Single Molecule Conductance, thermopower and Transition Voltage

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Circuit current offset and calibration:

In order to measure the thermoelectric effect of a single molecule, it is necessary to ensure that the offset current/voltage of the electric circuit is sufficiently stable during the measurement. Fig. S1a shows the schematics of the current preamplifier circuit used in the experiment, where resistor, R_M, represents the molecular junction, current source, I_{TE}, represents the thermoelectric current, U_{os} and I_{os} are the input offset voltage and current of the circuit, respectively.
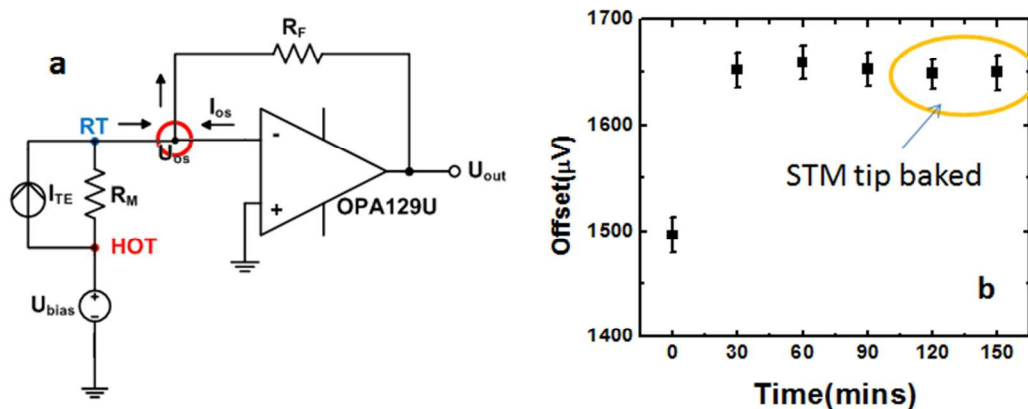

Fig. S1. (a) Circuit diagram of a current pre-amplifier used in the experiment. (b) The stability of the circuit offset.

Kirchhoff's current law at the circled node gives rise to

$$U_{out} = \frac{R_F}{R_M}(U_{os} - U_{bias}) + U_{os} - I_{os}R_F - I_{TE}R_F. \qquad (S1)$$

The total input current offset at zero applied bias, $I_{TE,m}$, is then given by

$$I_{TE,m} = \frac{U_{out}|_{U_{bias}=0}}{-R_F} = I_{TE} + I_{os} - U_{os}\left(\frac{1}{R_M} + \frac{1}{R_F}\right) = I_{TE} + I_0, \qquad (S2)$$

where $I_0 = I_{os} - U_{os}\left(\frac{1}{R_M} + \frac{1}{R_F}\right)$ is the total offset current due to the circuit itself.

The corresponding voltage offset including the thermoelectric effect is given by

$$U_{TE,m} = U_{TE} + I_{os}R_M - U_{os}R_M\left(\frac{1}{R_M} + \frac{1}{R_F}\right), \qquad (S3)$$

where $U_{TE} = I_{TE}R_M$.

In order to ensure that the measured voltage offset is independent of the molecular resistance, R_M, a large R_F was used (e.g., $R_F = 100 \times R_M$), and the measured voltage offset, $U_{TE,m}$, is expressed as

$$U_{TE,m} \approx U_{TE} + I_{os}R_M - U_{os} = U_{TE} + U_0, \qquad (S4)$$

where $U_0 = I_{os}R_M - U_{os}$ is the offset voltage due to the circuit, which remains constant if U_{os} and I_{os} are stable over time.

Fig. S1b plots the measured voltage offset of the circuit with a dummy resistor at the input to simulate the molecular junction. It shows that the circuit becomes stabilized in ~30 minutes after turning on the power. In addition, baking the STM tip by placing a heat source in close proximity (no direct contact) doesn't change the offset. We typically left the circuit on overnight to ensure maximum stability.

