Substrate and Tip Preparation

200 nm of Au is first sputtered onto freshly cleaved mica substrates, which are then flame annealed just before use using a hydrogen torch with a repetition rate of 1 Hz. Approximately 1 mM solutions of C_{60}, PCBM, and C_{70} in dichlorobenzene is prepared and sonicated to facilitate dissolving the fullerene molecules (>99% pure) before being drop cast (~10 µL) onto an annealed, Au-coated mica substrate where the solvent is allowed to evaporate under nitrogen. The STM tip is prepared from 250 µm diameter metal (>99.99% pure, Pt, Au, or Ag) wire. Just before use, the Pt and Au wire are cleaned by piranha and exposure to oxygen plasma then cut from the wire. Since Ag tarnishes and oxidizes, just before use, the Ag wire is flame annealed using a hydrogen torch to reduce the tarnish and oxide before being cut. The STM sample holder and electrical contacts are cleaned in a piranha bath, rinsed with deionized water and acetone, and dried under nitrogen to prevent contamination.

STM Conductance Measurements

Conductance measurements are performed using a modified STM setup that has been previously described in literature[1]. A +100 mV bias is applied between the initially separated tip and the substrate (ground referenced to the substrate) and a current amplifier monitors the conductance. The STM tip then approaches the molecule coated substrate until a conductance threshold of >6 G_0 is reached indicating contact with the surface. The STM tip is then retracted at a rate of ~1 nm/s eventually opening a 1D transmission channel corresponding to a conductance of G_0. The STM tip then continues to retract breaking that 1D channel, allowing for a molecule to bridge the gap. The tip continues to retract until a threshold conductance of $<10^{-5}$ G_0 is obtained suggesting only vacuum tunneling remains. Next the tip re-approaches the surface to form the next junction. >2000 junctions were gathered for each molecule and tip combination. Energy