Single-Molecule Junction Conductance through Diaminoacenes

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The study of electron transport through single molecules is essential to the development of molecular electronics. Indeed, trends in electronic conductance through organic nanowires have emerged with the increasing reliability of electron transport measurements at the single-molecule level. Experimental and theoretical work has shown that tunneling distance, HOMO-LUMO gap and molecular conformation influence electron transport in both saturated and π-conjugated nanowires. However, there is relatively little experimental data on electron transport through fused aromatic rings. Here we show using diaminoacenes that conductivity depends not only on the number of fused aromatic rings in the molecule, which defines the molecular HOMO-LUMO gap, but also on the position of the amino groups on the rings. Specifically, we find that conductance is highest with minimal disruption of aromaticity in fused aromatic nanowires.

We recently reported on the improved reliability and reproducibility of conductance measurements using amines instead of thiols or isonitriles in metal-molecule-metal junctions. Junctions are formed by breaking Au point contacts in a solution of diamines. Conductance measurements for diaminoacenes were recorded in 1,2,4-trichlorobenzene solution by repeatedly forming and breaking Au point contacts with a modified STM tip (Figure 1b, inset). Typically, diamines were sublimed under vacuum prior to use. Conductance traces measured as a function of tip-sample displacement reveal quantized conductance steps observed at integer multiples of $G_0$ ($2e^2/h$), the fundamental quantum of conductance. Many of the traces reveal steps at molecule-dependent conductance values below $G_0$ (Figure 1a) due to conduction through a single molecule bridging the gap between the two Au point-contacts. Repeated measurements give a statistical assessment of the junction properties presented as conductance histograms (Figure 1b) with the peak representing the most probable measured conductance value for the molecular junction.

Figure 1b shows representative conductance histograms resulting from several thousand conductance traces for three molecules, 1,4-diaminobenzene, 2,6-diaminonaphthalene and 2,6-diaminoanthracene along with a control histogram measured in the solvent alone. Peaks in the conductance histograms determined by Lorentzian fits to the data correspond to the most prevalent single molecule junction conductance. Figure 2 shows the measured conductance values for 5 different acenes. For the upper series, 1,4-diaminobenzene, 1,4-diaminonaphthalene and 9,10-diaminoanthracene, the conductance increases with increasing number of benzo rings, whereas in the lower series, 1,4-diaminobenzene, 2,6-diaminonaphthalene and 2,6-diaminoanthracene, the conductance decreases with increasing number of rings.

Figure 1. Representative conductance traces (a) and histograms (b) for 1,4-diaminobenzene (1), 2,6-diaminonaphthalene (2) and 2,6-diaminoanthracene (3). The lower inset illustrates 1,4-diaminonaphthalene binding in the metal-molecule-metal junction.

Figure 2. Plots of conductance ($G_0$, circles) and square of tunnel coupling ($eV^2$, X’s) vs. number of benzo rings (log scale). The inset shows experimental conductance values in the 2,6-diamine series with a linear abscissa.

We have demonstrated previously that the low bias conductance through polyphenyls attached to gold electrodes with amino groups is through a non-resonant tunneling process. Quantitative trends in the junction conductance have been analyzed using quantum chemistry calculations based on density functional theory for amines coupled to Au clusters to represent the electrodes. Frontier orbitals on the contact Au atoms are tunnel coupled through the molecular backbone resulting in a symmetric and antisymmetric pair split by $2t$. The conductance is
proportional to the square of the splitting.\(^\text{10}\) well representing trends observed in the conductance through amine linked junctions.\(^\text{3,5,11}\) The tunnel coupling was calculated for all the acenes in the experimental study with the results shown in Fig. 2. The trends for both series are accurately represented, strongly suggesting that non-resonant tunneling is responsible for the conductance measured in the acenes.

Interestingly, the 2,6 series conductance does not display the exponential dependence on length normally associated with tunneling.\(^\text{12}\) The inset in Fig. 2 shows a clear deviation and the calculations for longer acenes suggest a power law dependence (main panel, roughly \(r^{-1}\)). Most molecular bridges studied to date (alkanes, oligophenyls, oligophenyleneethynylene, etc.) exhibit modest changes in ionization potential (or HOMO energy) with length and a robust gap to the LUMO energy. In the McConnell picture the donor and acceptor levels (electrode Fermi energies) maintain a roughly constant separation from the bridge energy level independent of bridge length resulting in the exponential conductance. However, the acenes show a rapid reduction in ionization potential with increasing fused ring number. This has significant consequences, as suggested by a simple Hückel model calculation with constant \(\pi\) electron coupling parameter \(V\) (see supporting information). If the electrodes are electronically coupled \((I)\) at the 2 and 6 positions and the Fermi energies are aligned to the center of the HOMO-LUMO gap, the conductance does not drop exponentially with length (ring number, \(r\)).

\[
G = G_0(r+1)^2/((r+1)^2V^2 + \Gamma^2/4)^2
\]

In a similar way, the rise in conductance measured transverse to the acene (e.g. 9,10-diaminoanthracene) indicates systematic approach of the bridge HOMO to the electrode Fermi energy with increasing length. The quantitative trends observed in Fig. 2 depend on the final details of this energy alignment.

The conductivities follow the expected changes in aromatic stabilization when the diamines are oxidized to the dications (Figure 3). With 9,10-diaminoanthracene, there is an increase from one to two benzene rings on such oxidation, while with 2,6-diaminoacenes all benzenoid rings are lost on such oxidation to the dication.\(^\text{11}\) While this is a formalism, and the dications are from one to two benzene rings on such oxidation, while with 2,6-diaminoanthracene and 9,10-diaminoanthracene, there is an increase stabilization when the diamines are oxidized to the dications depend on the final details of this energy alignment.

Figure 3. Upon oxidation to the dication, 9,10-diaminoanthracene gains a benzene ring (left structure) whereas 2,6-diaminoanthracene loses a benzene ring (right structure).

In addition to establishing length-dependent conductances for diaminoacenes, this work demonstrates the importance of Hückel structures and aromatic stabilization in electron transport. Ongoing investigations are focused on determining the relationship between conductance and electrochemical properties of diaminoacenes. Our preliminary results indicate a relationship between oxidation potential and junction conductance.

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Supporting Information Available: Experimental details, conductance histograms and theoretical methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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