Supporting Information

Conductance and Geometry of Pyridine-Linked Single Molecule Junctions.

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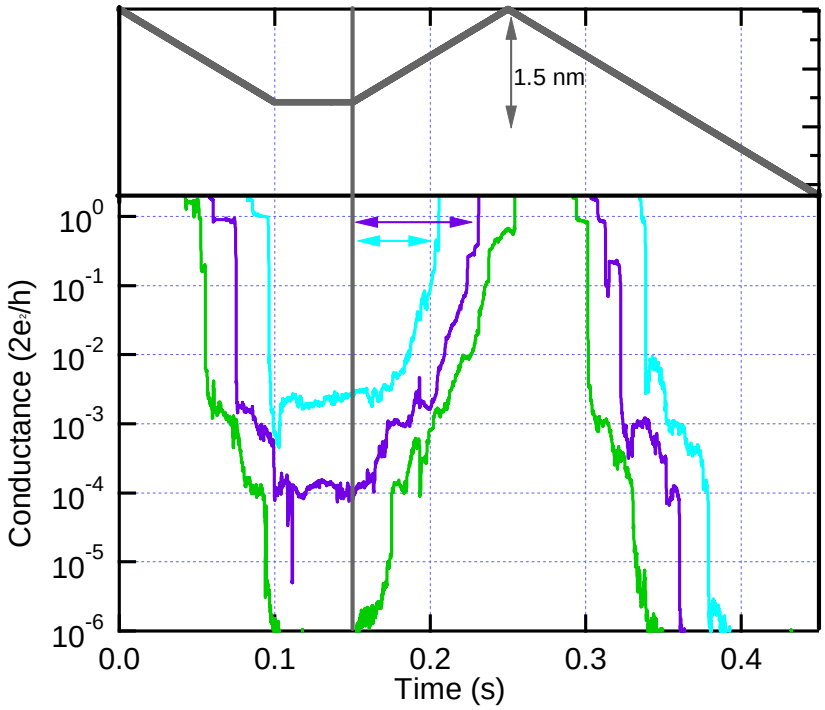
Experimental Procedure and Data Analysis:

The details of our experimental setup have been described previously[1]. Briefly, we prepare gold samples by evaporating 100 nm of gold onto freshly cleaved mica. During measurement, the sample is mounted on top of a single-axis piezoelectric positioner below a hand-cut gold tip in a home-built STM setup. The sample-tip junction is stretched and compressed with sub-nanometer precision by moving the substrate relative to the tip at a rate of 15 nm/s with the piezoelectric (Mad City Labs) while applying constant bias to the sample through a series resistor. The current in the tip is captured by a Keithly 428 current-voltage amplifier. The sample position is manipulated and data acquired at 40 kHz using a data acquisition board (National Instruments, PXI-4461) and custom-built software written in Igor (Wavemetrics, Inc). All position determinations were based on measurements with a built-in position sensor within our custom piezoelectric positioner. This position sensor was calibrated both by the

manufacturer and by us using laser interference measurements. We found the absolute values of the measured displacements to be accurate to within 5%.

We form metal-molecule-metal junctions by smashing the tip and substrate together until conductance exceeds 5 G_0 and then pulling them apart. All conductance traces acquired that reach a conductance below 5e-6 G_0 are then added to a linear binned histogram by an automated algorithm without any further data selection. Typically, 20000 traces are used to construct conductance histograms. Two-dimensional histograms are automatically generated[2] with the added requirement that a G_0 break is clearly identifiable in the trace (more than 90% of traces that start with a conductance greater than 1 G_0 and break satisfy this requirement). In two-dimensional histograms conductance is binned logarithmically with 100 bins per decade, while displacement is binned linearly for image clarity.

Push-Back Distance Measurements: To measure the push-back distance required for closing a metal-molecule-metal junction and to identify the distance between the gold electrodes when a molecule is bound, we measure conductance while the junctions are both opened and closed[3]. A typical manipulation ramp is shown in Figure S1, where the junction was first stretched by 1.5 nm, held at a fixed separation for 0.05 seconds, pushed back together and finally elongated by about 3 nm. Between successive ramps, the substrate and tip are smashed together to a conductance greater than 5 G_0 so that the previous junction geometry is fully disrupted. The ramp is repeated at least 10000 times to allow statistical analysis.

