Supporting Information for:

Single Molecule Rectification Induced by the Asymmetry of a Single Frontier Orbital

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Transmission Function: Tight-Binding Model

This section provides a derivation of Eq. (1) of the main text, giving an expression for the transmission function as a function of the applied bias potential for a tight binding model with a single transport channel. The Green's function for such a molecule in between the electron source and drain reservoirs (Figure 1) is

$$\mathscr{G}_{dev}(\varepsilon) = [\varepsilon - H_{dev} - \Sigma_T(\varepsilon)]^{-1} \tag{1}$$

where ε is the energy, H_{dev} is the molecular Hamiltonian, and Σ_T is the total self-energy of the contacts, which can be decomposed as the sum of the self-energy of the left and right lead contributions: $\Sigma_T(\varepsilon) = \Sigma_L(\varepsilon) + \Sigma_R(\varepsilon)$.

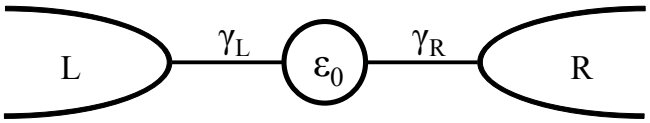

Figure 1: Scheme of a molecule with a single transport channel state $|\varepsilon_0\rangle$, coupled to the left (L) and right (R) electron reservoirs with coupling constants γ_L and γ_R, respectively.

The retarded and advanced Green's functions are

$$\mathscr{G}^{+}_{dev}(\varepsilon) = \frac{1}{\varepsilon - H_{dev} - \Sigma_T(\varepsilon)} \tag{2}$$

$$\mathscr{G}^{-}_{dev}(\varepsilon) = \frac{1}{\varepsilon - H_{dev} - \Sigma^{\dagger}_T(\varepsilon)} \tag{3}$$

The self-energy for the left (L) and right (R) contacts are

$$\Sigma_{L/R}(\varepsilon) = \Delta_{L/R} + i\Gamma_{L/R}(\varepsilon) \tag{4}$$

where the real part Δ can be approximated as $\Delta_L \simeq \frac{V}{2}$ and $\Delta_R \simeq -\frac{V}{2}$, with V the applied bias voltage. The total self-energy is

$$\Sigma_T(\varepsilon) \simeq i[\Gamma_L(\varepsilon) + \Gamma_R(\varepsilon)] \tag{5}$$

Considering there is only one state $|\varepsilon_0\rangle$ between the two contacts, we have $\langle\varepsilon_0|H_{dev}|\varepsilon_0\rangle = \varepsilon_0$, and the retarded and advanced Green's function take the form:

$$\mathscr{G}^{+}_{dev}(\varepsilon) = \frac{1}{\varepsilon - \varepsilon_0 - i[\Gamma_L(\varepsilon) + \Gamma_R(\varepsilon)]} \tag{6}$$

$$\mathscr{G}^{-}_{dev}(\varepsilon) = \frac{1}{\varepsilon - \varepsilon_0 + i[\Gamma_L(\varepsilon) + \Gamma_R(\varepsilon)]} \tag{7}$$

For either the left or right contact:

$$\Sigma(\varepsilon)_{L/R} = \gamma^{\dagger}_{L/R}\mathscr{G}^{+}_{L/R}\gamma_{L/R} = \gamma^{2}_{L/R}\mathscr{G}^{+}_{L/R} \tag{8}$$

where $\gamma_{L/R}$ is the coupling between the contact and the device, and $\mathscr{G}^{+}_{L/R}$ is the retarded Green's function of the contact. The seccond equality results from the fact that $\gamma_{L/R}$ and $\mathscr{G}^{+}_{L/R}$ commute in this particular case. Together with the expression $\Sigma(\varepsilon)_{L/R} = \Delta_{L/R} + i\Gamma_{L/R}(\varepsilon)$, we have:

$$\begin{aligned} \Delta_{L/R} + i\Gamma(\varepsilon)_{L/R} &= \gamma^{2}_{L/R}\mathscr{G}^{+}_{L/R}(\varepsilon) \\ \Longrightarrow \mathscr{G}^{+}_{L/R}(\varepsilon) &= \frac{\Delta_{L/R}}{\gamma^{2}_{L/R}} + i\frac{\Gamma_{L/R}(\varepsilon)}{\gamma^{2}_{L/R}} \end{aligned} \tag{9}$$

