour, but the threshold voltage at which the current begins to rapidly increase appears to be higher. In addition, like the room temperature measurements, a large forward bias leads to the formation of Au point contacts. However, at low temperature (10K), the Au point contact forms when the dissipation power reaches ~6 μW, higher than ~ 1.5 μW found at room temperature. These results suggest that the mechanisms may be a combination of both current-induced heat and force.

S5: (a) I-V curve of dipyrimidinyl-diphenyl diblock in UHV at 10 K. (b) Formation of Au point contact at large forward bias (gray line). Bias ramping rate is 1 V/s.
Resonant charge transport calculations

In order to provide insight into the nature of the rectification effect in chemically asymmetrical molecules, we performed first-principles calculations of atomic, electronic, and transport properties of gold/molecule junctions containing both symmetrical tetraphenyl and asymmetrical dipyrimidinyl-diphenyl diblock molecules. The molecular junction model was built by sandwiching the molecule between 4x4 (111) Au slabs. Then, density functional theory (DFT) within the Perdew, Burke, Ernzerhof (PBE) generalized gradient approximation was used to obtain the atomic and electronic structure of the junction.

In the case of dipyrimidinyl-diphenyl we found that the molecule, having the total length of 19.23 Å (measured between the anchoring sulphur atoms), is tilted by 38° with respect to the normal to the Au (111) surface. The individual rings are rotated with respect to each other and the dipyrimidyl block by a torsional angle of 30°, while the torsional angle between the pyrimidyl rings is zero. The symmetric tetraphenyl molecule is also tilted by 43.5°, the torsional angle between phenyl rings being 32°.

\[ M^0 \] and the corresponding molecular ions \( M^- \) and \( M^+ \). This widely-used method of calculation of EAs and IPs is referred to as the \( \Delta \)SCF method, and was shown during systematic studies across the large
database of organic molecules to achieve an accuracy of 0.1 – 0.2 eV by using DFT\textsuperscript{9-14}. Such a surprisingly good prediction of IPs and EAs is due to a fortunate cancellation of self-interaction errors during subtraction of the DFT total energies\textsuperscript{13}. Calculated IP and EA for the dipyrimidinyl-diphenyl molecule are 6.98 eV and 1.53 eV respectively, and those values for the tetraphenyl molecule are 6.50 eV (IP) and 0.75 eV (EA). The experimental information concerning ionization potential and electron affinity are currently unavailable.

The energy of the lowest hole energy level $\varepsilon_h$ at zero bias corresponds to the molecule’s ionization potential corrected by the interaction of the hole with its image charge in the electrodes. In the case of the dipyrimidinyl-diphenyl molecule, $\varepsilon_h$=-6.18 eV, while for the tetraphenyl molecule, $\varepsilon_h$=-5.7 eV. The lowest electron energy levels for both molecules are much higher ($\varepsilon_e$ = -2.33 eV and $\varepsilon_e$ = -1.55 eV) than the Fermi energies of the electrodes at zero bias, $\varepsilon_F^l = \varepsilon_F^r = -5.35$ eV (all the one-electron levels are referenced in respect to the vacuum level). Therefore, the resonant charge transfer in diblock molecule takes place through the hole resonant levels\textsuperscript{6-8} (see Fig. 6a of the manuscript).

The mechanism of resonant tunnelling via the hole resonant energy levels is the only mechanism that can explain experimentally observed high values of the current and the threshold character of the I-V curves. Hopping or polaronic mechanisms are not operational due to the following reasons. Both mechanisms require the localization of the extra charge due to its interaction with the dipole vibration modes of the molecule. Then, this charge moves through the molecule in the external electric field together with its polarization dressing (polaron mechanism) or by hopping between the localized charge traps (variable hopping mechanism). Our DFT calculations of the charged states of the molecule rule out any such charge localization:
the charged-state wave-functions, being of $\pi$-conjugated character, are delocalized over the entire molecule.

Several factors influence the hole states that determine the charge transport in the molecular junction. First, they are the charged states of the molecule, therefore, the hole energy levels are renormalized by the image potential due to the interaction of the positive charge $+e$, distributed over the molecule, with the metallic electrode. Second, due to electrostatic energy of the hole in the external electric field the levels are raised or lowered approximately as $-1/2 |e| V$ depending on the polarity of the bias $V$ applied at the right electrode. For simplicity we assume that the left electrode is grounded. The electrostatic energy and the image potential were calculated based on the distribution of the hole charge which was defined as the difference between the charge densities of the positively charged and neutral molecules obtained as a function of the applied voltage.

