

## Length dependence of charge transport in oligoanilines

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The conductance of aniline trimers, pentamers, and heptamers has been measured in a molecular junction as a function of the oxidation state of the molecules by making measurements under electrochemical potential control. The effective electronic decay length is too small to be consistent with simple tunnel transport in the neutral molecule and is even smaller in the oxidized molecule. Thus these molecules can act as relatively high conductance links even in the absence of the interchain hopping required for metallic behavior. © 2007 American Institute of Physics. [DOI: 10.1063/1.2472758]

Oligoanilines with well defined chain lengths are model compounds for studying the single molecule aspects of charge transport in polyaniline.<sup>1–3</sup> Single molecule measurements permit quantitative comparison with theory<sup>4</sup> and, when combined with electrochemical potential control, they permit quantitative measurements of the single molecule conductance as a function of the oxidation state of the molecule.<sup>5</sup> We previously studied an aniline heptamer<sup>5</sup> with subsequent studies of a trimer.<sup>6</sup> In this work, we present data for the conductance of a pentamer, which, taken together with data for the other oligomers, allow an effective electronic decay length  $\beta$  to be extracted from an exponential fit to the conductance versus length  $L$ ,  $G=A \exp(-\beta L)$ . The small values that are obtained for  $\beta$  ( $\sim 0.06 \text{ \AA}^{-1}$ ) are at least a factor of 5 smaller than the predictions of tunneling theory.<sup>7</sup> If interpreted in terms of a simple tunneling barrier, these values for  $\beta$  imply barrier heights less than  $k_B T$ . This situation was not altered significantly when electrochemical data were used to correct for the shift of the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap with the length of the molecule. Thus it appears that some other mechanism (such as hopping) contributes significant additional conductance even in these short oligomers. Even though crystalline samples are required for metallic conductance,<sup>8</sup> this enhanced conductance in isolated single molecules suggests that they could serve as “wires” for connecting electronic components over nanometer distances.

We synthesized the bithiolated pentamer [ $n=5$  in Fig. 1(a)] following the protocols previously described for the heptamer and trimer.<sup>5,6</sup> The backbone lengths (from sulfur to sulfur) of each oligomer are estimated to be 2.4 nm ( $n=3$ ), 3.5 nm ( $n=5$ ), and 4.7 nm ( $n=7$ ) using a monomer repeat distance of 5.73 Å.

The single molecule conductance of the pentamer was measured in a nonconducting solvent (toluene) and also in a supporting electrolyte (50 mM  $\text{H}_2\text{SO}_4$ ) as described

previously.<sup>5,6</sup> Briefly, a break junction is formed repeatedly by pushing a gold probe into a Au(111) substrate<sup>9</sup> and recording the current versus time as the probe is withdrawn. Steps in the trace of current versus time correspond to integer numbers of molecules trapped in the gap.<sup>10</sup> A partially insulated probe<sup>11</sup> permits operation of the system in a conducting electrolyte with surface potential under electrochemical control and the tip maintained at a fixed potential difference with respect to the surface.<sup>5</sup> The leakage current in the electrolyte through the insulated scanning tunneling microscope tip is 1–2 pA and thus negligible in our experiments. Potential control was maintained relative to a silver wire quasireference, calibrated and prepared as described earlier.<sup>5,6</sup> The reference was stable and reproducible to  $\pm 20$  mV.