The density of states (DOS) of the contact can be expressed by the imaginary part of the retarded Green's function of the contact: [1,2]

$$DOS(\varepsilon) = -\frac{1}{\pi}Im[\mathscr{G}^{+}(\varepsilon)] \tag{10}$$

therefore, we can write the imaginary part of the self-energy $\Gamma_{L/R}$ in terms of the contact DOS:

$$\begin{aligned} DOS_{L/R}(\varepsilon) = -\frac{1}{\pi}Im[\mathscr{G}^{+}_{L/R}(\varepsilon)] &= -\frac{1}{\pi}\frac{\Gamma(\varepsilon)_{L/R}}{\gamma^{2}_{L/R}} \\ \Longrightarrow \Gamma(\varepsilon)_{L/R} &= -\pi\gamma^{2}_{L/R}DOS_{L/R}(\varepsilon) \end{aligned} \tag{11}$$

Also,

$$\mathscr{A}_{L/R}(\varepsilon) = i[\Sigma_{L/R}(\varepsilon) - \Sigma^{\dagger}_{L/R}(\varepsilon)] = -2\Gamma_{L/R}(\varepsilon) \tag{12}$$

Therefore, the transmission function can be computed as:

$$\begin{aligned} T(\varepsilon) &= \mathscr{A}_L(\varepsilon)\mathscr{G}^{+}_{dev}(\varepsilon)\mathscr{A}_R(\varepsilon)\mathscr{G}^{-}_{dev}(\varepsilon) \\ &= 2\Gamma_L(\varepsilon)\mathscr{G}^{+}_{dev}(\varepsilon)2\Gamma_R(\varepsilon)\mathscr{G}^{-}_{dev}(\varepsilon) \\ &= \frac{4\Gamma_L(\varepsilon)\Gamma_R(\varepsilon)}{(\varepsilon-\varepsilon_0)^2 + [\Gamma_L(\varepsilon)+\Gamma_R(\varepsilon)]^2} \\ &= \frac{4\pi^2\gamma_L^2 DOS_L(\varepsilon)\gamma_R^2 DOS_R(\varepsilon)}{(\varepsilon-\varepsilon_0)^2 + \pi^2[\gamma_L^2 DOS_L(\varepsilon)+\gamma_R^2 DOS_R(\varepsilon)]^2} \end{aligned} \tag{13}$$

Under a voltage bias V, we have:

$$T(\varepsilon) = \frac{4\pi^2\gamma_L^2 DOS_L(\varepsilon-\frac{V}{2})\gamma_R^2 DOS_R(\varepsilon+\frac{V}{2})}{(\varepsilon-\varepsilon_0)^2 + \pi^2[\gamma_L^2 DOS_L(\varepsilon-\frac{V}{2})+\gamma_R^2 DOS_R(\varepsilon+\frac{V}{2})]^2} \tag{14}$$

Additional figures

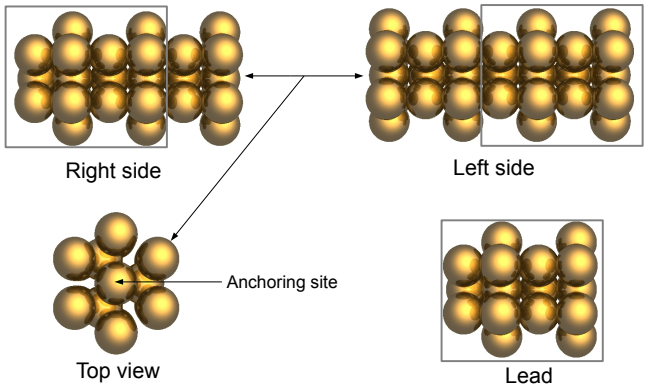

Figure 2: Leads used for building the extended systems described in the text. The Au lattice constant of the hcp lattice is 4.080 ÅThe face of the leads is the (111) surface.

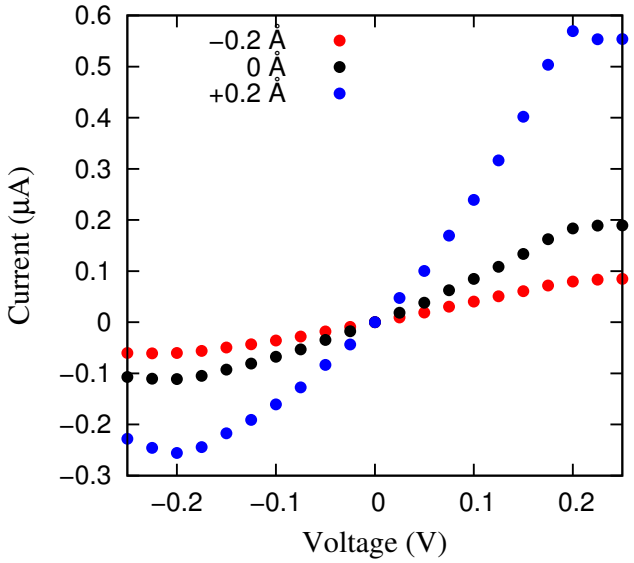

Figure 3: I-V curves for $\mathbf{Au}_L$**-S-Ph-amide-Ph-S-**$\mathbf{Au}_R$ for various different S-Au distances.