dispersive x-ray spectroscopy was acquired of new and used tips which showed no evidence of oxidation, tarnish, or contamination on any of the tips. Furthermore, no Au adhesion to the Pt or Ag tips was detected. This is because a withdraw conductance threshold of 6 G_0 does not produce sufficient pressure to cause the Au to plate the tip. Only data corresponding the withdraw sequence is analyzed; the $\log_{10}$ of this data normalized to G_0 is taken to represent the conductance trace. To help with data reduction, the second numerical derivative of each conductance trace is calculated after applying a Savitsky-Golay smoothing filter to reduce the increased variation associated with differentiation; this value corresponds to the curvature of the trace. Since sharp steps in conductance are expected, the base of each step should have a positive curvature and the tip of each step should have a negative curvature. Furthermore, exponential decay in current associated with tunneling should yield a straight line with a negative slope and thus zero curvature. Conductance data possessing a zero or positive curvature was excluded and only negative curvature data was placed in a histogram for further analysis (See Fig. S-1 for verification against 1,4-benzenediamine which has been well documented in literature[2]).
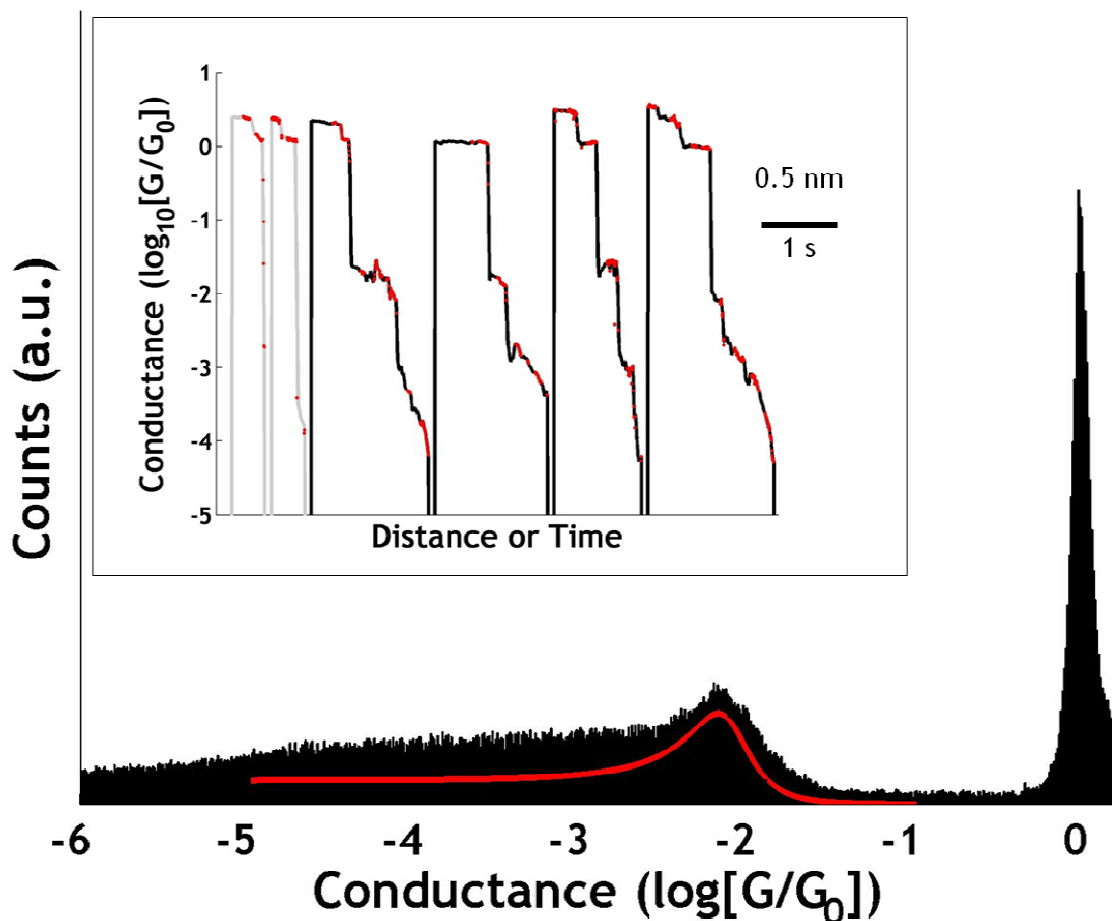
Figure S-1: Benzenediamine Conductance Verification. Conductance histogram of 1,4-benzenediamine with a single conductance peak at $6.5 \times 10^{-3} \pm 0.4 \times 10^{-3}$ G_0. The uncertainty is a measure of the full-width-half-maximum of a Lorentzian least-squares non-linear regression (red). This is in good agreement with literature therefore validating the accuracy of the STM conductance breakjunction. (Inset) Example conductance traces for a bare Au surface (grey) and a molecule coated surface(black). Using a curvature data reduction, only points with a negative curvature (red) are selected for histograms.

