Supplementary Information

Conductance of Molecular Junctions Formed with Silver Electrodes

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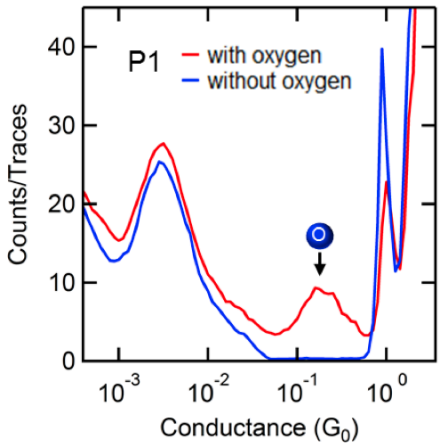
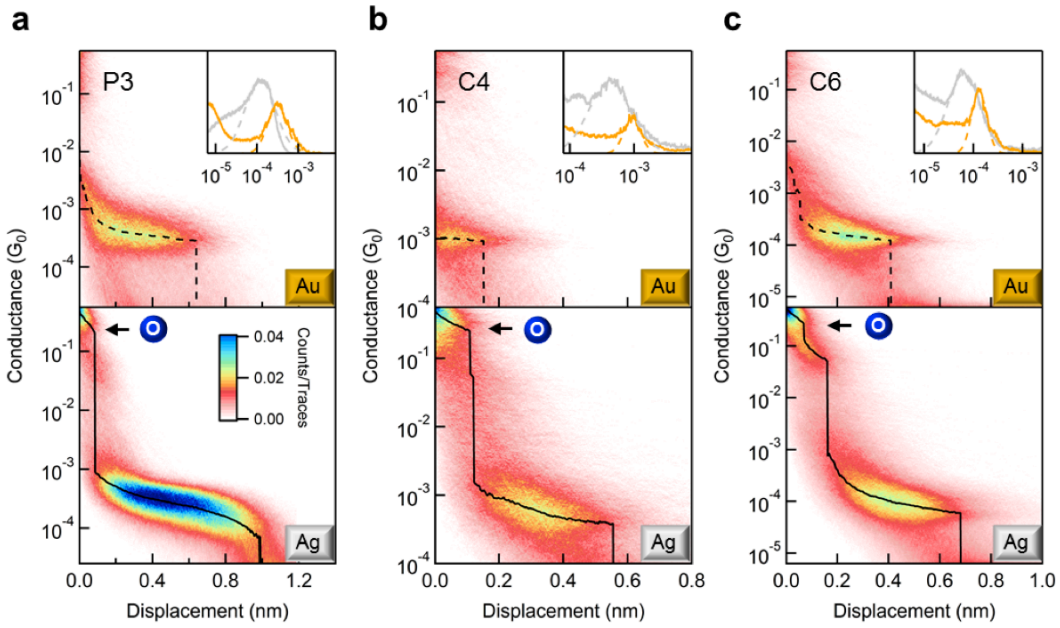
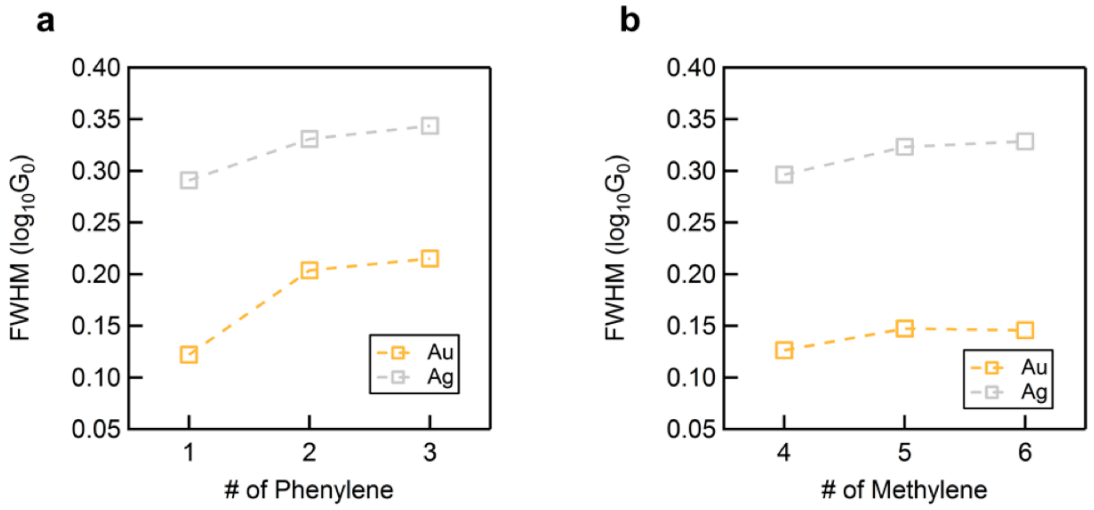


