

Correlation between HOMO Alignment and Contact Resistance in Molecular Junctions: Aromatic Thiols versus Aromatic Isocyanides

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Understanding electron transport in metal–molecule–metal (MMM) junctions is of great importance for the advancement of molecular electronics.¹ Critical factors that determine conductivity in a MMM junction include the nature of metal–molecule contacts and the electronic structure of the molecular backbone. While most junction experiments have utilized thiol (–S) metal contacts, theoretical studies of transport in conjugated molecules have addressed a number of surface linkers, including –O, –S, –CN (isocyanide), and –Se.² Here we report transport and electronic structure measurements on rigid, conjugated oligoacenes of increasing length with either thiol (–S) or isocyanide (–CN) linkers (Figure 1). We use conducting probe atomic force microscopy (CP-AFM) to measure transport and ultraviolet photoemission spectroscopy (UPS) to establish the valence electronic structure. We find that for these conjugated systems the Au–CN contact is more resistive than Au–S. The difference in contact resistance correlates with UPS measurements that show the highest-occupied molecular orbital (HOMO) of the isocyanide series is lower in energy (relative to the Fermi level of Au) than the HOMO of the thiol series, indicating the presence of a higher tunneling barrier at the contact for the isocyanide-linked molecules. By contrast, the difference in the HOMO positions for the two series of molecules does not appear to affect the length dependence of the junction resistance (i.e., the β value).

Au-coated AFM tips and flat Au substrates were prepared as described previously.³ Self-assembled monolayers (SAMs) of aromatic (benzene (Ph), 2-naphthalene (Naph), 2-anthracene (Anth)) thiols and isocyanides were grown on Au surfaces from 1 mM solutions in toluene for 24 and 6 h, respectively, rinsed thoroughly with toluene and acetonitrile, and dried under a stream of nitrogen. The SAMs have been extensively characterized, and the surface coverage of all of the molecules is comparable to within a factor of 10–20% (see Supporting Information). We formed each junction by bringing a Au-coated tip into contact with a SAM, as illustrated in Figure 1. For each Au–SAM–Au junction, the resistance was determined from the linear current–voltage relationship in the bias voltage range of –0.3 to 0.3 V. A tip radius of ~50 nm was used in all experiments, and the number of molecules in each junction was estimated to be ~100.⁴

Figure 2 shows representative semilog plots of junction resistance versus molecular length for both the –S and –CN oligoacene series. The data shown in Figure 2 were acquired with a single Au-coated AFM tip. Each resistance value represents the average of approximately 10 *I*–*V* traces. The linear fits in Figure 2 indicate that the data are well described by the typical nonresonant tunneling equation $R = R_0 \exp(\beta \cdot s)$,^{3a} where *R* is the junction resistance, *R*₀ is the effective contact resistance (the *y*-axis intercept), β is the length-dependent tunneling attenuation factor (the slope), and *s* is

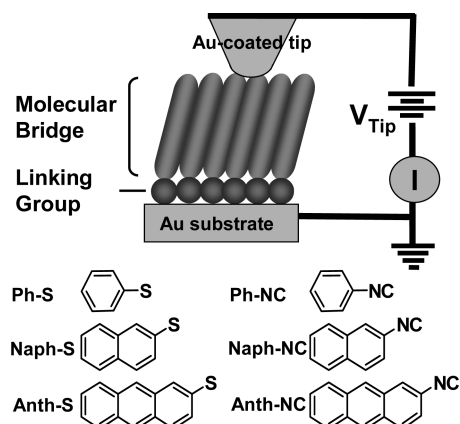


Figure 1. Illustration of a metal–molecule–metal junction formed using CP-AFM. A Au-coated tip is brought into contact with a SAM of aromatic molecules on a Au substrate. *I*–*V* traces are obtained over ± 0.3 V at a load of 2 nN. The molecular structures are shown at the bottom.

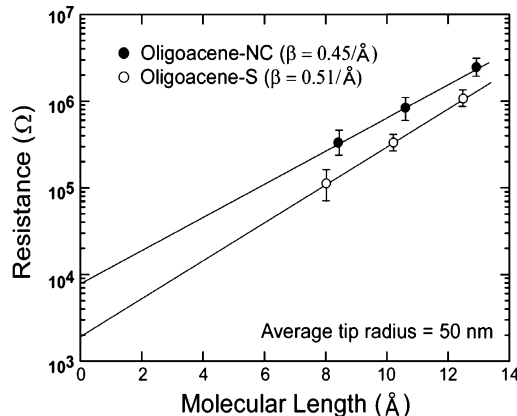


Figure 2. Semilog plot of resistance versus molecular length for Au/SAM/Au junctions. Each data point is the average of several *I*–*V* traces collected with a single AFM tip. The error bars represent one standard deviation. Straight lines show linear fits to the data.

the molecular length. Averages obtained from 10 sets of measurements (10 different tips) on each series are compiled in Table 1. The β values for the two series of molecules are the same ($0.5 \pm 0.1 \text{ \AA}^{-1}$) within experimental error and are in the expected range,⁵ but the effective contact resistance *R*₀ of the isocyanide series is about three times higher than that of the thiol series. *R*₀ is an aggregate contact resistance that includes the resistance of both the top and bottom contacts; because the top (tip–molecule) contact is likely to be similar for the two series, we ascribe the difference in the *R*₀ values to the difference in resistance between the Au–CN–oligoacene and Au–S–oligoacene contacts.

