Supporting Information

"Single-Molecule Circuits with Well-Defined Molecular Conductance"

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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 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 The sample was then withdrawn at a rate of 20 nm/s and the current and position data was recorded at a 40 kHz sampling frequency. Histograms were constructed from the current versus position traces by converting currents to conductances and binning the data as a function of conductance. The bin sized varied between 10^{-4} G_0 and $10^{-6}G_0$. All histograms were constructed from all collected traces with no selection whatsoever. For all histograms constructed, the counts were divided by the number of traces used to construct histograms so as to be able to compare histograms constructed from different number of traces for each molecule (the number of traces collected varied between 3000 and 12000 for different molecules).

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. All molecules and solvent were obtained from commercially available sources (Alfa Aesar and Sigma-Aldrich) with purity greater than 95%.

Additional Control Experiments:

In addition to the measurements reported in the main text, we also performed control experiments on the following molecules: 1,2 Benzenediamine, 1,3 Benzenediamine and butylamine (See Figure below). Within our measurable conductance range (~5 G_0 − $5 \times 10^{-5} G_0$), set so as to be able to measure a conductance greater than G_0 when pushing the electrodes together and to clear see the G_0 conductance step of Au, we do not see any difference between these histograms and those of clean gold. This implies that we either do not bind these molecules between the two Au electrodes that are being pulled apart, as can be expected for butylamine which has only one amine endgroup, or that the conductance of these molecules is below our measuring range (which could be the case for 1,3 benzenediamine). We believe that former of these two possibilities is more likely for the aromatics.

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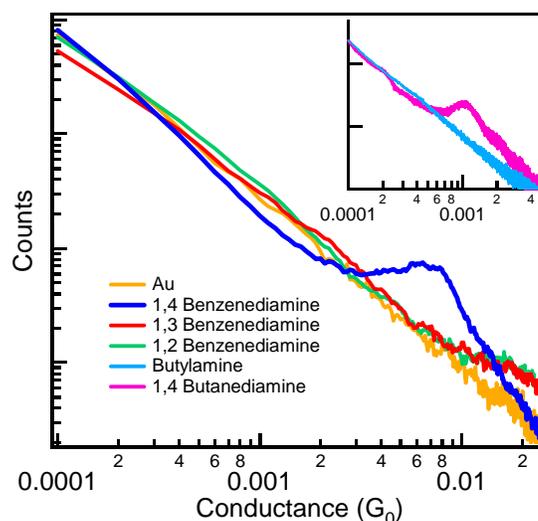
DFT Calculation Details:

The generalized gradient approximation (GGA) as formulated by Perdew, Burke and Ernzerhof was used.[1] The molecule and finite cluster calculations were done with Jaguar v5.0[2] using a 6-31g** basis for the light atoms and a lacvp** basis for Au.[3] Except where specified, complete geometric relaxation was performed. The periodic slab calculations were done using pseudopotentials[4] and a planewave basis set with Abinit v4.2.[5, 6] A 20 Ha kinetic energy cutoff defined the basis set size. The Brillouin zone for the Au(111):2x2 surface unit cell was sampled by a 4x4 grid. The basic supercell consisted of 4 monolayers of Au and 8 monolayers of vacuum, to which adatoms and molecules were added on one surface. The calculated lattice parameter of bulk Au (4.182 A) was used. The surface layer for the flat surface relaxes outward by 2.6%. With the addition of an Au adatom in the hcp hollow site, the coordinating surface atoms are drawn towards the adatom by about 0.02 A. The final adatom to surface atom bond length is 2.78 A. The ammonia and 1,4 butanediamine calculations on the surface were performed for a structure which maintained one mirror plane orthogonal to the surface and through the molecule.

For the case of ammonia, detailed, high quality correlated electron calculations for the radical $AuNH_3$ give a binding energy for the Au to the ammonia of 0.78 eV[7]. Our molecular calculations with the GGA give 0.71 eV, including a small counterpoise correction, similar to the GGA results of Lambropoulos et al[7] and reasonably close to the accurate result. We find that ammonia binds to the Au(111) surface at the a-top site, with a calculated binding energy of 0.4 eV, similar to a similar recent calculation[8]. This includes a small correction (0.08 eV) for additional intermolecular dipole-dipole interactions to obtain the dilute limit.[8] The result is in reasonable agreement with the binding energy inferred from temperature programmed desorption, 0.43 eV in the dilute limit[9]. However, the ammonia is calculated to bind to an Au adatom (hcp hollow site)

much more strongly, viz. by 0.7 eV. This agrees qualitatively with the broad range of ammonia adsorption energies observed on rough Au surfaces[10].

