Supporting Information

Additional Experimental Details:

The substrates were Au(111) prepared by evaporating 100nm Au on mica in an ultrahigh vacuum system at a rate of 0.1nm/sec. Each substrate was annealed in hydrogen flame immediately before use. The STM used in the experiment was a Pico-STM from Molecular Imaging. Model DS345 Function generator (Stanford Research System) was used to add the AC modulation signal ($A_0 \cos(\omega t)$) to the linear PZT driving voltage. The measured current was decomposed into DC (I_{DC}) and AC (I_{AC}) components with a band-pass filter. α was obtained from the amplitude of the AC component, and conductance histogram was constructed by the method mentioned in the manuscript.

When measuring the I-V curve, the tip was brought close to the substrate surface until the current reaches a set point. The AC modulation was then turned on, and both the AC response and DC current were monitored with a digital oscilloscope. We adjusted the tip-substrate distance by changing the set point. When the distance was appropriate, the AC response started to blink between a large value (~10 nm^{-1}) and a smaller value (~2 nm^{-1}). When the AC response was stabilized at the lower value, a molecular junction was formed between the substrate and tip. We then turned off the feedback loop and measured the current while sweeping the bias voltage. The AC modulation was continuously applied to the tip so that we could determine if the molecule remained bridged between the tip and substrate during the IV measurement.

Control experiment:

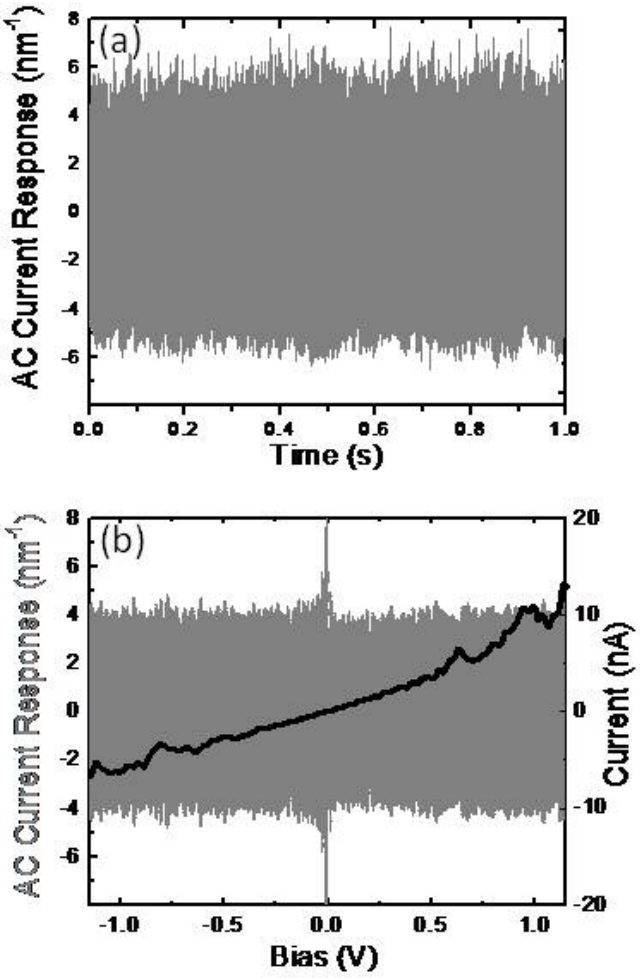

Figure: Control experiment. (a) AC component of the current recorded by placing the STM tip near a bare Au substrate in mesitylene. The bias is fixed at -50 mV, and the initial current set point is 0.8 nA. (b) DC (right axes) and AC (left axes) components of current vs. bias voltage of the same surface. The modulation frequency and amplitude are 2 kHz and 0.05 nm, respectively.