STM Thermopower Measurements

Thermopower measurements were performed using a modified STM setup that has been previously described in literature[3]. Molecules are first captured between an STM tip held at ambient temperature and the Au substrate heated to ΔT above the ambient temperature. To capture molecules a voltage bias of +120 mV is applied between the initially separated STM tip and substrate (ground referenced to substrate). As the tip advances towards the surface, conductance is monitored with a current amplifier. Once the threshold conductance is exceeded, a junction has been formed, and a switch disconnects the current amplifier and voltage bias in favor of a voltage amplifier. Since thermopower is insensitive to the number of molecule (intrinsic property) in the junction, capturing one of a few molecules does not significantly change the result. The induced thermoelectric voltage due to thermopower of the junction is measured between the tip and the substrate. Statistics are accumulated through >500 serial approach-withdrawal sequences at each ΔT (for $\Delta T \sim$ 0, 5, 10, 15, 20, and 30K). Voltage associated with incomplete isolation of the current amplifier resulting with a voltage offset at $\Delta T=0$ is rejected because thermopower reflects the slope of the voltage vs. ΔT not its absolute value. ΔT occurs across the

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junction, and not within the tip or substrate when a molecule is present[3]; when a molecule is not present, ΔT occurs across the STM tip (see Figs. S-2 through S-4). For further verification of this, thermopower was measured with the STM tip in brief contact with the substrate in the absence of molecules. Measured metal-metal thermopower voltages reproduce accepted thermopower values for Au, Ag, Pt, and Cu. Furthermore, the temperature dependence of thermopower on the STM tip over the temperature range of interest is small compared to the thermopower of the heterojunction and within the error in thermopower.
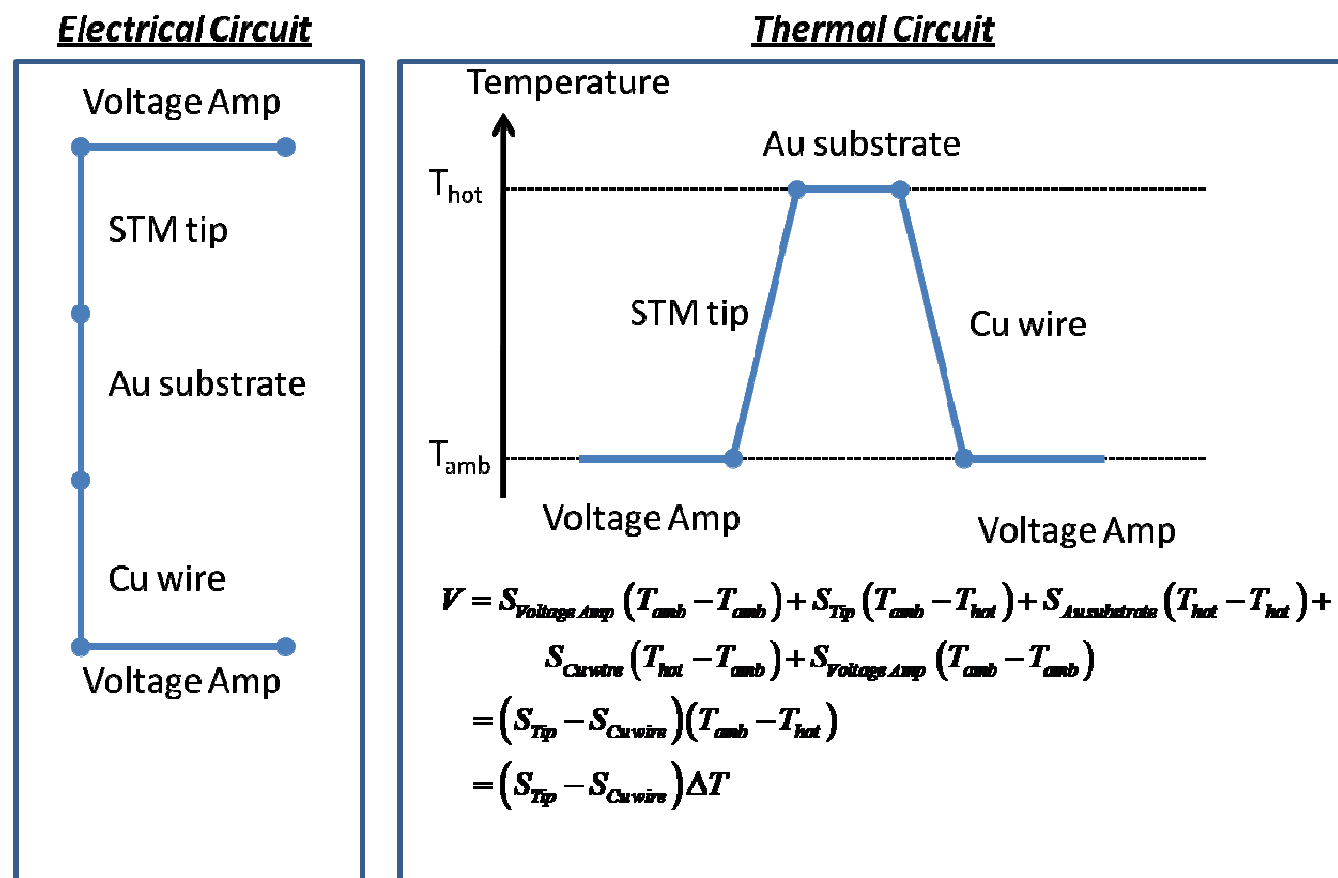
Electrical Circuit

Voltage Amp

STM tip

Au substrate

Cu wire

Voltage Amp

Thermal Circuit

$$V = S_{Voltage\ Amp}\left(T_{amb} - T_{amb}\right) + S_{Tip}\left(T_{amb} - T_{hot}\right) + S_{Au\ substrate}\left(T_{hot} - T_{hot}\right) +$$
$$S_{Cu\ wire}\left(T_{hot} - T_{amb}\right) + S_{Voltage\ Amp}\left(T_{amb} - T_{amb}\right)$$
$$= \left(S_{Tip} - S_{Cu\ wire}\right)\left(T_{amb} - T_{hot}\right)$$
$$= \left(S_{Tip} - S_{Cu\ wire}\right)\Delta T$$