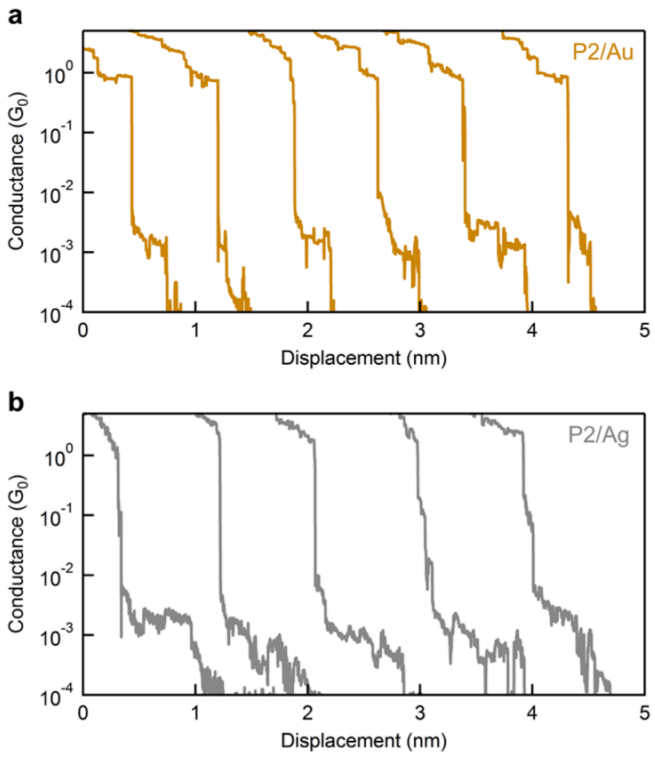
SI Figure S1: Normalized conductance histogram of traces with the oxygen feature (red curve, ~4000 traces) and traces without the oxygen feature (blue curve, ~3000 traces) for **P1** measured with Ag electrodes. Traces were sorted using an automated algorithm. Traces without the oxygen feature were required to have fewer than 50 data points in a region between $0.07G_0$ and $0.7\ G_0$.



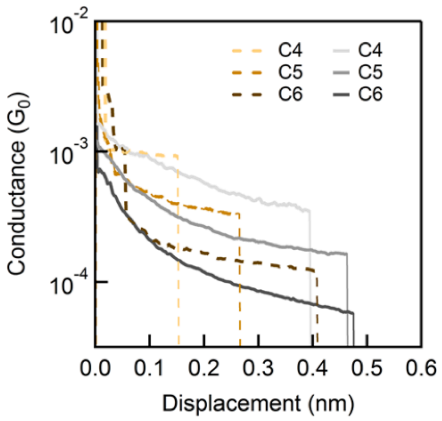
SI Figure S2: Normalized two-dimensional (2D) conductance histograms for **P3** (a), **C4** (b) and **C6** (c) measured with Au (upper panel) and Ag (lower panel) electrodes. Insets in upper panel are conductance profiles and Gaussian fits (dashed curves) determined from 2D histograms over a width of 0.05 nm centered at the end of the molecular feature.