Relationship between thermopower and energy level alignment:

The transmission function for a molecular junction can be described in terms of Lorentian functions, given by

$$\tau(E) = \sum_n^N \frac{\Gamma_{n,1}\Gamma_{n,2}}{\left(\Gamma_{n,1}+\Gamma_{n,2}\right)^2/4+(E-\varepsilon_n)^2}, \qquad (S5)$$

where ε_n is the energy level of the nth molecular orbital, and $\Gamma_{n,1}$ and $\Gamma_{n,2}$ describe the couplings of the nth molecular orbital to first and second electrodes, respectively.

Assuming that molecule-electrode contacts are symmetric and the HOMO of the molecule dominates the charge transport, then Eq. S5 can be simplified as

$$\tau(E) = \frac{\Gamma_H{}^2}{\Gamma_H{}^2+(E-\varepsilon_H)^2}, \qquad (S6)$$

where ε_H is the energy level of the HOMO, and Γ_H is the coupling of the HOMO to the electrodes.

If further assuming that Γ_H is energy-independent (the wideband approximation), the thermopower can be expressed as,

$$S_{junction} = -\frac{\pi^2 k_B^2 T}{3|e|}\frac{\partial \ln(\tau(E))}{\partial E}\bigg|_{E=E_F} = \frac{\pi^2 k_B^2 T}{3|e|}\frac{2(E_F-\varepsilon_H)}{\Gamma_H{}^2+(E_F-\varepsilon_H)^2}. \qquad (S7)$$

From the works by Bâldea (Refs. S1 and S2), the transition voltage is

$$|e|V_t = \frac{2}{\sqrt{3}}(E_F-\varepsilon_H) + \frac{11}{\sqrt{3}}\frac{\Gamma_H{}^2}{3(E_F-\varepsilon_H)}. \qquad (S8)$$

For weak molecule-electrode coupling, $(E_F-\varepsilon_H)^2 \gg \Gamma_H{}^2$, the thermopower is given by

$$S_{junction} \approx \frac{\pi^2 k_B^2 T}{3|e|}\frac{2}{(E_F-\varepsilon_H)}. \qquad (S9)$$

Since the transition voltage reflects the energy barrier height of the molecular junction, we have

$$|e|V_t \approx \frac{2}{\sqrt{3}}(E_F - \varepsilon_H). \quad \text{(S10)}.$$

Combining Eqs. S9 and S10, the thermopower at 300K is

$$S_{junction} \approx \frac{4\pi^2 k_B^2 T}{3\sqrt{3}e^2} \frac{1}{V_t} \approx \frac{A}{V_t}, \qquad \text{(S11)}$$

where $A = 16.93 \ \mu V \cdot V/K$.

Correlation analysis

As a measure of dependence between two sets of data X and Y, the Pearson's correaltion coefficient is defined as:

$$r_{xy} = \frac{\sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y})}{(n-1)s_x s_y} \quad \text{(S12)}$$

where x_i and y_i are individual data points in X and Y ($i = 1, 2, ..., n$), $\bar{x}$ and $\bar{y}$ are the sample means of X and Y, and s_x and s_y are the sample standard deviation of X and Y. r_{xy} varies between -1 and 1, indicating the degree of linear dependence between X and Y. If X and Y are uncorrelated, r_{xy} will be zero. And r_{xy} is 1 in the case of a perfect positive linear correlation and -1 in the case of a perfect negative linear correlation.