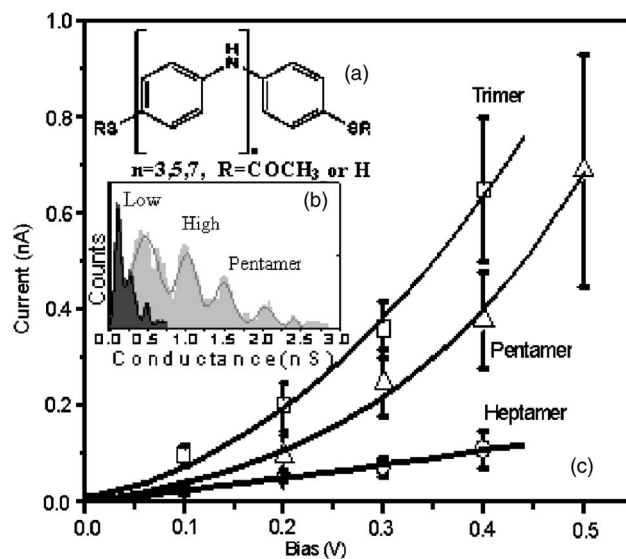


FIG. 1. (a) Molecular structure. (b) High conductance (light gray) and low conductance (gray) histograms of pentamer based on several thousand current-distance curves at  $V=200$  mV in toluene. The peaks correspond to one, two, three, and five molecules in the gap. The gray and black curves are Gaussian fits to the histogram peaks for the high conductance and low conductance data, respectively. (c) Current-voltage characteristics for trimer (squares), pentamer (triangles), and heptamer (circles) in toluene. Data are for the high conductance series of peaks in the conductance histograms. The solid lines are fits to polynomials. Error bars are the width of the first peak in the conductance histograms.

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TABLE I. Electrochemical data for aniline oligomers.

Molecule	Oxidation potential (V) <sup>a</sup>	
	1st ( $E_{ox}/E_{red}$ )	2nd ( $E_{ox}/E_{red}$ )
Trimer	0.33/0.30	0.76/0.67
Pentamer	0.28±0.02 /0.24±0.01 <sup>b</sup>	0.71±0.01 /0.66±0.03 <sup>b</sup>
Heptamer	0.17/0.15	0.6/0.57

<sup>a</sup>In 50 mM H<sub>2</sub>SO<sub>4</sub> acid, scan rate of 100 mV/s, and vs Ag wire.

<sup>b</sup>Based on average of eight experiment runs.

The oxidation potentials of this series of molecules depend on their length,<sup>12</sup> indicative of changes in electronic structure with length. Our data (Table I) are in reasonable agreement with previously published data.<sup>13</sup> Our electronic measurements were confined to the potential region that includes only the first oxidation peak because this is stable over many cycles. The potential of the first oxidation peak,  $V_p$ , depends linearly ( $R=0.98$ ) on the number of monomers,  $N$ ,

$$V_p = 0.46 - 0.04N \text{ V} \quad \text{versus Ag wire.} \quad (1)$$

The single molecule conductance was determined from a histogram of the values of the measured conductances [Fig. 1(b)] as described elsewhere.<sup>6</sup> The recorded current depends sensitively on the nature of the contacts, and it is not unusual to observe more than one series of peaks, corresponding to different types of atomic geometry at the connection.<sup>4,14-16</sup> We found only one series in the case of the heptamer<sup>5</sup> and two (a low and a high conductance series) in the case of the trimer.<sup>6</sup> Two values of conductance were also found for the pentamer, as shown by the two histograms in Fig. 1(b). If the single series for the heptamer corresponds to the “low” value, we would expect to detect steps at yet higher current multiples but we find no evidence for it, so we conclude that the measured heptamer data belong to the “high” conductance set. Therefore, in what follows we confine our attention to this high conductance data set so that we can make meaningful comparisons across the entire series of molecules.

Figure 1(c) shows current-voltage,  $I(V)$ , characteristics of the three oligoanilines in toluene for the high conductance data set. The shape of  $I(V)$  is distinctly nonlinear for both trimer and pentamer. The heptamer characteristic is fitted by  $i=GV$  where  $G=0.27$  nS. The pentamer and trimer are fitted by  $i=G_1V+G_2V^2$  where  $G_1=-0.14$  (pentamer) and  $0.3$  nS (trimer) and  $G_2=2.95$  (pentamer) and  $3.16$  nA/V<sup>2</sup> (trimer). Electric-field induced changes of structure might account for this effect<sup>17</sup> (though it does not scale linearly with field).

We plot the conductance of these neutral molecules versus  $N$  in Fig. 2. In order to accommodate the nonlinear characteristics, we have plotted separate data for each bias [Fig. 2(a)=0.2 V, Fig. 2(b)=0.3 V, Fig. 2(c)=0.4 V]. At low bias, the decay is fitted quite well by an exponential [solid line in Fig. 2(a)],

$$G = A \exp(-\beta_N N), \quad (2)$$

where  $A$  is the contact conductance and can be obtained from the fitting. The fit is less good at the two higher biases [Figs. 2(b) and 2(c)]. The fits yield  $\beta_N=0.33\pm0.1$  (0.2 V),

