SUPPORTING INFORMATION for

Energy Level Alignment in Molecular Tunnel Junctions by Transport and Spectroscopy: Self-Consistency for the Case of Alkyl Thiols and Dithiols on Ag, Au, and Pt Electrodes

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Figure S1. Film thicknesses as a function of the number of repeat units.

Figure S2. Low bias resistance of Metal-CnDT-Metal junctions.

Table S1. Summary of the main results for CnDT CP-AFM junctions.

Figure S3. Linear and semilog I-V plots of Metal-CnDT-Metal junctions.

Figure S4. Transition voltages $V_{t_{\pm}}$ of Metal-CnDT-Metal junctions.

Table S2. Results of calculated energies of the molecular orbitals.

Figure S5. Molecular orbital spatial distributions for CnT and CnDT molecules.

Figure S6. Length ($n$) dependence of orbital energies for isolated CnT, CnDT, and Cn molecules.

Figure S7. UPS of CnT and CnDT SAMs on metals.

Figure S8. The normalized UPS of CnT SAMs on metals.

Figure S9. The normalized UPS of CnDT SAMs on metals.

Figure S10. The calculation of the change of the work function via UPS.
Charge Transport in the Low Bias Range. Our results for the low bias resistance are presented in Figure S2. In discussing these results, we will separately consider the impact of the molecular length (n) and the contact (metal) nature. For homologous molecular series, the two aforementioned effects can be conveniently disentangled by expressing the low bias resistance $R = R_n$ analyzed as follows

**Figure S1.** Film thicknesses (on Au) as a function of the number of repeat units. (A) The estimated molecular length (black) and measured thickness (blue) of CnT ($n=7, 8, 9, 10, 12$) SAMs. (B) The estimated molecular length (black) and measured thickness (blue) of CnDT ($n=8, 9, 10$) SAMs. Monolayer thicknesses were measured by ellipsometry. The estimated molecular lengths were calculated using Cambridge Scientific ChemBio 3D assuming a trans configuration of the molecules oriented normal to the substrate; the Au−S bond length was taken to be 2.35 Å.

**Figure S2.** (A) Semilog plot of low bias resistance of Metal-CnT-Metal ($n=7, 8, 9, 10, 12$) and Metal-CnDT-Metal ($n=8, 9, 10$) junctions versus repeat units n. Semilog plot of resistance R and contact resistances $R_c$ versus the work functions of the bare electrodes for (B) CnT and (C) CnDT. Metal= Ag, Au and Pt.
\[ R_n = R_c \exp(\beta n L_0) \]  

(S1)

Here \( R_c \) is the effective contact resistance, \( \beta \) is the tunneling decay parameter, \( L_0 \approx 1.2 \ \text{Å} \) is the repeat unit length, and \( n \) is the number of repeating units. The exponential length dependence shown in the equation represents a general feature of off-resonant tunneling. From the slope of the semilogarithmic plot of \( R = R_n \) versus \( n \), one can determine the tunneling attenuation factor \( \beta \), while its intercept at \( n = 0 \) gives the effective contact resistance \( R_c \). Low bias resistances of CnDT as well as the values of \( \beta \) and \( R_c \) for the various types of junctions are shown in Table S1. The absolute values of resistance for CnT and CnDT are smaller than our previous data by half an order of magnitude, while the precision is substantially increased, as witnessed by the much smaller standard statistical deviation.\(^2\,^3\) This could be related to the fact that our present CP-AFM experiments were done in Ar filled glove box (\( \text{H}_2\text{O}, \text{O}_2 < 0.1 \ \text{ppm} \)), unlike in the previous measurements performed in ambient environment.

**Table S1.** Summary of the main results for CnDT CP-AFM junctions: the \( \beta \) value in \( \text{Å}^{-1} \), contact resistance \( R_c \) and the low bias resistance \( R \) of the junctions in \( \Omega \), transition voltages \( V_{t\pm} \) in \( \text{V} \). The corresponding data for CnT are in ref. 4.