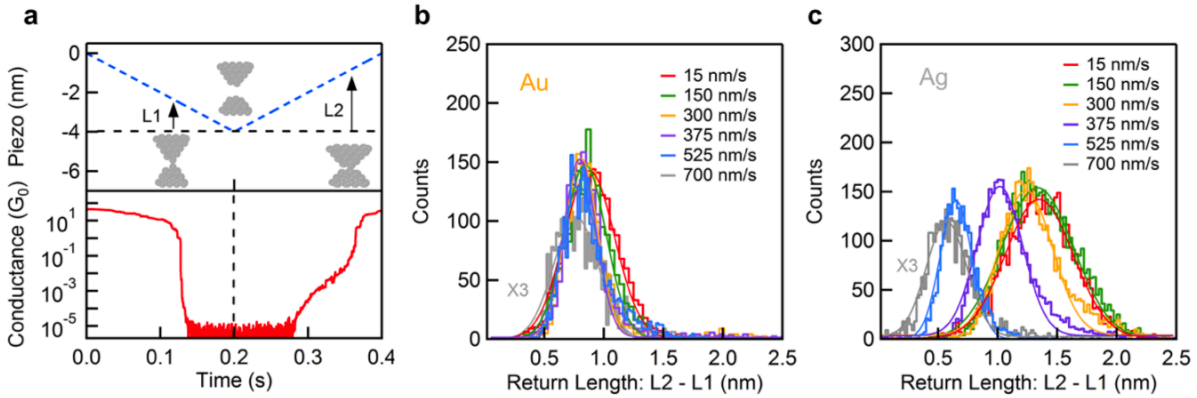
SI Figure S3: Full width at half maximum (FWHM) of conductance profiles determined from 2D histogram for the oligophenyl series (a) and the alkane series (b) with Au and Ag electrodes. These widths were determined from the profiles shown in the inset of Figure 2 and SI Figure S2.



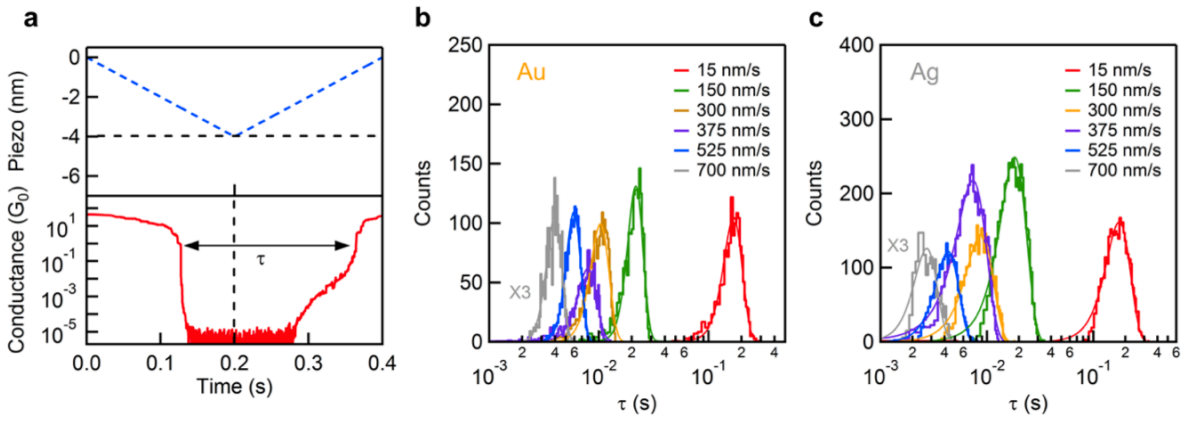
SI Figure S4: Sample traces of **P2** junctions measured with Au (a) and Ag (b) electrodes.