Figure S-2: Metal-Metal Thermopower Analysis. Electrical and thermal circuit analysis for a metal-metal junction between the STM tip and the Au substrate demonstrating the origin of the thermoelectric voltage in the measurement system. Here it is assumed that the temperature drop occurs primarily over the metal electrodes that contact the heated substrate. Note that the thermopower contribution from the Cu wire is first subtracted from the data to yield the thermopower of tip.
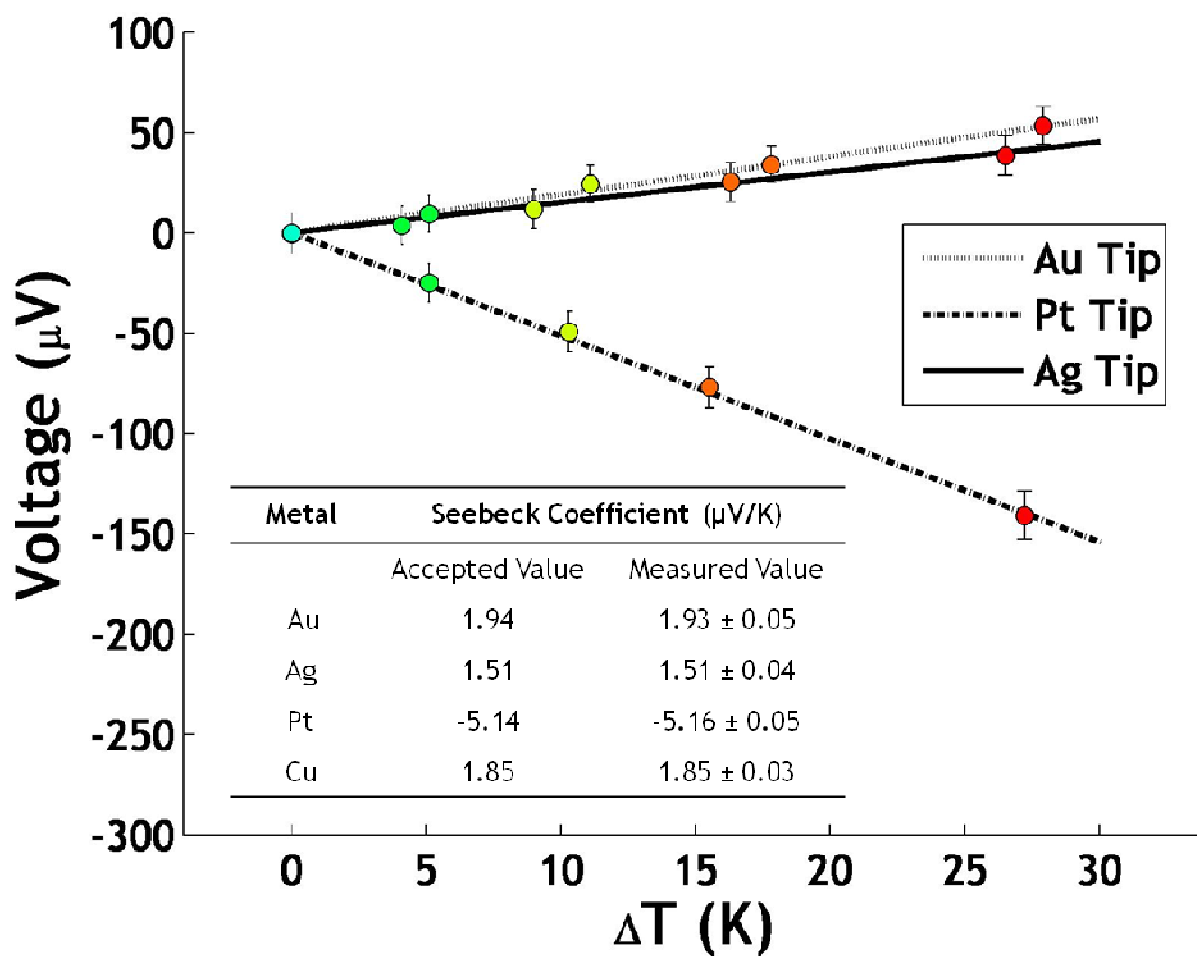
Metal	Seebeck Coefficient (µV/K)	
	Accepted Value	Measured Value
Au	1.94	1.93 ± 0.05
Ag	1.51	1.51 ± 0.04
Pt	-5.14	-5.16 ± 0.05
Cu	1.85	1.85 ± 0.03

