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]

$$Z = Z' + jZ'' \tag{1}$$

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

$$Z = |Z| e^{j\phi} \tag{2}$$

where $|Z|$ is the modulus of the complex impedance and ϕ 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

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

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

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

Here ω is the angular frequency in rad/sec. Now connecting a series resistance R_C, the above expression (4) gets modified to[1,2]

$$Z = \left(R_C + \frac{R}{1 + \omega^2 R^2 C^2} \right) - j \left(\frac{\omega C R^2}{1 + \omega^2 R^2 C^2} \right) \tag{5}$$

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.[4, 5]. We fitted the curves using eq 1 in main text and the value of β is obtained. We note that in all impedance measurements the geometrical junction area was 9.6×10^2 μm^2.

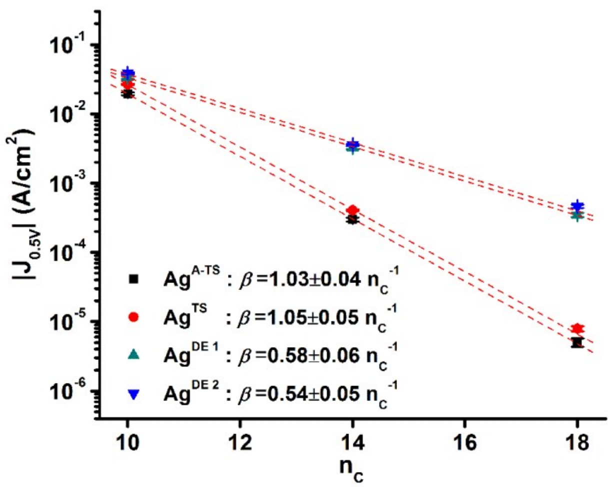

Figure S1: The length dependence of |*J*| at 0.50 V for SAM-based tunneling junctions formed on different bottom surfaces.

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.

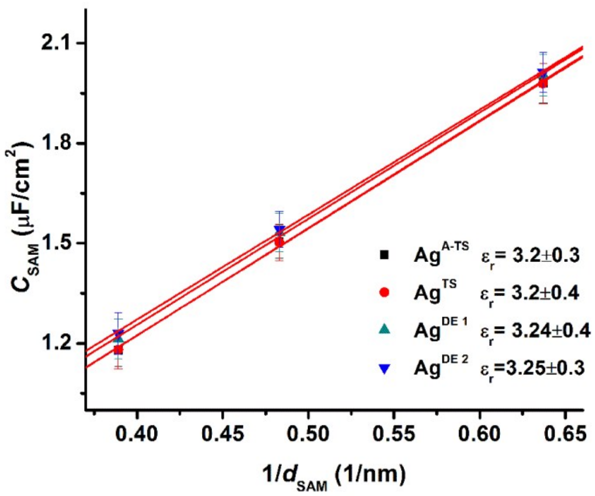

Figure S2: C_{SAM} vs. 1/d plots for SAM-based tunneling junctions formed on different bottom surfaces.

Bearing Volume calculation: To capture more detailed information of the surface topography, we use previously reported method, bearing volume (BV)[3], 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[3] 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 = $N_{gr} \times A_{gb} \times$ 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.