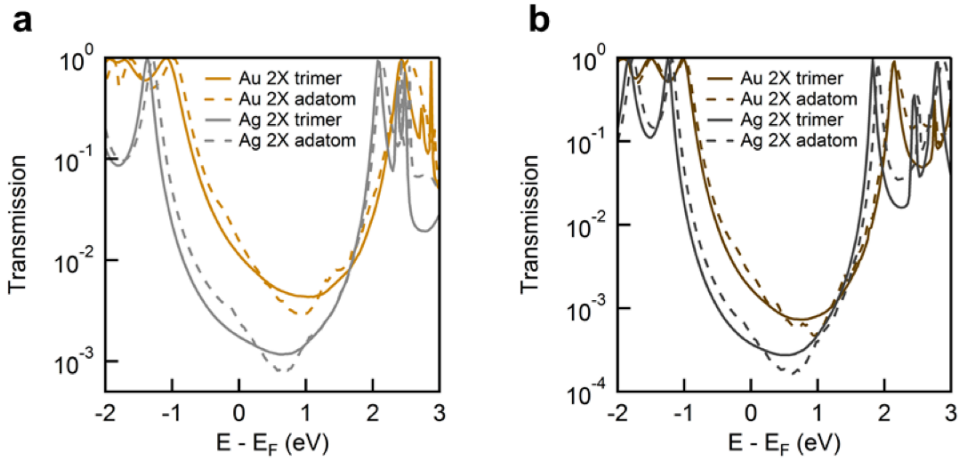
SI Figure S5: Conductance profiles determined from the 2D histograms for the alkane series measured with both Au electrodes (dashed curves) and Ag electrodes (solid curves).



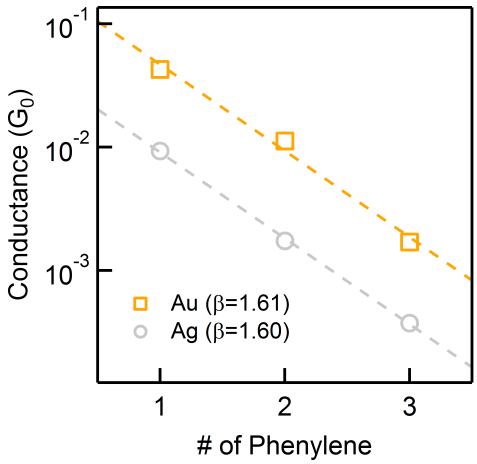
SI Figure S6: (a) Sample piezo ramp (blue dashed line in the upper panel) and simultaneously acquired conductance trace (red curve in the lower panel) used to measure the gap opened up in a metal point contact after rupture. Histograms of return length (L2-L1) measured with Au electrodes (b) and Ag electrodes (c) using different piezo ramp speeds. The histograms are fit with Gaussians (solid curves) to determine the most frequently measured return length for each piezo ramp speed.



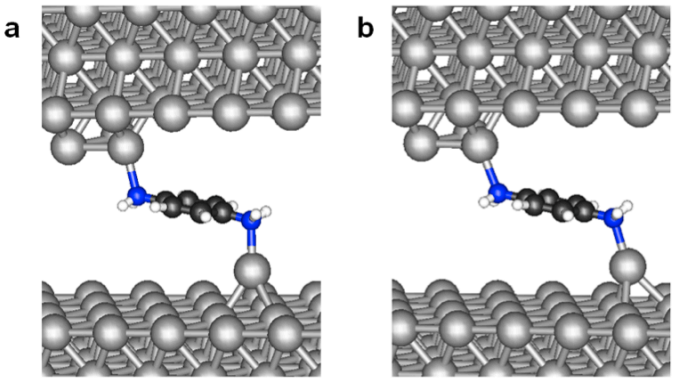
SI Figure S7: (a) Sample piezo ramp (blue dashed line in the upper panel) and simultaneously acquired conductance trace (red curve in the lower panel) used to measure the gap opened up in a metal point contact after rupture. Histograms of time (τ) between contact rupture and reformation measured with Au electrodes (b) and Ag electrodes (c) using different piezo ramp speeds. The time axis is shown on a log scale. The histograms are fit with Gaussians (solid curves) to determine the most frequently measured τ for each piezo ramp speed.



SI Figure S8: Transmission curves for **P2** (a) **P3** (b) with Au and Ag junctions using adatom/adatom (dashed line) and trimer/trimer (solid line) tips.



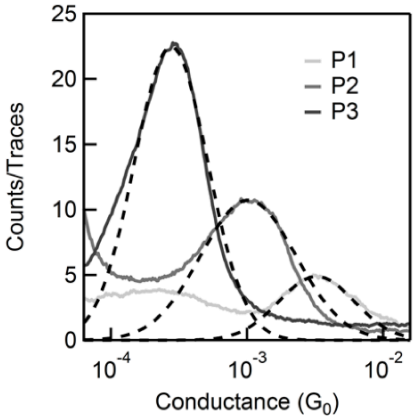
SI Figure S9: Conductance values calculated from density functional theory (DFT) for oligophenyls with both Au (square) and Ag (circle) electrodes using trimer/trimer tips.