The electrostatic contribution of the energy level shift at bias $V$ is calculated as 
\[ \int \rho_h(r,V) \phi_{ext}(r,V) \, dr, \]
where $\rho_h(r,V)$ is the hole charge distribution and $\phi_{ext}(r,V)$ is the external electrostatic potential due to the applied bias. The energy levels of the excited hole states were obtained taking into account the relative positions of the occupied orbitals of the neutral molecule with respect to the highest occupied molecular orbital (HOMO). Fig. S6a shows the hole energy levels for dipyrimidinyl-diphenyl and tetraphenyl molecules as a function of the electric field. The red horizontal line corresponds to the fixed Fermi level of the grounded left electrode $\varepsilon_F^L = -5.35 \text{ eV}$ (minus the work function of Au (111)), and the red inclined line is the Fermi level of the right electrode $\varepsilon_F^R = \varepsilon_F^L - |e| V$, see Fig. 6 in the manuscript. The hole energy levels contribute to the current, if they are close or within the current energy window represented by these two red lines. In both asymmetric and symmetric molecules, the hole energy levels
approach the current energy window at non-zero bias which results in the threshold behaviour of I-V characteristics: current is zero up to some turn-in voltage. The levels start to contribute to the current even if they are outside the current energy window because they are broadened by the coupling of the electronic and vibrational degrees of freedom for the molecule.

S6: DFT calculations; (a) Hole energy levels as a function of the applied bias (blue curves) and the current energy window specified by the Fermi energies of the left ($\varepsilon_F^l$) and right ($\varepsilon_F^r$) electrodes (red lines). (b) Probabilities of hole transfer from the molecule to the right and left electrodes. The anode is at the right electrode at $V>0$ and at the left electrode at $V<0$.

The resonant tunnelling current is calculated as a sum of contributions from each resonant hole level that are either close or within the current energy window,

$$ I = \sum_i I_i \cdot I_i(V) = \gamma_{\Delta}(V) \cdot \Phi(-\delta\varepsilon_i + \varepsilon_r)/\sigma $$  

(5)
Where $\delta \varepsilon_i$ is the energy of the hole level referenced by the Fermi energy of the anode (the right electrode at the positive bias and the left electrode at the negative bias), and $\gamma^i_a(V)$ is the probability of hole transfer from the anode to the molecule at voltage $V^{6,8}$,

$$\gamma_a(\varepsilon_h) = \frac{2\pi}{\hbar} |\langle \psi_h(r,V) | U_a | \psi_a(r) \rangle|^2 \rho(\varepsilon_h^2)$$  \hspace{1cm} (6)

Here $\psi_h(r,V)$ is the asymptotics of the hole wave function in anode region, $U_a$ is the electron potential in the metal and $\psi_a(r)$ is the corresponding electron wave function. The error function $\Phi$ in (5) describes the line shape of the hole level $i$ due to the electron-vibron interactions in the course of the charge transfer transition. Such electron-vibron interactions result in the level broadening that involves the reorganization energy $\varepsilon_r$ and the temperature $T$, $\sigma = 2\sqrt{\varepsilon_r k_B T}$. The reorganization energy was found to be weakly dependent on $V$, $\varepsilon_l \approx 0.08$ eV for dipyrimidinyl-diphenyl and $\varepsilon_l \approx 0.06$ eV for tetraphenyl. Fig. S6b shows the bias dependence of $\gamma_a(V)$ for the first ground state hole level, which corresponds to the HOMO of the neutral molecule. This is the level that first approaches and enters the current energy window, see top panel of Fig. S6a. The bias dependence is markedly asymmetric in the case of dipyrimidinyl-diphenyl, which is mostly due to the asymmetry of the corresponding hole wave function, $\gamma^i_a(V) \propto |\psi_h^i(r_a,V)|^2$. The initial electronic asymmetry due to the differing chemical compositions of the dipyrimidinyl and diphenyl blocks is amplified as the molecule experiences the external electric field. In contrast, the tetraphenyl molecule exhibits perfectly symmetric behaviour because both ends of the molecule are chemically and electronically equivalent.

The current-voltage characteristic for dipyrimidinyl-diphenyl molecule shown in Fig. S7a clearly displays rectification behaviour, i.e. the large current at positive bias and small current at negative bias. The characteristic feature of theoretical I-V curve is the asymmetry in turn-on
(threshold) voltage: the current starts to increase from zero at $V_{th} \approx 0.7\,\text{V}$ at positive bias and at $V_{th} \approx 1.2\,\text{V}$ at negative bias, which is one of the consequences of the asymmetrical behaviour of the hole wave functions in the external electric field.

**S7:** Calculated $I(V)$ characteristics: (a) for the dipyrimidinyl-diphenyl and (b) for tetraphenyl molecules.

The theoretical rectification ratio at 1.5 V is $I(+1.5\,\text{V})/I(-1.5\,\text{V}) \approx 2.5$. The asymmetry becomes less pronounced at larger biases above 1.5 V due to additional contributions of hole levels other than that of HOMO. It is also seen from Fig. S7b that the I-V curve for tetraphenyl is perfectly symmetric. Thus, we come to the conclusion that the rectification behaviour of the diblock dipyrimidinyl-diphenyl molecule is due to the strong asymmetrical localization of the hole ground state wave function in the electric field. This is the consequence of the original electronic structure which reflects the underlying chemical differences between the dipyrimidinyl and diphenyl blocks.
References


3. The tip-sample distance was roughly estimated considering a classical 1-D tunneling gap for the STM junction and taking a local energy barrier ~1 eV for Au. Molecular length of 0.8 nm is considered for C8dithiol.