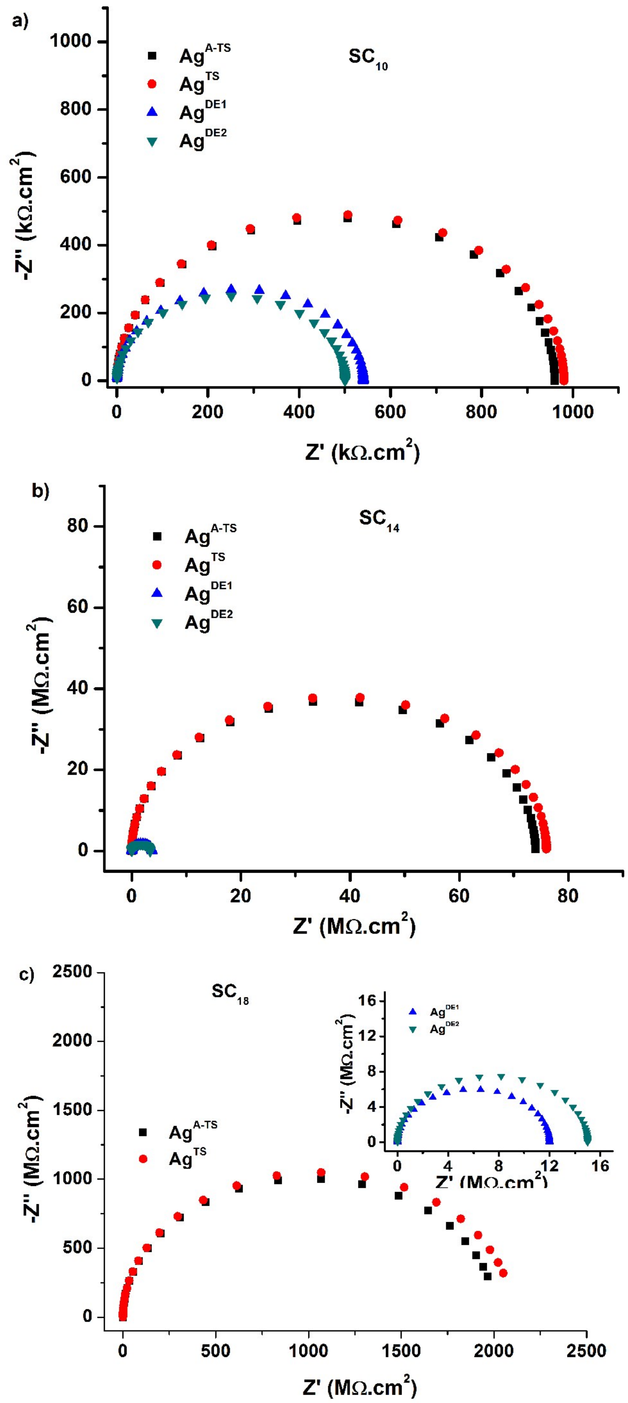

Figure S3: Nyquist plots for SAM-based tunneling junctions formed on different bottom surfaces.

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}).