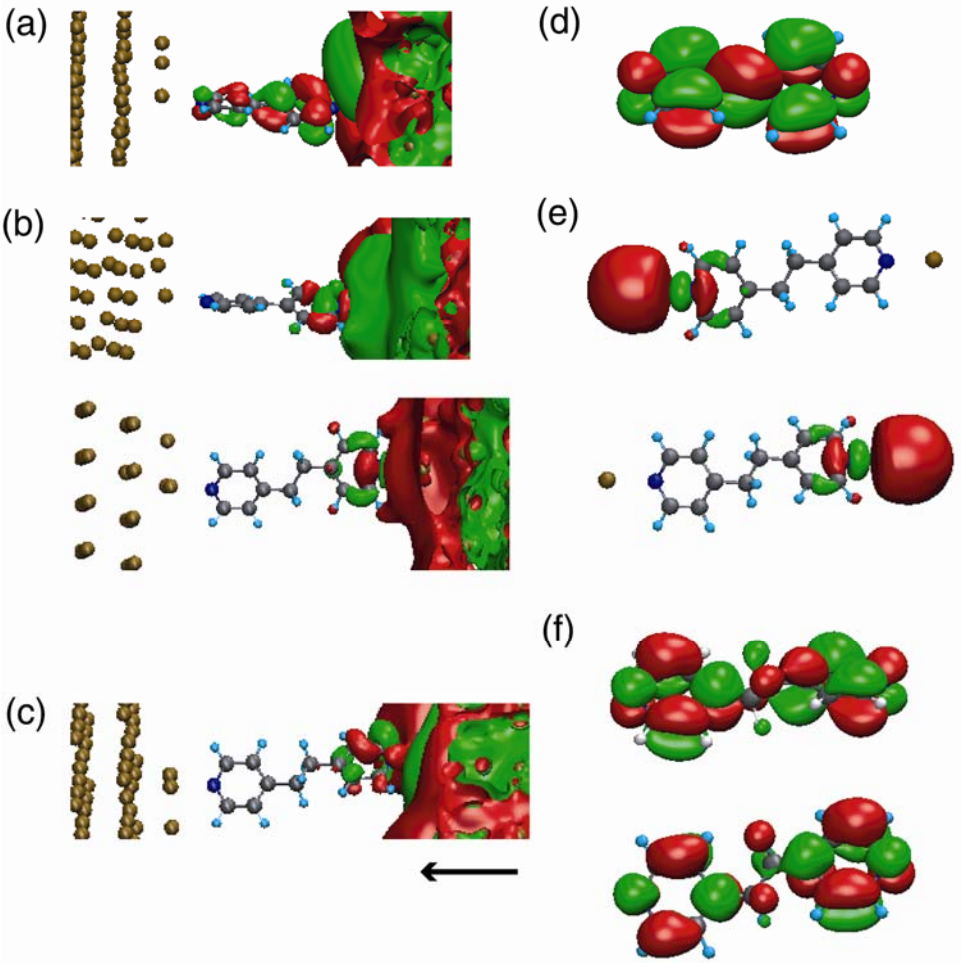


SI FIGURE S1: Upper panel: The piezo manipulation ramp used for push-back distance measurements. The junctions are first stretched by 1.5 nm, then held at a constant separation for 0.05 seconds, pushed back by 1.5 nm and finally stretched out by about 3 nm. Lower Panel: Typical conductance traces recorded with the push-back ramp in the presence of molecule **2**. Some junctions are fully broken during the hold portion (green), while others exhibit conductance above the noise level (purple and blue). All junctions that exibit a stable conductance signature during the hold (where the standard deviation of the conductance in that region does not exceed 150% of the average conductance) were included in the analysis; this includes junctions where the hold conductance did not correspond to either a high or a low conductance configuration. In this figure, the blue trace exhibits a hold conductance consistent with the high conductance geometry, whereas the purple shows a conductance consistent with the low G peak.

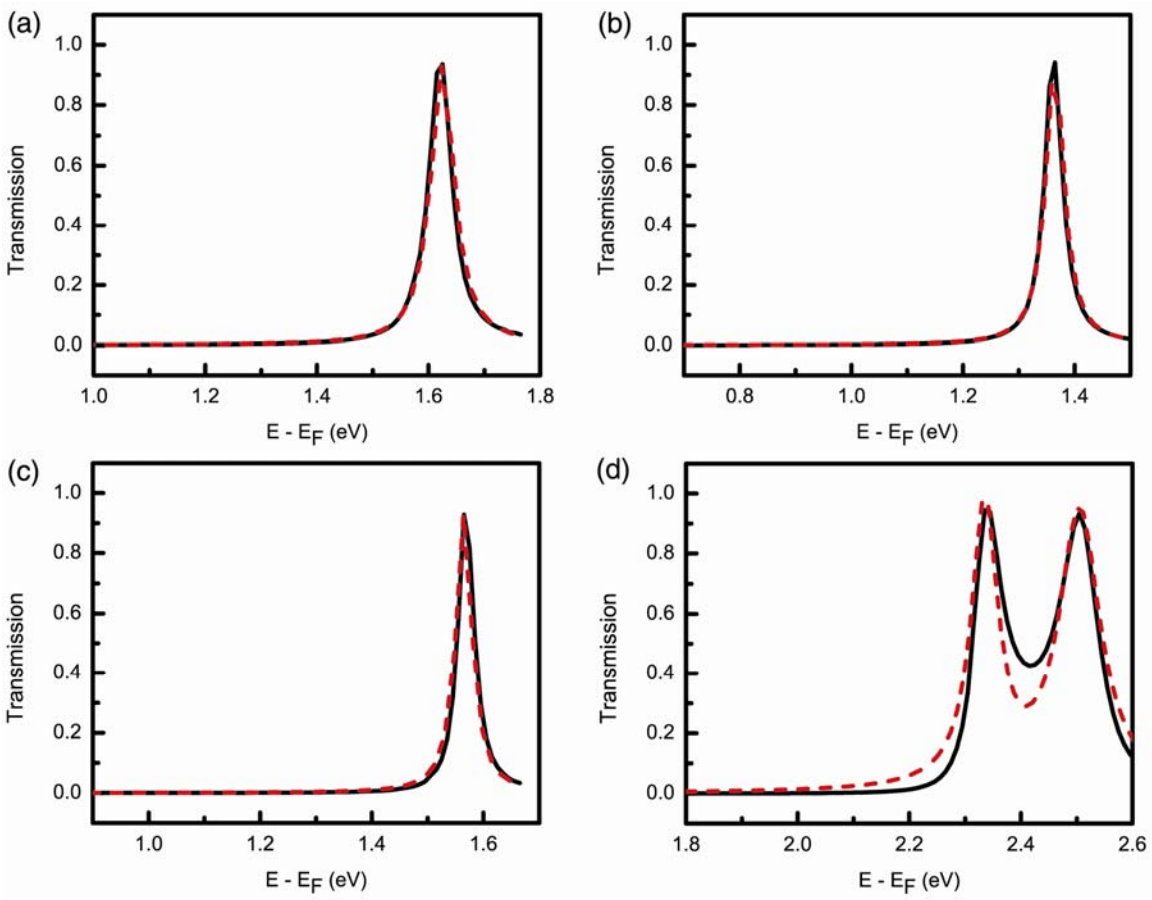
Push back analysis to correlate junction conductance to gold-gold separation was performed by an automatic algorithm which averages the conductance of the last quarter of the hold portion (0.013 sec) of each trace and finds the push-back distance necessary to reform a junction with a conductance of $0.5G_0$. Sample traces obtained during the pull-