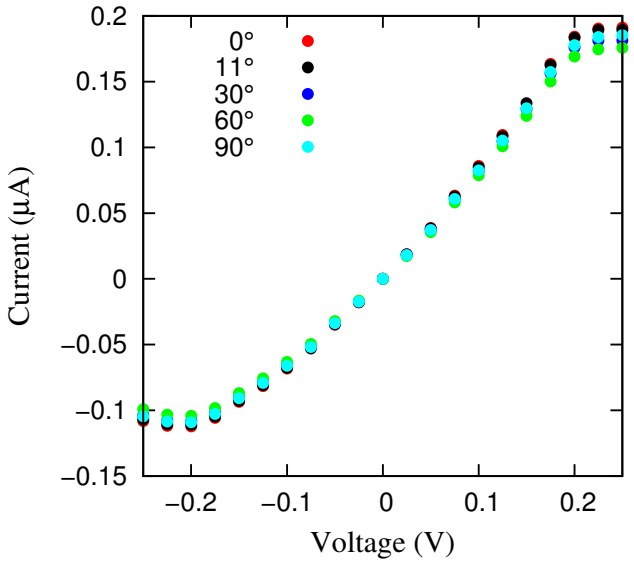

Figure 4: I-V curves for **Au$_L$-S-Ph-amide-Ph-S-Au$_R$** for various rotational orientations of the molecule with respect to the contact.

Coordinates of isolated studied systems

HS-Ph-amide-Ph-SH

C	-4.67450400	-0.20420200	-0.02467400
C	-3.94683100	-1.37807200	-0.25661100
C	-3.97529100	0.98643100	0.19883800
C	-2.55787700	-1.35169100	-0.26369100
H	-4.46321200	-2.31750500	-0.42910000
C	-2.58231400	1.01979600	0.19793000
H	-4.51604700	1.91156900	0.37587200
C	-1.85676200	-0.15745000	-0.03641000
H	-2.01053000	-2.27430200	-0.44378100
H	-2.05262700	1.94605300	0.36696900
N	-0.44817600	-0.21925000	-0.04407200
H	-0.06535500	-1.12745300	-0.26018600
C	0.46070200	0.80995600	0.07599500
O	0.14115700	1.99055500	0.17789900
C	1.90237500	0.39152300	0.05640800
C	2.84562000	1.36365600	-0.30164600
C	2.36007000	-0.88709700	0.40603100
C	4.20176300	1.06435900	-0.34469600
H	2.49064000	2.35922700	-0.54465400
C	3.71692900	-1.19356900	0.37559500
H	1.66776300	-1.65122300	0.74868600
C	4.65036000	-0.22121900	-0.00911500

H	4.91104300	1.83270500	-0.63736800
H	4.05145800	-2.18570700	0.66308500
S	-6.46079400	-0.30232900	-0.04553100
S	6.37123600	-0.68625000	-0.03993900
H	-6.69517500	0.96005400	0.36047800
H	6.85750900	0.51962300	-0.39088700

HS-stilbene-SH optimized structure

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C	2.54100100	0.99647700	0.08251800
C	3.92175800	1.13386600	0.07667900
C	-1.92731100	0.27005100	0.00583500
C	-2.77637100	1.38995500	-0.07054300
C	-4.16061200	1.26307600	-0.07673900
C	-4.75058900	-0.00475600	-0.00324500
C	-3.92248000	-1.13392000	0.07803800
C	-2.54059100	-0.99547400	0.08304500
H	-4.78271700	2.15114300	-0.13898500
H	-4.35793200	-2.12702500	0.14100800
H	-1.93177000	-1.89117300	0.15416800
C	-0.47878900	0.47533900	0.00353700
C	4.16138900	-1.26321800	-0.07487800
C	4.75064400	0.00377100	-0.00307100
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H	1.93187400	1.89195400	0.15218400
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H	-0.17694600	1.52127300	-0.00666500
S	6.51738200	0.26104500	-0.00153000
S	-6.53308800	-0.10589100	-0.01224900
H	6.86950300	-1.03368900	-0.11836900
H	-6.61935100	-1.44845000	0.05164000

HS-stilbene-SH twisted structure

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H                  2.21919300    2.33061900    0.00349000
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Sample imput file with the coordinates for the full system of Au_L-S-Ph-amide-Ph-S-Au_R

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References

(1) Zahid, F.; Paulsson, M.; Datta, S. In *Advanced Semiconductor and Organic Nano-Techniques III: Physics and Technology of Molecular and Biotechnology Systems*; Morkoç, H., Ed.; Academic Press: San Diego, 2003; Chapter 1 - Electrical Conduction through Molecules, pp 1 – 41.

(2) Economou, E. *Green's Functions in Quantum Physics*, 3rd ed.; Springer Series in Solid-State Sciences; Springer, 2006.