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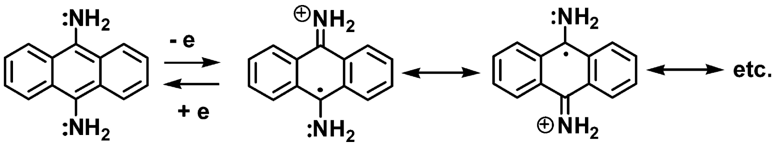

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Oxidation Potentials Correlate with Conductivities of Aromatic Molecular Wires

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An important step in building molecular electronics is to establish the relationship between electronic structure and conductivity.[1−3] Understanding how electrons are transported through molecules will allow us to control current and to design more efficient devices. Previously,[4] we showed that conductance through diamine molecular wires depends on the placement of amino group contact points for gold electrodes, and that conductance is highest with minimal disruptions of aromaticity. Here we show that conductivity is related to the ease with which electrons are abstracted from diamine molecular wires, using experimental data rather than theoretical estimates, and over 3 orders of magnitude.

The dependence of junction conductance on the redox state of a molecule has been studied by measuring conductance as a function of gate voltage or source/drain bias.[5−8] Our approach involves measuring conductivities of single molecules and comparing their electrochemical oxidation potentials using cyclic voltammetry (CV). Conductivities of single molecules can be determined accurately and reproducibly by repeatedly forming and breaking Au point contacts in a solution of diamines using a modified STM at ambient temperature.[9,10] Peaks in the conductance histograms constructed from raw data determine the most probable conductance of each molecule.

The diamines in our study contained biaryl or fused aromatic rings between amino groups. Figure 1a illustrates 9,10-diaminoanthracene binding in the metal−molecule−metal junction. Electrochemical potentials were recorded at ambient temperature in acetonitrile solution using a platinum disc working electrode and Ag/AgNO$_3$ reference electrode with tetrabutylammonium perchlorate as supporting electrolyte. CV traces for 9,10-diaminoanthracene (**1**), 1,4-diaminonaphthalene (**2**), and 1,4-diaminobenzene (**3**) are shown in Figure 1b. Most of the diamines in this study showed two reversible one-electron redox couples similar to those in Figure 1b. Some diamines showed irreversibility or unclear second oxidation peaks (reflecting subsequent chemical processes), but all gave clear first oxidation peaks. In Figure 1c, we plot, on a semilog scale, the measured molecular conductance (G_0) against the oxidation potential ($E_{1/2}$) for 22 molecules studied. We find that the conductivity correlates inversely with the first oxidation potential, reflecting the fact that both quantities are functions of the N−N distance and of the nature of the intervening conjugated systems. However, replacement of aromatic CH hydrogens in **3** or **6** with electron-withdrawing groups such as cyano, halo, or trifluoromethyl groups significantly increased oxidation potentials but had only a small affect on conductivity relative to changes in N−N distance (see below).

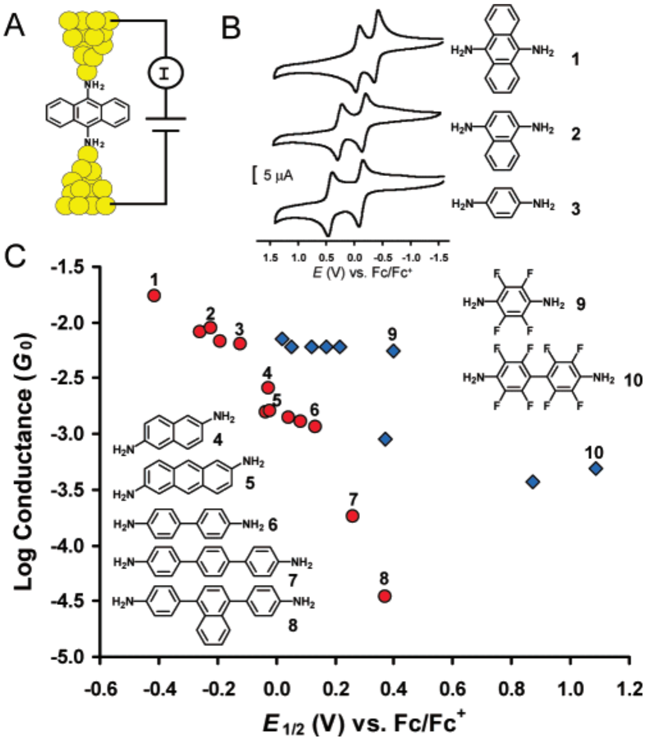

Figure 1. Illustration of 9,10-diaminoanthracene binding in the junction (a) and cyclic voltammograms (b) for diamines **1**−**3**. Cyclic voltammetry was performed at ambient temperature in CH$_3$CN containing 0.1 M Bu$_4$NClO$_4$ at 100 mV s^{-1} using a platinum disc working electrode and Ag/AgNO$_3$ reference electrode. In (c), conductance (G_0) is plotted versus first oxidation potential ($E_{1/2}$) on a semilog scale with diamines **1**−**8** and methyl-substituted diamines as red circles. The blue diamonds represent phenylene and biphenylene diamines with electron-withdrawing substituents. See Supporting Information for more details.