Figure S-3: Metal-Metal Thermopower Measurements. Measured thermoelectric voltage of the measurement system for Au, Pt, and Ag STM tips in contact with a Au substrate. Lines represent the accepted thermopower values thus validating the accuracy of the measurement approach with different metal tips. This further suggests that the temperature drop in the system occurs primarily through the STM tip.
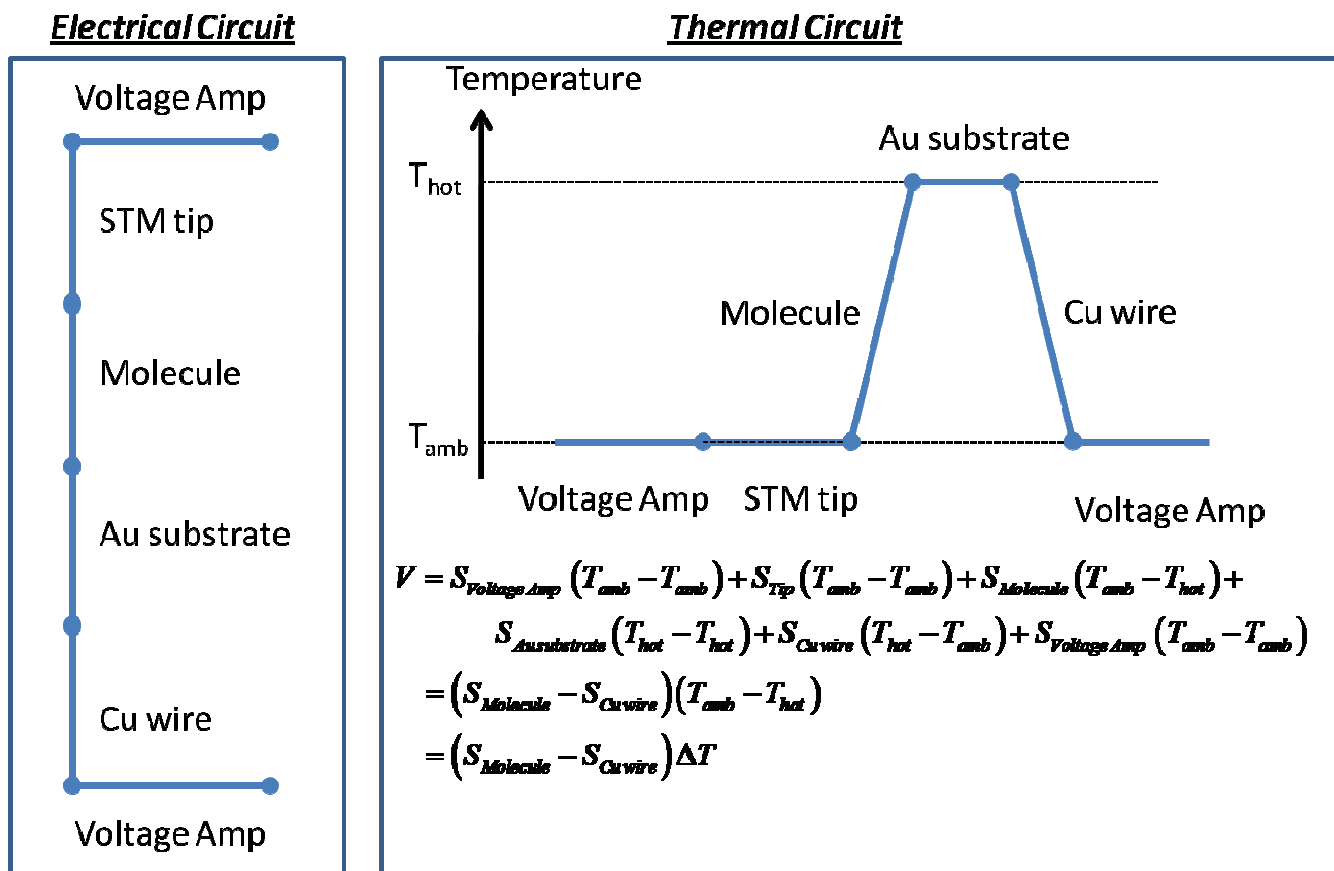
Electrical Circuit   **Thermal Circuit**