SI Figure S10: Optimized structures of **P1** with Ag electrodes for a horizontal junction with the Ag adatom located near neighboring hollow sites. The electrode separation is 10.65 Å (see Fig. 5c). The binding energy of structure (a) is higher than that of structure (b) by ~0.09 eV.

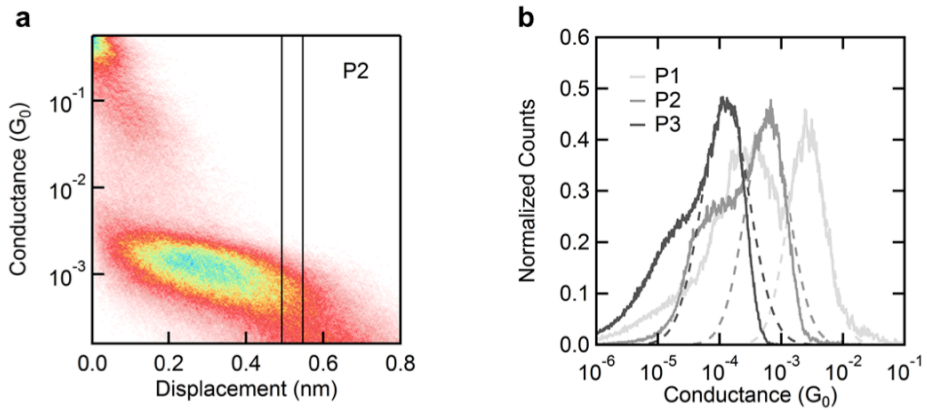
Data Analysis Details:

Determining the conductance values from log-binned histograms: The most-probable conductance can be obtained from a Gaussian fit to the molecular peaks in logarithmically binned histograms. From Gaussian center (g_c) and the Gaussian width (w), the most probable conductance value (G_c) of a log-normal distribution in a linear histogram can be determined following Huber et al.[1] as: $\log(G_c) = g_c - \ln(10)w^2$.



SI Figure S11: Logarithmically binned conductance histograms (solid lines) for the oligophenyl series (**P1-P3**) measured with Ag electrodes showing Gaussian fits (dashed lines) to the data.

Determining the conductance of a fully extended junction from 2D Histogram: To isolate the conductance of a fully extended junction, we determine the conductance from a profile of the 2D histograms. This region within a 0.05 nm window at the end of the conductance feature, demarcated by the solid lines shown SI Figure S11a, is integrated along the displacement axis to generate a conductance shown in SI Figure S11b for **P1**-**P3**. A Gaussian is fit to this profile as shown and its center value and width are used to determine the most frequently measured conductance value of a fully elongated junction as detailed above following Reference 1.



SI Figure S12: (a) 2D conductance histogram of **P2** measured with Ag electrodes. The vertical lines indicate the end of the molecular feature. (b) Conductance profiles determined from 2D histogram for all oligophenyls studied. Dashed curves indicate Gaussian fits to these profiles.

Theoretical Calculation Details:

Basis Set Superposition Error (BSSE) corrections: The calculation of the junction binding energies include counterpoise corrections to the BSSE.[2] We calculate the energy of each fragment (molecule and metal electrodes) in the presence of ghost orbitals of the other fragment. We find these BSSE counterpoise corrections to be significant, reducing the junction binding energy by ~0.5 eV for both Au and Ag junctions, most of which (approximately 0.4 eV) is provided by the ghost atoms of the metal substrate.

References:

(1) Huber, R.; Gonzalez, M. T.; Wu, S.; Langer, M.; Grunder, S.; Horhoiu, V.; Mayor, M.; Bryce, M. R.; Wang, C. S.; Jitchati, R.; Schonenberger, C.; Calame, M. *J. Am. Chem. Soc.,* **2008,** 130, (3), 1080-1084.

(2) van Duijneveldt, F. B.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Lenthe, J. H. *Chem. Rev.,* **1994,** 94, (7), 1873-1885.