Supporting Information

Chain length and temperature dependence of alkanedithiol molecular conductance under ultra high vacuum

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SI-1. Control curves

Control curves were acquired over freshly sputtered and annealed gold samples before molecular deposition from solution. Aside from noise, these curves were always featureless and did not demonstrate evidence of molecular bridge formation i.e. current plateaus. **Figure SI-1** shows a set of such control curves along with the resulting current histogram. In the histogram, the edge of the noise limit peak can be seen below abscissa values of -1 and the amplifier saturation peak can be observed at roughly 5.3. There are no other statistically significant peaks.

Figures SI-2a and **SI-2b** show an area density plot and histogram, respectively, for an unfiltered dataset acquired from an 1,6-hexanedithiol sample. Both plots demonstrate very clear evidence of molecular bridge formation. The gradients of the linear portions of the two area density plots are the same within experimental error, consistent with a stable STM tip and constant barrier height. (However, the plot with the deposited molecules is broader than that for the clean gold.)

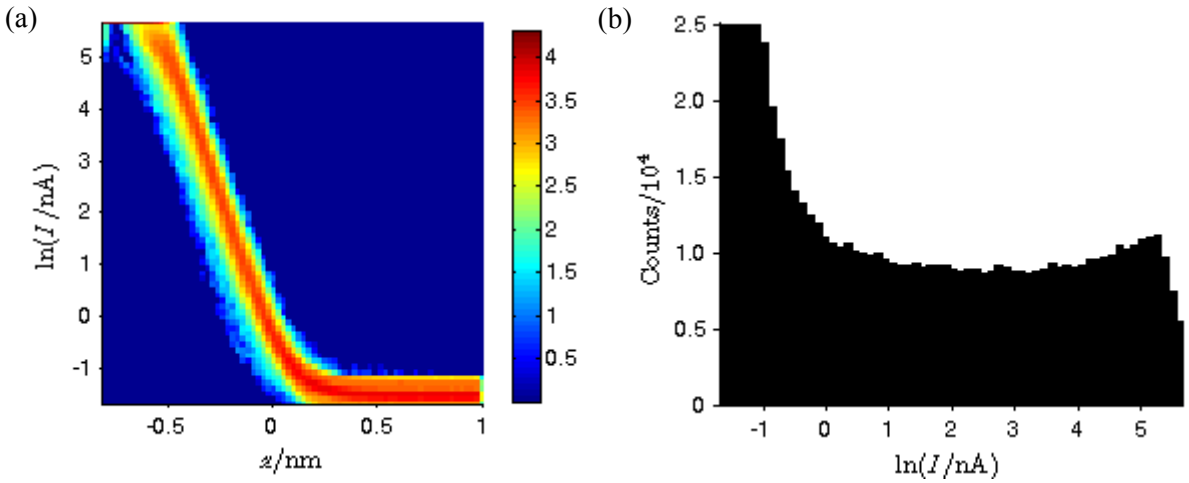

Figure SI-1: a) An area density plot (logarithmic) for 1500 consecutive control *I*(*z*) curves taken over freshly cleaned gold with a gold tip biased at 0.3 V. b) A logarithmic histogram of the curves.

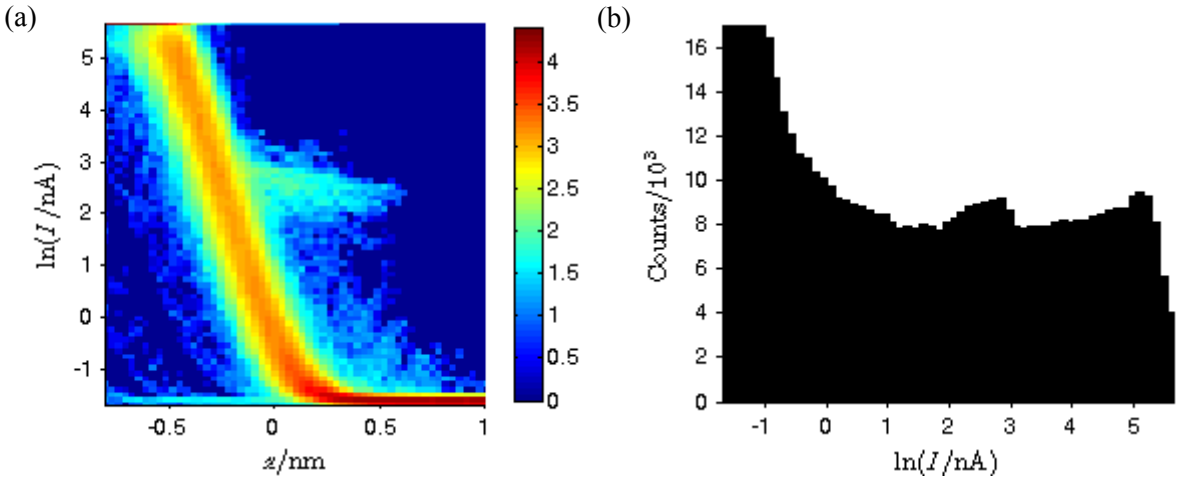

Figure SI-2: (a) An area density plot (logarithmic) for 1500 consecutive *I*(*z*) curves taken over an HDT sample with a gold tip biased at 0.3 V. (b) A logarithmic histogram of the curves. A very obvious molecular 'arm' can be seen in (a) which results in a broad molecular peak in (b).