For the case of 1,4 butanediamine, an initial study was performed using a single Au to represent the adatom. The Au binds to the N lone pair with a bond length of 2.29 A, a Au-N-C bond angle of 120 degrees and an energy of 0.6 eV, similar to the ammonia case. This suggests binding of the 1,4 butanediamine to the a-top site of the flat surface, oriented so that the N lone pair is vertical, placing the backbone of the molecule about 34 degrees from vertical. However, the forces predominately direct the molecule away from the surface slab and the molecule is either not bound or only weakly physisorbed (<0.1 eV binding) in this orientation. The binding to the adatom on the surface slab was then considered. The initial geometry was taken from the cluster calculation and the relaxed adatom on the slab, with the molecule placed with the N lone pair approximately vertical and the torsion angle defined by the surface Au atom, the Au adatom, the N and the first C being zero. An initial structural relaxation with residual forces less than 0.1 eV/A gave a binding energy of 0.32 eV. However, the very soft angular degrees of freedom make finding the absolute minimum difficult. Exploration by pivoting around the Au adatom to systematically open the Au-Au-N bond angle gave structures with larger binding energy, up to 0.48 eV, giving the present estimate for the binding energy to the adatom.

The flexibility of the angular degrees of freedom for binding to the adatom was further explored in the context of the junction scenario illustrated in Fig. 4a. Each contact was modeled by an Au_5 cluster taken from the optimized adatom structure optimized using the periodic slab calculations and consisting of the adatom, 3 atoms from the surface layer and one atom from the sub-surface layer. The structure of the cluster was frozen and the bonding to the 1,4 butanediamine determined by energy minimization, only constrained by C_2 symmetry that assured the contact

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geometry was the same.   The Au-N bond length is 2.32 A, the Au-N-C bond angle 117 degrees and the Au-Au-N bond angle 120 degrees. The orientation illustrated in Fig. 4a, Au-Au-N-C torsion angle of 180 degrees, is slightly higher (<0.01 eV) in energy than the 0 degree torsion angle case. For this five atom Au cluster model of the electrode, there are two nearby frontier orbitals responsible for the tunneling. The tunneling induced splitting was averaged for the two to get a measure of the overall coupling across the molecular junction for this case.

1.   Perdew, J. P.; Burke, K.; Ernzerhof, M. *Physical Review Letters* **1996,** 77, (18), 3865-3868.
2.   *Jaguar* 5.0; Schrodinger, L.L.C., Portland, OR, 1991-2003.
3.   Wadt, W. R.; Hay, P. J. *Journal of Chemical Physics* **1985,** 82, (1), 284-298.
4.   Fuchs, M.; Scheffler, M. *Computer Physics Communications* **1999,** 119, (1), 67-98.
5.   Gonze, X.; Beuken, J. M.; Caracas, R.; Detraux, F.; Fuchs, M.; Rignanese, G. M.; Sindic, L.; Verstraete, M.; Zerah, G.; Jollet, F.; Torrent, M.; Roy, A.; Mikami, M.; Ghosez, P.; Raty, J. Y.; Allan, D. C. *Computational Materials Science* **2002,** 25, (3), 478-492.
6.   The ABINIT code is a common project of the Université Catholique de Louvain, C. I., and other contributors. URL: http://www.abinit.org.
7.   Lambropoulos, N. A.; Reimers, J. R.; Hush, N. S. *Journal of Chemical Physics* **2002,** 116, (23), 10277-10286.
8.   Bilic, A.; Reimers, J. R.; Hush, N. S.; Hafner, J. *Journal of Chemical Physics* **2002,** 116, (20), 8981-8987.
9.   Kay, B. D.; Lykke, K. R.; Creighton, J. R.; Ward, S. J. *Journal of Chemical Physics* **1989,** 91, (8), 5120-5121.
10.   Richton, R. E.; Farrow, L. A. *Journal of Physical Chemistry* **1981,** 85, (24), 3577-3581.