$$V = S_{Voltage\,Amp}\left(T_{amb}-T_{amb}\right)+S_{Tip}\left(T_{amb}-T_{amb}\right)+S_{Molecule}\left(T_{amb}-T_{hot}\right)+$$
$$S_{Au\,substrate}\left(T_{hot}-T_{hot}\right)+S_{Cu\,wire}\left(T_{hot}-T_{amb}\right)+S_{Voltage\,Amp}\left(T_{amb}-T_{amb}\right)$$
$$=\left(S_{Molecule}-S_{Cu\,wire}\right)\left(T_{amb}-T_{hot}\right)$$
$$=\left(S_{Molecule}-S_{Cu\,wire}\right)\Delta T$$

Figure S-4: Metal-Molecule-Metal Thermopower Analysis. Electrical and thermal circuit analysis for a metal-molecule-metal junction between the STM tip and the Au substrate demonstrating the origin of the thermoelectric voltage in the measurement system. Here it is assumed that the temperature drop occurs primarily over the molecule. Note that the thermopower contribution from the Cu wire is first subtracted from the data to yield the thermopower of tip.

Contamination and Electrode Purity Verification

In these experiments the tips and substrates were prepared as described above. To summarize, the Au and Pt tips were cleaned in a bath of piranha and then cleaned in an oxygen plasma. Since Ag oxidizes, it cannot be cleaned by piranha or in an oxygen plasma. For that reason, Ag is cleaned in a hydrogen flame where any Ag_2O or Ag_2S is reduced to Ag metal and any contaminants are incinerated. Tips were fabricated from metals wires that are >99.99% pure. We performed energy dispersive x-ray spectroscopy (EDS) in an SEM as elemental analysis of the tips to verify that trace metals, oxides, and sulfur tarnish were not present. Three tips (one of each metal) were used as a control and designated as "new tips". The remaining three tips were used in the STM and conductance experiments on a bare Au substrate were performed and designated as "used tips." A drop of dichlorobenzene was placed on the surface and allowed to evaporate to test for contamination in the same solvent that was used to dissolve the fullerenes. Steps at 1, 2, 3, and 4 G_0 were observed and ~1000 approach and withdraws were acquired for each tip. The upper conductance threshold was set to ~6 G_0. After these approach and withdraw sequences, EDS spectrum (Figs. S-5) of the "used tips" were gathered. The "new tips" only showed x-ray peaks corresponding to Ag, Au, and Pt respectively. No oxygen, sulfur, or trace metal peaks were observed. The tips are indeed pure and free of contamination. Al peaks are routinely present in this SEM resulting from the Al sample stage. The "used tips" show nearly identical EDS spectrum to the "new tips". Screenshot (Fig. S-5, right) of the EDS spectrum (red) with built-in peak