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>Quantity</th>
<th>C8DT</th>
<th>C9DT</th>
<th>C10DT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag-Ag</td>
<td>( R )</td>
<td>6.39×10(^6)</td>
<td>1.61×10(^7)</td>
<td>5.76×10(^7)</td>
</tr>
<tr>
<td>( \beta = 0.92 \ \text{Å}^{-1} )</td>
<td>( V_{t} )</td>
<td>1.42</td>
<td>1.41</td>
<td>1.45</td>
</tr>
<tr>
<td>( R_c \approx 8.8 \times 10^2 )</td>
<td>( V_{t+} )</td>
<td>1.43</td>
<td>1.40</td>
<td>1.47</td>
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<tr>
<td>Au-Au</td>
<td>( R )</td>
<td>9.16×10(^5)</td>
<td>2.24×10(^6)</td>
<td>8.33×10(^6)</td>
</tr>
<tr>
<td>( \beta = 0.90 \ \text{Å}^{-1} )</td>
<td>( V_{t} )</td>
<td>1.28</td>
<td>1.20</td>
<td>1.23</td>
</tr>
<tr>
<td>( R_c \approx 1.5 \times 10^2 )</td>
<td>( V_{t+} )</td>
<td>1.31</td>
<td>1.27</td>
<td>1.26</td>
</tr>
<tr>
<td>Pt-Pt</td>
<td>( R )</td>
<td>2.05×10(^5)</td>
<td>5.62×10(^5)</td>
<td>1.90×10(^6)</td>
</tr>
<tr>
<td>( \beta = 0.91 \ \text{Å}^{-1} )</td>
<td>( V_{t} )</td>
<td>1.11</td>
<td>1.15</td>
<td>1.06</td>
</tr>
<tr>
<td>( R_c \approx 3.2 \times 10^1 )</td>
<td>( V_{t+} )</td>
<td>1.12</td>
<td>1.13</td>
<td>1.08</td>
</tr>
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</table>
**Analysis of I-V traces and Determination of the Model Parameters.** Figure S3 displays representative $I-V$ characteristics of our CP-AFM junctions based on CnDT ($n=8, 9, 10$) with Ag contacts. For a more comprehensive examination of transport properties, we investigated the full $I-V$ characteristics over the interval $\pm 1.6$ V ($\pm 2.0$ V for Ag/Ag junctions), recasting them as curves of $V^2/|I|$ versus $V$ (Figure 3C). This approach is an alternative reformulation of transition voltage spectroscopy (TVS), as it can be shown that the voltage at peak maximum and the transition voltage $V_t$ (defined as the bias at the minimum of the Fowler–Nordheim plot) are mathematically identical. Averaged $I-V$ traces and TVS plots of alkane dithiols are shown in Figure S3. $I-V$ curves for CnDT are practically symmetric around the origin [$I(-V)=-I(V)$], accordingly, the transition voltages at positive ($V_t^+>0$) and negative ($V_t^-<0$) biases for CnDT have within errors the same magnitude (cf. Table S1).

The presently reported $V_t$ values for CnDT junctions with Au electrodes are consistent with previously reported data for alkyl dithiols in STM break junctions. For a given metal contact, our data show no significant length dependence of $V_t$ (Figures S4), which is consistent with the length independent band gap of molecules possessing saturated hydrocarbon backbone. On the other hand, the absolute values of $V_t$ slightly decrease with increasing work function of the contact electrodes.
Figure S3. Representative linear and semi-log plots of average $I-V$ curves and transition voltage spectra for (A, B, C) Ag-$C_n$DT-Ag, and (D, E, F) Au-$C_n$DT-Au and (G, H, I) Pt-$C_n$DT-Pt junctions ($n=8, 9, 10$).

Figure S4. Transition voltages of M-$C_n$DT-M (M=Ag, Au, Pt; n=8, 9, 10) junctions as a function of (A) molecular length and (B) bare electrode work functions.
**Figure S5.** Molecular orbital (MO) spatial distribution of molecules. (A) HOMO and (B) HOMO-1 spatial distribution of C7T, C8T, C9T, C10T and C12T. (C) HOMO, (B) HOMO-1 and (D) HOMO-2 spatial distribution of C8DT, C9DT and C10DT. The HOMO-2 of CnDT is the counterpart of HOMO-1 in the case of CnT. Figures here generated with GABEDIT.¹¹

**Table S2.** Results of ab initio OVGF¹²,¹³ quantum chemical calculations using 6-311++g(d,p) basis sets¹⁴,¹⁵ as implemented in GAUSSIAN 16¹⁶ for relevant MO energies (in eV) of isolated molecules of CnT, CnDT, and alkanes (Cn; i.e. without thiol ends).

