Supporting Information

Bottom-Electrode Induced Defects in Self-Assembled Monolayer (SAM)-Based Tunnel Junctions affect only the SAM Resistance, not the Contact Resistance or SAM Capacitance

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Modeling Impedance spectra: Impedance $Z$ is a more general concept than resistance and can be expressed as\(^{1,2}\)

$$Z = Z' + jZ''$$  \hspace{1cm} (1)

where $Z'$ and $Z''$ are the real and imaginary part respectively. One can express $Z$ in polar form as

$$Z = |Z|e^{j\phi}$$  \hspace{1cm} (2)

where $|Z|$ is the modulus of the complex impedance and $\phi$ represents the phase difference which appears between the applied voltage and measured current.

Consider a simple network comprising of resistance $R$ and capacitance $C$ connected in parallel. In this case the complex impedance $Z$ is given by

$$\frac{1}{Z} = \left(\frac{1}{R} + j\omega C\right)$$  \hspace{1cm} (3)

The expression 3 can be separated into real and imaginary parts as,

$$Z = \frac{R}{1 + j\omega RC} = \frac{R}{1 + \omega^2 R^2 C^2} - j\left(\frac{\omega CR^2}{1 + \omega^2 R^2 C^2}\right)$$  \hspace{1cm} (4)

Here $\omega$ is the angular frequency in rad/sec. Now connecting a series resistance $R_c$, the above expression (4) gets modified to\(^{1,2}\)

$$Z = \left(\frac{R_c + \frac{R}{1 + \omega^2 R^2 C^2}}{1 + \omega^2 R^2 C^2}\right) - j\left(\frac{\omega CR^2}{1 + \omega^2 R^2 C^2}\right)$$  \hspace{1cm} (5)

The above scenario is shown in figure 1c in main text.
**Tunneling decay coefficient:** Figure S1 shows the dependence of tunneling current at 0.5 V for molecular junctions on different bottom surfaces as a function of molecular chain length. For our experiments, we only used junction that had their $J(V)$ characteristics within one log-standard deviation from the log-mean $J(V)$ curve which are reported in reference 3. All impedance measurements were repeated 3 times using 3 different junctions following previously reported procedures reported elsewhere. We fitted the curves using eq 1 in main text and the value of $\beta$ is obtained. We note that in all impedance measurements the geometrical junction area was $9.6 \times 10^2 \, \mu m^2$.

![Figure S1: The length dependence of $|J|$ at 0.50 V for SAM-based tunneling junctions formed on different bottom surfaces.](image)

**Capacitance vs 1/d:** Figure S2 shows the capacitance plot as a function of 1/d. The capacitance follows the linear dependence with 1/d and fitting to eq 6 of main text. We estimated the dielectric constant of the SAMs using eq 6.
**Figure S2:** $C_{\text{SAM}}$ vs. 1/d plots for SAM-based tunneling junctions formed on different bottom surfaces.

**Bearing Volume calculation:** To capture more detailed information of the surface topography, we use previously reported method, bearing volume (BV), to determine the quality of the electrode surfaces. The value of rms is determined by AFM images of 5×5 µm$^2$ as shown in Figure 2. We used a so-called “split and count” method to estimate the grain size ($A_{gr}$). Briefly, we divided the AFM images into small boxes and counted the number of small boxes occupied by each grain. The relative number of grains ($N_{gr}$) is then determined by normalization of $A_{gr}$ to the largest grain size. We determined the width of the grain boundaries ($d_{gb}$) using the line-scans. We calculated the average radius of the grains ($R_{gr}$) by $R_{gr} = (A_{gr}/\pi)^{0.5}$. Then, the area of the grain boundary ($A_{gb}$) is then estimated by $A_{gb} = \pi(R_{gr} + d_{gb})^2 - \pi R_{gr}^2$. Finally, the BV is calculated using $BV = N_{gr} \times A_{gb} \times \text{rms}$. 
Nyquist plots: The Nyquist plots of SAM based molecular junctions are shown in figure S3. The semi-circular plots suggest the presence of parallel RC elements in the equivalent circuit.
**Figure S3:** Nyquist plots for SAM-based tunneling junctions formed on different bottom surfaces.

**Equivalent circuit parameters as a function of BV:** The equivalent circuit parameters ($R_{SAM}$, $R_C$ and $C_{SAM}$) are presented in figure S4 and S5 as a function of BV. The capacitance and contact resistance shows no significant change with BV while $R_{SAM}$ shows orders of magnitude change with BV for long chain molecules ($SC_{14}$ and $SC_{18}$).
**Figure S4:** Plots of $R_{\text{SAM}}$ as a function of BV for junctions with SC$_{10}$, SC$_{14}$ and SC$_{18}$ SAMs.
Figure S5: Plots of $R_C$ and $C_{\text{SAM}}$ a function of BV for junctions with SC$_{10}$, SC$_{14}$ and SC$_{18}$ SAMs.
Table S1. Summary of surface topography of different bottom-electrodes.

<table>
<thead>
<tr>
<th>Surfaces</th>
<th>rms (nm)</th>
<th>$N_{gr}$</th>
<th>$A_{gb}$ (nm$^2$)</th>
<th>BV (nm$^3$)</th>
</tr>
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<tr>
<td>Ag$^{A-TS}$</td>
<td>0.5</td>
<td>1.0</td>
<td>$1.6 \times 10^5$</td>
<td>$8 \times 10^4$</td>
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<tr>
<td>Ag$^{TS}$</td>
<td>0.7</td>
<td>1.2</td>
<td>$1.6 \times 10^5$</td>
<td>$1 \times 10^5$</td>
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<td>Ag$^{DE,1}$</td>
<td>2.1</td>
<td>48</td>
<td>$2.4 \times 10^4$</td>
<td>$2 \times 10^6$</td>
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<tr>
<td>Ag$^{DE,2}$</td>
<td>4.8</td>
<td>4.6</td>
<td>$1.2 \times 10^5$</td>
<td>$3 \times 10^6$</td>
</tr>
</tbody>
</table>

Note: The values of $N_{gr}$ and $A_{gb}$ are taken from reference 3.

References