identification show that Au lines (indicated by blue and yellow placement lines) are not present in the Ag and Pt tips and clearly align with the Au tip spectrum. We also note that sulfur peaks are not present as we indicated by a yellow placement line. $K\alpha$, $L\alpha$, and $M\alpha$ energies for Pt and Au are close, however, the instrument resolution is more than sufficient to observe, detect, and auto assign elements to these peaks. Au plates onto Pt and Ag by hard-pressing, the pressures here were limited by our threshold conductance (~6 G_0), and did not result in any transfer of Au onto the tips. Finally, no light elements were visible verifying the absence of contamination. For thermopower measurements the approach threshold is 0.1 G_0 making metal-metal contact and cross contamination of metals an impossibility.
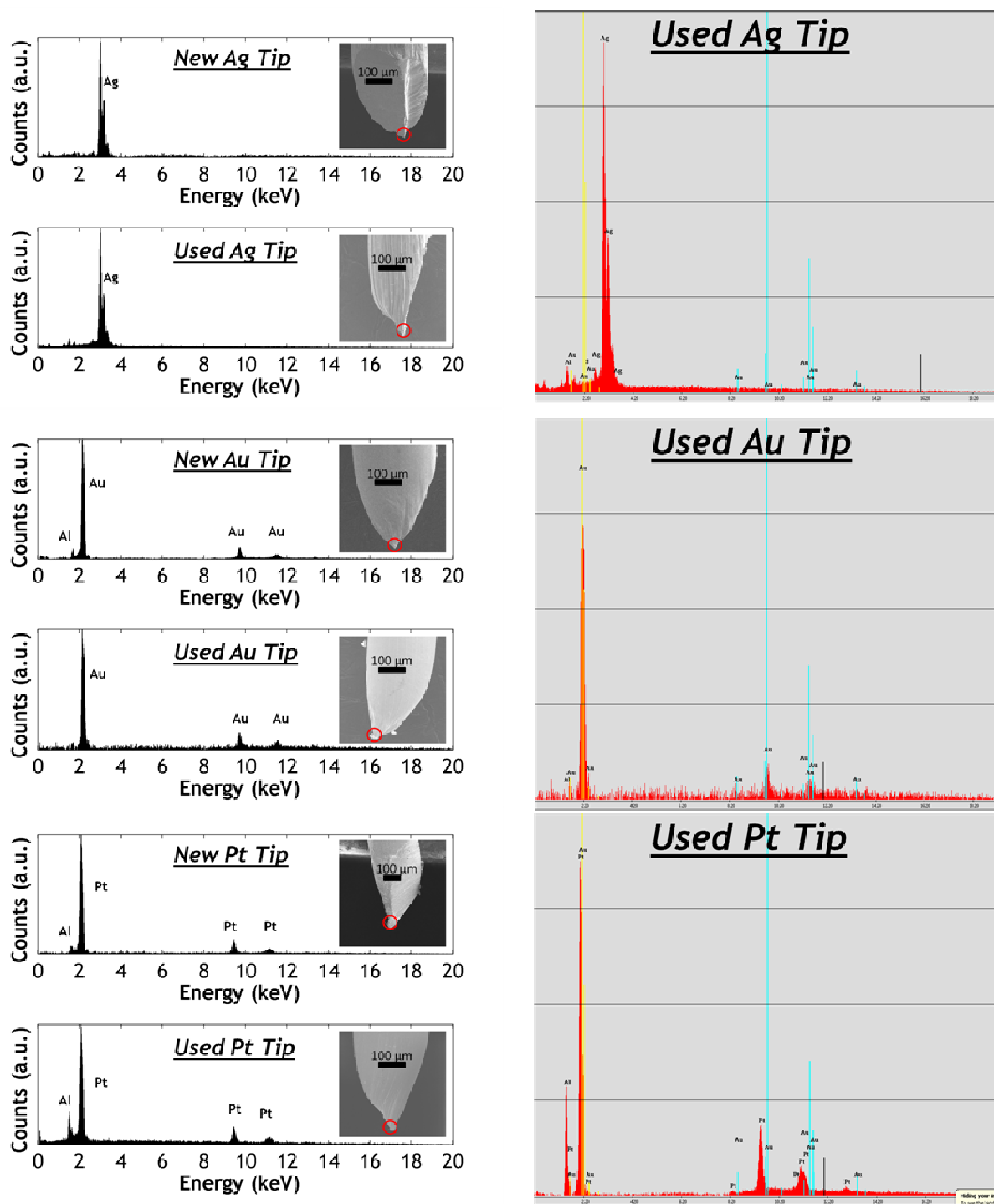
Figure S-5: **EDS Spectrum.** (Left) EDS spectrum comparing "new" and "used" tips showing the purity of the tips free of contamination. (Right) Screenshots of "used" tips showing the automated peak identification. There is no evidence that the Au substrate is picked up during measurements.

Supplemental References

1.   Jang, S. Y.; Reddy, P.; Majumdar, A.; Segalman, R. A. *Nano Letters* **2006,** 6, (10), 2362-2367.
2.   Venkataraman, L.; Klare, J. E.; Nuckolls, C.; Hybertsen, M. S.; Steigerwald, M. L. *Nature* **2006,** 442, (7105), 904-907.
3.   Reddy, P.; Jang, S. Y.; Segalman, R. A.; Majumdar, A. *Science* **2007,** 315, (5818), 1568-1571.