<table>
<thead>
<tr>
<th></th>
<th>CnT</th>
<th>CnDT</th>
<th>Cn</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td>HOMO</td>
<td>HOMO-1</td>
<td>HOMO≈HOMO-1</td>
</tr>
<tr>
<td>7</td>
<td>-8.935</td>
<td>-10.818</td>
<td>-8.989</td>
</tr>
<tr>
<td>8</td>
<td>-8.933</td>
<td>-10.659</td>
<td>-8.977</td>
</tr>
<tr>
<td>10</td>
<td>-8.93</td>
<td>-10.414</td>
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</tr>
<tr>
<td>11</td>
<td>-8.93</td>
<td>-10.328</td>
<td>-8.953</td>
</tr>
<tr>
<td>12</td>
<td>-8.929</td>
<td>-10.25</td>
<td>-8.949</td>
</tr>
</tbody>
</table>
Figure S6. Calculated energies of (A) HOMO, HOMO-1 of isolated CnT and HOMO of isolated Cn versus the 1/n; (B) HOMO (essentially degenerate with the HOMO-1) and HOMO-2 of isolated CnDT and HOMO of isolated Cn versus the 1/n (n is the number of the carbons, here n=7, 8, 9, 10, 11, 12).
S1.2. UPS measurement.

The UPS measurements were performed in the same system as XPS and using a He I light source (21.2 eV). During data collection, the pressure was lower than $1.0 \times 10^{-5}$ Pa. The UPS spectra were collected using 1.3 eV pass energy, 0.05 eV/step, 20 s dwell time per step, and a take-off angle set to $45^\circ$.

**Figure S7.** UPS spectra of (A) bare Ag, Au and Pt, (B) CnDT on Ag, Au and Pt and (C) CnT on Ag, Au and Pt.
Figure S8. UPS spectra of \( C_n T \) on (A) Ag, (B) Au, and (C) Pt substrates. \((n = 7, 8, 9, 10, 12)\) Binding energies are referenced to the Fermi level, \( E_F = 0 \) eV. The spectral intensity of SAM-coated metal substrates was normalized to the intensity of bare metal substrates at 0 eV. The crossing points of the red lines indicate the onsets of the HOMOs; the numbers in eV are the values of the HOMO-Fermi energy offsets.
Figure S9. UPS spectra of CnDT on (A) Ag, (B) Au and (C) Pt substrates. \( n = 8, 9, 10 \) Binding energies are referenced to the Fermi level, \( E_F = 0 \) eV. The spectral intensity of SAM-coated metal substrates was normalized to the intensity of bare metal substrates at 0 eV. The crossing points of the red lines indicate the onsets of the HOMOs; the numbers in eV are the values of the HOMO-Fermi energy offsets.
The abscissa of Figure S10 is the binding energy relative to $E_{\text{Fermi}}$, the Fermi level of the bare Au substrate, for the Fermi edge of SAM overlayers should align with that of the substrate. In Figure S10A, the position of the secondary electron cut off is determined by the linear extrapolation. From this figure 10 we can determine the work functions of C10T on Au: $\Phi_{\text{C10T/Au}} = 21.2 - \Phi_{\text{width}}$, where 21.2 eV is the emission energy of the light source of He I and $\Phi_{\text{width}}$ is the width of the spectrum of C10T/Au, Fermi level to secondary electron cut off. The difference in Figure S10B ($\Delta\Phi$) is defined as the change of the work function by the SAM modification. The secondary electron cutoff shifts to higher binding energy and therefore increases the width of the UPS spectrum of the C10T/Au compared to bare Au, resulting in a decrease of the work function of the surface.
Reference:


(16) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.;