Supporting Information for:

Variability of Conductance in Molecular Junctions: J. Ulrich, D. Esrail, W. Pontius,

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Experimental Details:

The STM was constructed from a home-built tip holder mounted on top of a single-axis piezoelectric positioner (Physik Instrumente). A bias of 100mV was applied between a cut Au wire tip and an Au substrate placed on top of the piezoelectric positioner and the resulting current was converted to a voltage with a current amplifier (Keithley 428). Data collection and control of the piezoelectric positioner were done by means of a data acquisition board (National Instruments, PXI-4461) driven by a customized program using Igor software (Wavemetrics Inc.) For the conductance trace measurements, the substrate approached the tip until a set conductance larger than G_0 was measured to ensure that the Au/molecule/Au junction from the previous measurement was completely destroyed. The sample was then withdrawn at a rate of 20 nm/s and the current and position data was recorded at a 40 kHz sampling frequency.

The Au samples were prepared by coating a freshly cleaved mica substrate with 200 nm of 99.999% pure Au (Alfa Aesar) using an thermal evaporator (Edwards/BOC) and cleaned in a UV/O_3 cleaner for 10 minutes just prior to use. An Au wire (0.25 mm diameter, Alfa Aesar 99.999% purity) was mounted in the tip holder and cut just before immersion into the solution. Before any measurements with molecules, the Au substrate was characterized in air to ensure that no features due to contaminations were seen in the conductance histogram below G_0. For the measurements in solution, 1,4-benzenedithiol (Alfa Aesar),1,6 hexanedithiol (Fluka), 1,4 benzenedimethanthiol (Sigma-Aldrich), 1,2 benzenedimethanethiol (Sigma-Aldrich), and 4-methylbenzylmercaptan (Sigma-Aldrich) was dissolved

in 1,2,4-trichlorobenzene (Sigma-Aldrich) and a few drops were added to a freshly cleaned Au substrate.

The samples for the MCBJ experiments were fabricated similar to a procedure given by Ruitenbeek *et al*. (Rev. Sci. Instrum. **67**, 108 (1996)). Eighteen parallel Au wires 30 nm thick with a 100 nm constriction were patterned onto a polyimide layer on top of a flexible Cu/Be bronze substrate using standard electron beam lithography. Subsequently the polymer under the narrow part of the wire was removed in an O_2-plasma to form a 1 µm long bridge. The samples were then mounted in a bending mechanism inside a He-flow cryostat, cooled down to 30 K, and characterized before the deposition of the molecules. In a typical run, 1000 current versus time traces were recorded on one wire while, during each one, a motorized micrometer was bending the substrate over a range of 3 mm at a constant speed of 0.15 mm/s. The translation ratio was roughly estimated from the sample geometry as 3×10^{-6} and from the exponential slope of the current versus time trace as 4×10^{-6} (assuming a vacuum barrier of 4 eV). A bias voltage of 100mV was applied and the current was recorded in time intervals of 2 ms using a semiconductor parameter analyzer (HP) set to a fixed current measurement range. Before collecting each trace, the electrodes were moved back into contact and a 2 V bias was applied for 2 s to erase the memory of the preceding break.

After the control experiment on clean Au wires, the BDT molecules were applied to the electrodes by dipping the sample for 5 minutes into a 1 mM solution in ethanol, rinsing it with ethanol and blowing it dry with N_2. Immediately after that, the samples were returned to the vacuum of the cryostat and characterized in the same way with the molecules.

For the IV measurements with the MCBJ, the electrodes were slowly (~0.2 nm/s) approached while the current was monitored at a constant bias voltage (10 mV), and stopped when the current versus

displacement characteristics changed abruptly from exponential to a plateau. The electrodes were then kept fixed and multiple IV curves were measured.

Fitting Algorithm:

For each breaking trace, the conductance region between 0.1 G_0 and $\sim 10^{-4}$ - 10^{-6} G_0 (1.1 times the detection limit) was selected. For the exponential decay, a straight line was fit to the logarithm of this selected data. For fitting a piecewise constant function to this data, the positions of the steps were first determined by looking for peaks higher than a set threshold in the derivative of the logarithm of the data. For each trace, this threshold was taken to be the 10 % of the height of the largest peak in the derivative of the data, corresponding to the drop from conductance larger than 0.1 G_0 to a conductance below 0.1 G_0. An upper limit of 15 was set on the number of steps. A piecewise constant function was then fit to the data by keeping the step positions fixed and minimizing the least square deviation. Since there are no independent fitting parameters for the piecewise constant function, we use the least squares deviation to compare how close the each of the fits is to the raw data.

Note: For requests of the raw data collected in these experiments, please contact the corresponding author.