It is not immediately obvious that the junction resistance for the oligoacenes should be well described by $R = R_0 \exp(\beta \cdot s)$, which

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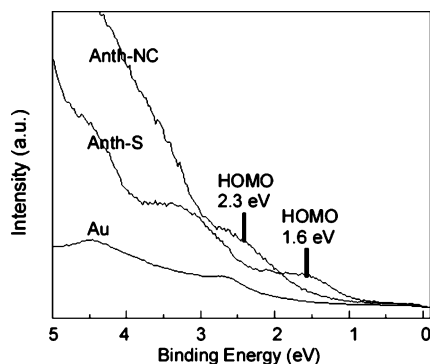


Figure 3. Ultraviolet photoelectron spectra for SAMs of Anth-S and Anth-NC along with bare gold. Binding energy is referenced to E_{Fermi} , and the intensities of the raw spectra were normalized at E_{Fermi} .

Table 1. Length-Dependent Tunneling Attenuation Factors (β) and Contact Resistances (R_0) for Each Molecular Series

molecular series	β (\AA^{-1})	R_0 (Ω)
oligoacene-S	0.50 (± 0.09)	1.3 (± 1.2) $\times 10^3$
oligoacene-NC	0.49 (± 0.08)	3.6 (± 1.9) $\times 10^3$

Table 2. Energy Offsets ($E_{\text{Fermi}} - E_{\text{HOMO}}$) of SAMs on Au (eV)

	$E_{\text{Fermi}} - E_{\text{HOMO}}$		$E_{\text{Fermi}} - E_{\text{HOMO}}$
Ph-S	2.0	Ph-NC	3.3
Naph-S	1.8	Naph-NC	2.8
Anth-S	1.6	Anth-NC	2.3

also works well for aliphatic systems. The HOMO–LUMO gap of the oligoacene backbone decreases substantially with increasing number of rings, and this changing electronic structure presumably should change the β value. However, the influence of the changing molecular electronic structure on transport depends on where the Fermi level lies in the HOMO–LUMO gap, as has been pointed out theoretically.^{2b,6} The linear dependence in Figure 2 may suggest that the Fermi level is too far from a molecular energy level to impact β substantially.^{3a,7} The apparent linear dependence may also be simply a consequence of the small range of molecular lengths (8–13 \AA) that we have probed. Interestingly, recent work on molecular junctions based on highly conjugated carotene molecules also demonstrated similar length-dependent resistance and a well-defined β parameter.⁸ Spectroscopic and electrochemical electron-transfer studies have established that electron-transfer rates through conjugated bridges of varying lengths can be well-characterized by a β value, typically less than 0.5 \AA^{-1} .^{7,9}

To probe the electronic structure of the SAMs on Au, UPS spectra were taken with HeI ($h\nu = 21.2 \text{ eV}$) radiation incident at 50° from the sample normal. Photoemitted electrons were collected at normal emission with a pass energy of 4.45 eV. All spectra were acquired at an applied bias of -7 V on the sample, and the energy scale was referenced to the Fermi level of Au (E_{Fermi}). The intensities of the raw spectra were normalized at E_{Fermi} . Figure 3 shows UPS spectra of SAMs of Anth-S, Anth-NC, and bare Au. The clean bare Au was prepared by dipping thermally evaporated polycrystalline Au in a piranha solution for 10 min, washing with deionized water, and then immediately transferring to the UPS vacuum chamber. Its work function was 4.9 eV. Note that the HOMO level of Anth-S lies closer to E_{Fermi} than Anth-NC by 0.7 eV. We found a similar shift in the energy offset ($E_{\text{Fermi}} - E_{\text{HOMO}}$) for naphthalene and benzene derivatives (Table 2). That is, $E_{\text{Fermi}} - E_{\text{HOMO}}$ was greater for the isocyanide species than for the corresponding thiol species

of the same length. We also found that within each series $E_{\text{Fermi}} - E_{\text{HOMO}}$ decreased with molecular length, consistent with expectation.

We propose that the offset $E_{\text{Fermi}} - E_{\text{HOMO}}$ for the $-S$ and $-NC$ series is the reason for the difference in contact resistance between aromatic thiols and isocyanides. The smaller offset observed for the aromatic thiols should produce more effective coupling between states in the metal and the HOMO level of the molecules, thereby reducing the effective barrier to tunneling at the contact.¹⁰ However, one could have anticipated that a smaller offset would also affect β , particularly because the HOMO states for both the thiol and isocyanide compounds are delocalized across the linking group and the aromatic system.¹⁰ The dependence of β on Fermi level position has not been examined experimentally for conjugated systems beyond what is reported here, though theoretical work suggests a strong dependence may be expected.^{10,11} Elucidating the precise dependence of R_0 and β on energy level alignment will require further experiments in which electronic structure and transport measurements are coupled with synthesis of homologous molecules having systematically varying electron affinities or ionization potentials. We note that preliminary UPS and CP-AFM measurements in our laboratory on oligophenylene thiols and isocyanides yield similar results to what we have reported here for the oligoacene systems.

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Supporting Information Available: Synthesis of molecules and structural characterization of SAMs using ellipsometry, XPS, UPS, and ATR-FTIR. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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