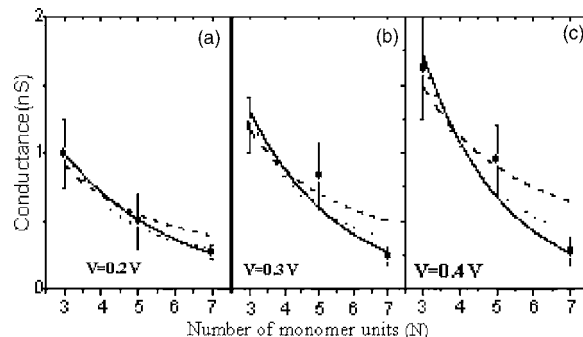


FIG. 2. Conductance as a function of oligomer length derived from the data in Fig. 1. Because of the nonlinearity of the  $I(V)$  curves, these data are shown for three different biases [(a) 0.2 V, (b) 0.3 V, and (c) 0.4 V]. The solid line is a fit to a simple exponential function [Eq. (2)]. The dotted line is a fit to a variable-barrier model [Eq. (4)]. The dashed line is a fit to a  $1/N$  model for hopping conductance.

$\beta_N=0.39\pm0.12$  (0.3 V), and  $\beta_N=0.47\pm0.15$  (0.4 V). Taking each monomer to be  $5.7 \text{ \AA}$  leads to  $\beta=0.06-0.08 \text{ \AA}^{-1}$ , depending on the bias. This is at least five times smaller than the value calculated in first-principles tunneling calculations ( $\beta=0.3-0.4 \text{ \AA}^{-1}$ ),<sup>7</sup> a remarkably large discrepancy.

What do such small decay lengths mean? We can understand the decay length for a simple tunneling system in terms of the energy gap  $\Delta E$  between the Fermi level of the electrodes and the HOMO (or LUMO, which ever is closer) in terms of a simple model.<sup>18</sup> With  $\Delta E$  in eV and the tunnel gap  $L$  expressed in  $\text{\AA}$ ,

$$G = A \exp(-1.02\sqrt{\Delta E L}), \quad (3)$$

from which we see that  $\Delta E \sim \beta^2/1.04$ . Our experimental values for  $\beta$  would yield values for  $\Delta E$  on the order of 5 mV, clearly not compatible with the rather low room-temperature conductances observed in the neutral molecules.

The simple model of Eq. (3) neglects the dependence of the electronic states on the length of the molecule [Eq. (1)]. The (inappropriate) particle-in-a-box model gives  $\Delta E \sim 1/L^2$  which would lead to non-length-dependence for  $G$ . Thus, we must take into account the length dependence of  $\Delta E$  in fitting these data. We can make a better model of the length dependence of  $\Delta E$  using the electrochemical data summarized by Eq. (1). These are a measure of the energy difference between the state being oxidized and the Fermi energy of the electrode and can be connected with the energy of states that mediate tunneling.<sup>19</sup> Thus we will use Eq. (1) but scale the constant part by a factor  $\gamma$  to take into account the energy shift between relaxed and unrelaxed states and to avoid the need to try to relate electrochemical potentials to an absolute scale. This leads to the following expression for the length dependence of the conductance:

$$G = A \exp(-\sqrt{(0.46\gamma - 0.04N)N}). \quad (4)$$

Fits using this function yield the dotted lines in Fig. 2 with  $\gamma=1.00\pm0.07$  (0.2 V),  $0.98\pm0.27$  (0.3 V), and  $1.07\pm0.27$  (0.4 V). The corresponding value of  $\beta_N$  now varies with  $N$  and spans the range  $\beta_N=0.58$  ( $N=3$ ) to  $\beta_N=0.42$  ( $N=7$ ). Again, using a monomer length of  $5.7 \text{ \AA}$ , this corresponds to  $\beta=0.1-0.07 \text{ \AA}^{-1}$ . These values are still three to four times less than predicted by a tunneling theory<sup>7</sup> and the corresponding  $\Delta E$  turns out to be only a little bit bigger than the  $\sim 5$  mV produced by the simple exponential fit.