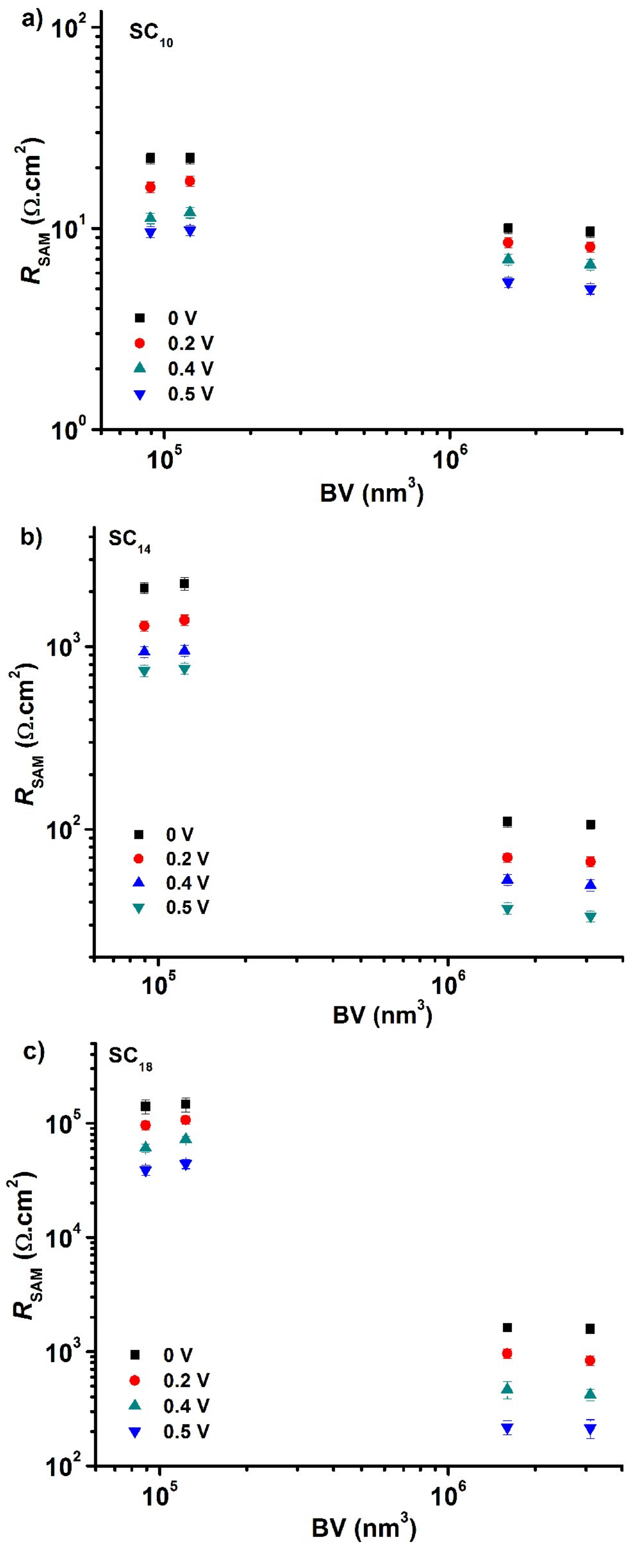

Figure S4: Plots of R_{SAM} as a function of BV for junctions with SC_{10}, SC_{14} and SC_{18} SAMs.

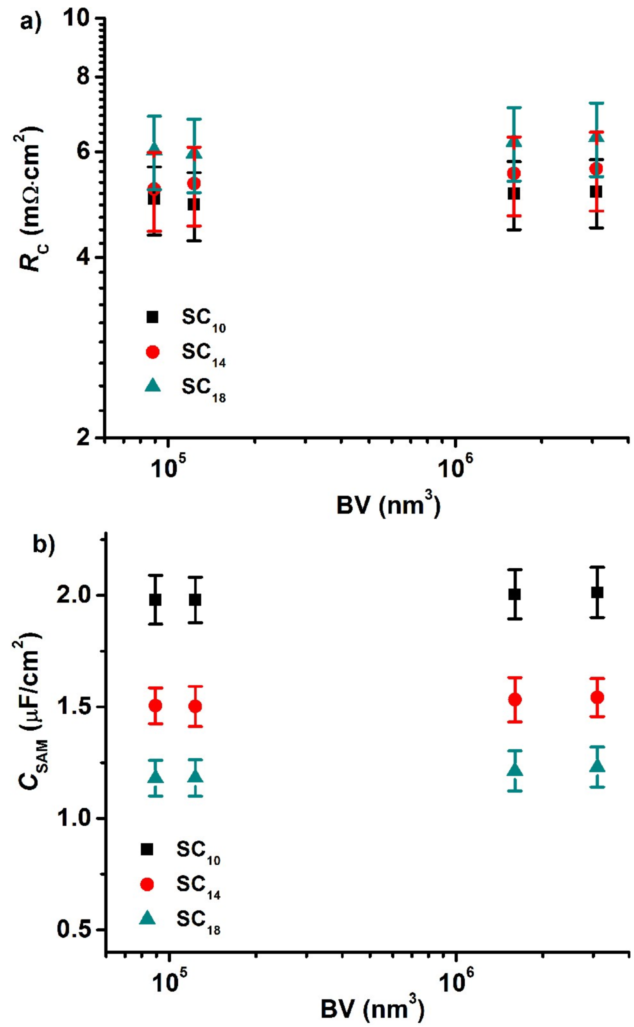

Figure S5: Plots of R_C and C_{SAM} a function of BV for junctions with SC_{10}, SC_{14} and SC_{18} SAMs.

Table S1. Summary of surface topography of different bottom-electrodes.

Surfaces	rms (nm)	N_{gr}	A_{gb} (nm^2)	BV (nm^3)
$Ag^{A\text{-}TS}$	0.5	1.0	1.6×10^5	8×10^4
Ag^{TS}	0.7	1.2	1.6×10^5	1×10^5
$Ag^{DE,1}$	2.1	48	2.4×10^4	2×10^6
$Ag^{DE,2}$	4.8	4.6	1.2×10^5	3×10^6

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

References

1. J. R. Macdonald and W. B. Johnson, In *Impedance Spectroscopy*; John Wiley & Sons, Inc.: 2005, p 1.
2. C. S. S. Sangeeth, A. Wan and C. A. Nijhuis, *J. Am. Chem. Soc.,* 2014, **136**, 11134.
3. L. Yuan, L. Jiang, B. Zhang and C. A. Nijhuis, *Angew. Chem., Int. Ed.*, 2014, 53, 3377-3381.
4. C. S. S. Sangeeth, A. Wan and C. A. Nijhuis, *Nanoscale*, 2015, **7**, 12061-12067.
5. L. Jiang, C. S. Sangeeth and C. A. Nijhuis, *J Am Chem Soc*, 2015, **137**, 10659-10667.