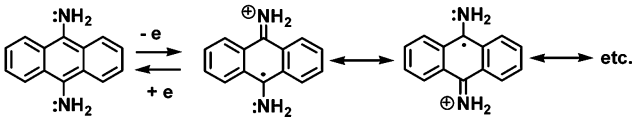

Figure 2. Resonance structures of electrochemically generated cation radical of 9,10-diaminoanthracene (**1**).

The correlation in Figure 1c implies that as an electron becomes easier to remove the conductivity improves. One possible factor is that converting a diamine to its cation radical (Figure 2) causes changes in aromaticity related to those we have invoked previously for electrical conduction.[4] For example, conductivity through biphenylene units (e.g., benzidine, **6**) was lower than through 2,6-diaminonaphthalene (**4**) because two benzene rings are disrupted by electrical conduction in biphenyl systems as opposed to one benzene and one benzenoid ring in naphthalene, and the same factors make one-electron oxidation also easier in the naphthalene system.

However, the correlation between conductivity and oxidation potential also implies that, during electronic conduction, partial electron abstraction at the drain (reflecting electron delocalization across the junction) precedes electron injection at the source in the

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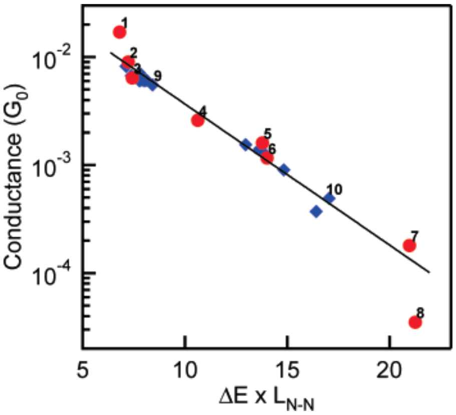

Figure 3. Plot of measured conductance versus $\Delta E \times L$. The fitting parameter E_{Au} is 3.5 eV. Note the fit of compounds **9** and **10**.

electron-rich systems. The molecules therefore have a slight positive charge in their conducting state but less so in compounds such as **9** and **10**. This interpretation is supported by the increased conductivities of diamines containing electron-donating methyl substituents on the aromatic rings. This further supports the indication that electron transport through these diamines is analogous to hole transport in metal−insulator−metal films, or that the HOMO is the molecular level dominating transport in this system.[11] Electron-withdrawing substituents as in **9** and **10** make diamines more difficult to oxidize electrochemically because they lower the HOMO energy and destabilize positive charge. Thus there is less p-doping of the wire by electron abstraction into the drain during conduction in such cases.

The correlation between conductivities and oxidation potentials can be analyzed further by considering the mechanism for electron conduction through these systems. The low bias conductance through diamine molecules attached to gold electrodes is through nonresonant tunneling or super-exchange.[9,10] Tunneling rates decrease exponentially, both with increasing molecular length and with the barrier for tunneling. For the molecules studied, the tunneling distance is roughly the N−N separation and, in a square tunnel barrier limit, barrier height can be approximated as the energy difference between the Au Fermi level and the molecular HOMO level.[11,12] In this tunneling limit, the measured conductance data (G) can be expressed in terms of the N−N length (L) and the position of the molecular HOMO level as follows:

$$G \propto \exp(-\Delta E \times L) \text{ where } \Delta E = \sqrt{E_{\text{HOMO}} - E_{\text{Au}}}$$

The HOMO energy levels (E_{HOMO}) were estimated relative to that of ferrocene ($E_{\text{HOMO}} = 4.8$ eV) from the measured first oxidation potentials.[13] In Figure 3, we plot G against $\Delta E \times L$ using E_{Au} as a fitting parameter. Quite surprisingly, the measured conductance of all molecules in Figure 1c correlates with the estimated position of the molecular HOMO level within this model. The fitting parameter, $E_{\text{Au}} = 3.5$ eV, obtained from this model is however significantly lower than the work function of clean Au(111) (5.3 eV).[14] This can be expected for the following reasons. First, the estimation of E_{HOMO} from the oxidation potential does not include solvent and image charging effects, which could play a crucial role and change the actual HOMO energies relative to vacuum.[15] Second, the tunneling model used here does not account for changes in the barrier across the molecular junction and is therefore too simple. Finally, the actual work function of a gold point contact in a solution of a molecule could be significantly different from that of Au(111) under ultrahigh vacuum conditions.[16] Nonetheless, the linear dependence of the fit ($R = 0.98$) supports the fact that nonresonant tunneling transport in this system is through the HOMO level.[11] Interestingly, the two data points that deviate the most are molecules **1** and **8**. In the case of **1**, it is possible that the HOMO level is sufficiently close to the Fermi level of gold that we see deviations from tunneling transport. For molecule **8**, we believe that the internal twists are significant, possibly indicating that transport is through the σ system in addition to the π system.

In summary, we find an excellent correlation between junction conductivities and electrochemical oxidation potentials, indicating that the HOMO level is indeed responsible for tunneling transport through these diamines. This supports the idea that conductivity is affected by changes in aromatic stabilization and that the electron-rich molecules have some positive charge in their conducting states. This relationship between electronic structure and conductivity gives insight into the mechanism of electron transport in organic molecules comprising aromatic ring units. We are now exploring the predicted higher conductivities of molecular wires containing antiaromatic units.

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Supporting Information Available: Experimental details and cyclic voltammetry data. This material is available free of charge via the Internet at http://pubs.acs.org.

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