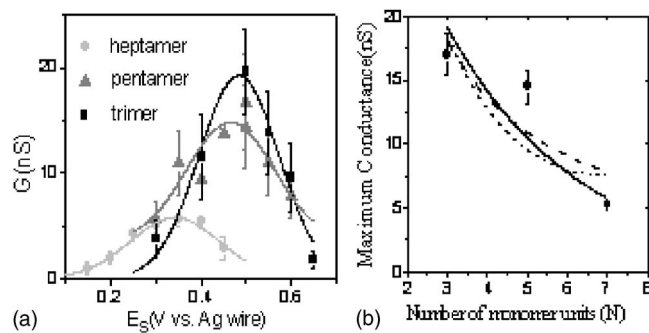


FIG. 3. (a) Single molecule conductance of trimers (black squares), pentamers (gray triangles), and heptamers (light gray circles) as a function of surface potential  $E_s$  for the high conductance series. The lines are fits to Eq. (5) using the parameters listed in Table II. These data are taken from histograms of thousands of measurements on single molecules. The molecules are on Au(111) in 50 mM  $H_2SO_4$ . The applied bias is 50 mV. (b) Conductance decay with oligomer length for the oxidized oligomers. Values are for the maximum conductance ( $G_M$ ) obtained by fitting data to Eq. (5). All data were obtained in 50 mM  $H_2SO_4$  under potential control. The fits are to Eq. (2) (solid line), Eq. (4) (dotted line), and the  $1/N$  dependence expected for hopping (dash line).

The above discussion assumes that the mechanism is indeed tunneling. A hopping mechanism would lead to  $G=A/N$  (Ohm's law, shown by the dashed line in Fig. 2). These fits are not as good as the tunneling models, suggesting that pure hopping is also not the only contributor to transport in these molecules.

We also measured the potential dependence of the single molecule conductance of the pentamer, finding it to be strongly dependent on potential  $E_s$  with a peak in the vicinity of the first oxidation potential. Our previous data for  $G$  vs  $E_s$  were fitted with a quadratic dependence of conductance on potential.<sup>5,6</sup> We found that a Gaussian gave a somewhat better fit:

$$G = A_0 + G_M \exp\left(-2 \frac{(E_s - E_s^M)^2}{w^2}\right). \quad (5)$$

Here,  $E_s^M$  is the surface potential at which the molecule has maximum conductance and  $w$  determines the width of the conductance peak. Fits to the conductance versus potential,  $G(E_s)$ , data for all of the molecules measured are shown in Fig. 3(a), and the corresponding fitting parameters are listed in Table II ( $A_0$  is close to 0 in all cases and is not shown). The data were taken at a small (50 mV) bias applied across the substrate to tip gap in order to avoid disturbing the local potential.<sup>20</sup> Clearly, Eq. (5) describes the potential depen-

TABLE II. Important parameters for the Gaussian fits to the dependence of the single molecule conductance on potential ( $G_M$ ,  $E_s^M$ , and  $w$ ). Here,  $E_s^M$  is the surface potential at which the molecule has maximum conductance.  $G_M$  and  $w$  determine the width of the conductance peak.

	$G^M$ (nS)	$w$	$E_s^M$
Trimer high	$19 \pm 2$	$0.18 \pm 0.02$	$0.48 \pm 0.01$
Pentamer high	$15 \pm 1$	$0.2 \pm 0.1$	$0.47 \pm 0.01$
Heptamer high	$6 \pm 1$	$0.21 \pm 0.05$	$0.34 \pm 0.01$

dence of the single molecule conductance well.

This work, taken together with the two previous studies,<sup>5,6</sup> also allows us to examine the conductance decay for the oxidized molecule at its peak conductance ( $E_s = E_s^M$ ). We have plotted the peak value of the conductance for the trimer, pentamer, and heptamer in Fig. 3(b) [error bars are relatively small because the entire data set was fitted, see Eq. (5)]. It is clear that the data are not well fitted by any of the models (exponential, variable energy barrier, and hopping). The exponential fit yields  $\beta_N = 0.3 \pm 0.1$ , corresponding to  $\beta = 0.06 \text{ \AA}^{-1}$ . The variable-barrier model [Eq. (4)] yields  $\gamma = 0.6 \pm 0.5$ . This is substantially less than the value of  $\sim 1$  found in the neutral molecule, reflecting a significant shift of electronic levels on oxidation of the molecules.

In summary, we have measured the single molecule conductance of three lengths of aniline oligomer. These data yield apparent decay lengths that are smaller by at least a factor of 5 than the predictions of tunneling theory and inconsistent with reasonable values of tunneling barrier. Thus, it appears that there is a significant additional contribution to the conductance of these molecules from another process (such as hopping) even in these very short molecules and even in the absence of the interchain hopping that dominates conductance in the bulk material. Thus, these molecules would serve remarkably well as short connectors in nanoscale electronic circuitry.

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