hold-push procedure are shown in Figure S1, where the push-back distances are marked with arrows. Only traces where the conductance during the last quarter of the hold portion did not vary by more than 150% of the average conductance in that portion of the trace were considered. Overall, about 60% of all traces in a sample of at least 10000 were included in the analysis. Hold conductance values from all the included traces were binned logarithmically and plotted against an averaged push-back distance corresponding to the range of each conductance bin. Finally, all the push-back values in included traces where the hold conductance fell within the full width of the low conductance peak position were included in the histograms shown in Figure 3B. The peak position of each histogram corresponds to the most frequently observed electrode separation for the low conductance geometry for each molecule.

Supplemental Theory Figures and Table



SI Figure S2 (a-c) Eigenchannel wavefunctions at E_F. Isocontours are taken at 2.5% of the maximum value for a-b, and 1.25% of the maximum value for c. The arrow in c denotes the direction of incident states on the junctions. (d-f) Gas phase molecular orbital wavefunctions. Isocontours are taken at 10% of the maximum value. (a) molecule **1** junction, eigenchannel wavefunction with LUMO character shown in (d); (b) junctions for molecule **1** (top) and **4** (bottom): eigenchannel wavefunctions with molecular σ character shown in (e): top: HOMO and bottom: LUMO of molecule **4** bonded to 2 Au atoms. (c) molecule **4** junction, eigenchannel wavefunction with no clear σ or π character; (f) LUMO (top) and LUMO+1 (bottom) of gas-phase molecule **4**.



SI Figure S3. (a-c) Lorentzian fits (red dashed) to transmission peaks in GGA+Σ transmission spectra for molecules **1-3** respectively. (d) Fit (red dashed) corresponding to the sum of two Lorentzians for GGA+Σ transmission for molecule **4**.

Junction	HOMO (eV)	LUMO (eV)
Molecule **1**	**-5.9**	**1.6**
Molecule **2**	**-4.0**	**1.4**
Molecule **3**	**-4.5**	**1.6**
Molecule **4**	**-5.6**	**2.3**

SI Table 1. HOMO and LUMO levels in the junction, referenced relative to E_F. The HOMO levels in the junction are obtained by diagonalizing the molecular sub-matrix of the Hamiltonian. For weakly-coupled molecule-metal systems, the eigenvalues of the molecular sub-Hamiltonian are a good approximation to the molecular resonance levels in the junction, as we have found for the LUMO (within 0.1 eV of resonances found in the transmission spectra).

References

1. Ulrich, J.; Esrail, D.; Pontius, W.; Venkataraman, L.; Millar, D.; Doerrer, L. H. *Journal of Physical Chemistry B,* **2006,** 110, (6), 2462-2466.
2. Kamenetska, M.; Koentopp, M.; Whalley, A.; Park, Y. S.; Steigerwald, M.; Nuckolls, C.; Hybertsen, M.; Venkataraman, L. *Physical Review Letters,* **2009,** 102, (12), 126803.
3. Quek, S. Y.; Kamenetska, M.; Steigerwald, M. L.; Choi, H. J.; Louie, S. G.; Hybertsen, M. S.; Neaton, J. B.; Venkataraman, L. *Nature Nanotechnology,* **2009,** 4, (4), 230-234.