Single molecule transition voltage spectroscopy

After obtaining the I-V curves for single molecular junctions (Figs. S2a and S2d), one can get 4 G-V curves by dividing current by bias (Figs. S2b and S2e). As thousands of curves need to be processed within reasonable time, all G-V curves are fitted using second order polynomial before re-plotting using ln(I/V2) vs. 1/V axes, known as Fowler-Nordheim plot (Figs. S2c and S2f). The corresponding bias at minimum point in such plot is the transition voltage, which is a measure of the energy difference between the frontier molecular orbital and the electrodes' Fermi energy.
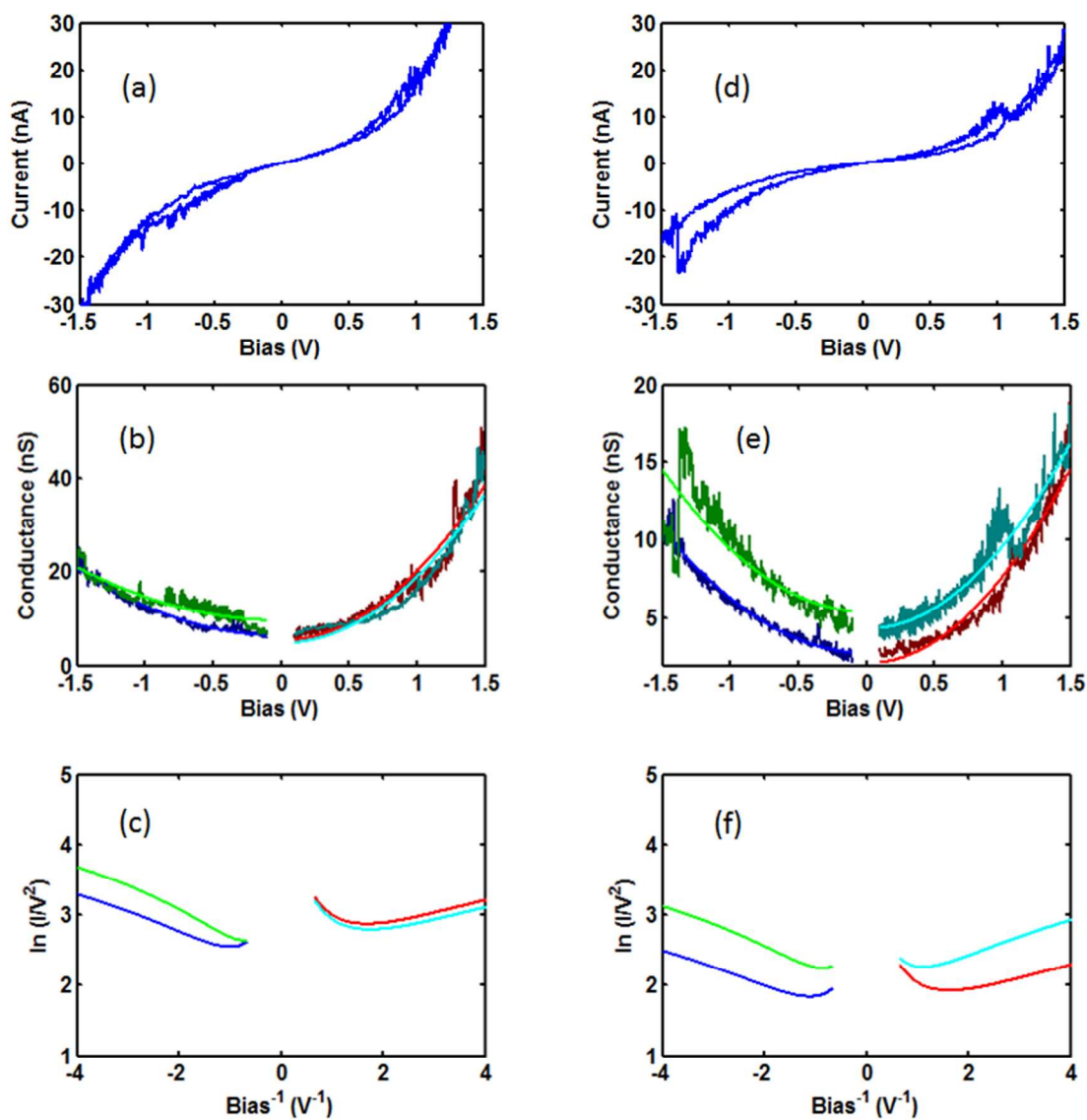
Fig. S2. Examples of I-V, G-V and TVS curves for DMS molecule.

References

S1.   Bâldea, I. *Journal of the American Chemical Society* **2012,** 134, (18), 7958-7962.
S2.   Bâldea, I. *Chemical Physics* **2012,** 400, (0), 65-71.