The effect of molecular conformation on single molecule conductance: measurements of \( \pi \)-conjugated oligoaryls by STM break junction\(^\dagger\)

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Measurements of molecular break junction reveal quantitatively the correlation between the single-molecule conductance and the conformation of \( \pi \)-conjugated molecules with 6–18 conjugated double bonds.

Although the conformation of molecules has long been held to be a major factor that influences the electron transporting properties,\(^1\)–\(^6\) only very recently, Venkataraman and co-workers first unveiled the effect of torsion angles on the conductance of biphenyls by constraining the dihedral angles between the neighboring aryl rings.\(^6\) Unambiguous experimental findings associated with the deformation and stretching of \( \pi \)-conjugated molecules are yet unavailable because the studies of single-molecule conductance focus mostly on saturated alkane chains,\(^6\)–\(^12\) para-derivatized benzenes,\(^6,12-15\) DNA oligonucleotides,\(^16,17\) peptide,\(^18\) rigid OPEs,\(^19\) ligand-supported metal strings,\(^20,21\) and short oligomers.\(^16,17\) These model systems have either ill-conductive chains or rigid frameworks which do not yield a readily discernible correlation of the single-molecule conductance to the conformational stretching along the molecular long axis. Herein, we manifest this effect by designing conjugated and relatively flexible oligoaryls (Fig. 1) with alternating benzene-furan units, synthesized by the bidirectional iterative annulation protocol that allows precisely controllable conjugation length toward rationally tailored molecular wires.\(^22\)–\(^24\)

The single-molecule junction conductance was measured by recording currents at a fixed bias voltage across a metal–molecule–metal assembly configured by STM break junction (scanning tunneling microscopy). The experimental procedures and data treatment are referred to the thorough account in literature.\(^6\)–\(^8,18,20,25\)–\(^29\)

Briefly, molecular junctions were repeatedly generated by bringing a gold STM tip into and out of contact (5–10 nm s\(^{-1}\)) with a gold substrate in toluene containing the compound (1 mM) of interest. When the STM tip was dipped onto the substrate, the current increased drastically, revealing that a point contact between the gold electrodes was created. During withdrawal of the tip, the gold contact was broken and a gold bridge was pulled out. The cross-section of the bridge was eventually thinning to that of a single strand of gold atoms and the gold chain was subsequently broken.\(^30\) The corresponding conductance traces exhibited quantized steps which were integral multiples of the fundamental conductance, \( G_0 = 2e^2/h \approx 77.4 \mu \text{S} \) or \((12.9 \text{ k} \Omega)^{-1}\), where \( e \) is the electron charge and \( h \) is Planck’s constant.\(^30\) In the absence of molecules, the conductance traces showed exponential decay associated with the tip displacement, attributed to the tunneling event between the electrodes. Upon the formation of the tip-substrate gap in the presence of diol molecules, the thiol headgroups at the molecular termini might bind simultaneously onto the gold electrodes. The conductance traces responding to the tip withdrawn from the gold substrate \( (I(s) \text{ curves}) \) appeared a stepwise and quantized fashion, suggesting the presence of integer numbers of molecules in between the junction. The \( I(s) \) profiles were recorded by a NanoScope built-in program and exported as ASCII files. Each trace had 5120 data points which were converted into conductance after being divided by the applied bias voltage. Experimental details by Tao and Lindsay\(^8,28\) should be strictly followed to acquire better defined traces, in particular, by taking special care in the preparation of sharp tips and flat substrate.

The single-molecule resistance of compound I is 20.9 ± 2.9 M\( \Omega \) in a good agreement with 21 M\( \Omega \) of the literature value.\(^13\) For oligoaryls II–V, Panels (a)–(d) of Fig. 2 show their general \( I(s) \) features, significantly different than those of ill-conductive polymethylene chains\(^3,28\) or rigid molecules.\(^20,28\) For comparison, displayed in Fig. 2(e) and (f) are typical stepwise traces, respectively, for octanethiol and a rigid metal string complex, \([\text{Co}((\mu_1\text{-dpn})_2\text{NCS})_2]^{20}\) whose \( I(s) \) traces comprise reasonably smooth and clean steps. Note that when the STM tip is pulled

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away from the substrate, the bridging molecule is concomitantly stretched out. For Compounds II–V, the I(s) steps appear extended longer than those in panels (e) and (f) (see Table 1), ascribed to the relatively long and flexible framework of the oligoaryls. More than one-third of the I(s) curves exhibits a peak near the step edge where the breakdown of the molecule-to-electrode contact takes place. At some point prior to the junction breakage, the molecule might develop a better conjugated conformation such as ideal bond angles and co-planarity which improve the π-electron propagating along the chain and should be accounted for the peaks in the I(s) traces. Note that nearly two-third of the I(s) traces do not exhibit isolated peaks. Regardless whether the isolated peak is present, all I(s) traces of Compounds II–IV fluctuate pronouncedly while those of rigid molecules appear smooth (e.g. Fig. 2(f)), providing a strong support for the correlation between the molecule conductance and the corresponding conformation.

Table 1 summarizes the single-molecule conductance for compounds I–V. Two types of conductance values, G and Gpeak, are derived by the following manner. The former is decided by exponential decay and with plainly tunneling decay to facilitate the determination of conductance histograms (Fig. 2(a)–(d)) which exclude are derived by the following manner. The former is decided by exponential decay and with plainly tunneling decay to facilitate the determination of conductance histograms (Fig. 2(a)–(d)) which exclude

$$G = \frac{2e^2}{\hbar} \sim 77.4 \, \mu\text{s}, \text{the fundamental conductance unit,}^{30} \text{where } e \text{ is the electron charge and } h \text{ is the Planck’s constant.}$$

Table 1 Conductance and $\Delta G/G$ of π-conjugated oligoaryls I–V

<table>
<thead>
<tr>
<th>$n$</th>
<th>$G_{10^{-3} G_0}$</th>
<th>$G_{\text{peak}}/10^{-3} G_0$</th>
<th>$\Delta G/G$ (%)</th>
<th>$\Delta x/\text{nm}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>62 ± 2</td>
<td>NA</td>
<td>NA</td>
<td>0.09 ± 0.05</td>
</tr>
<tr>
<td>II</td>
<td>13 ± 2</td>
<td>14.4 ± 2.5</td>
<td>11 ± 3</td>
<td>0.33 ± 0.11</td>
</tr>
<tr>
<td>III</td>
<td>6.5 ± 0.6</td>
<td>3.1 ± 1.4</td>
<td>25 ± 6</td>
<td>0.38 ± 0.12</td>
</tr>
<tr>
<td>IV</td>
<td>2.5 ± 0.2</td>
<td>3.6 ± 0.8</td>
<td>44 ± 14</td>
<td>0.47 ± 0.14</td>
</tr>
<tr>
<td>V</td>
<td>0.8 ± 0.1</td>
<td>1.4 ± 0.2</td>
<td>75 ± 18</td>
<td>0.57 ± 0.19</td>
</tr>
</tbody>
</table>

$G_0 \sim 77.4 \, \mu\text{s or (12.9 kΩ)}^{-1}$. NA not available. $\Delta G = G_{\text{peak}} - G$, where $G$ was obtained from all traces except those exhibiting simple exponential decay and $G_{\text{peak}}$ was averaged from those with a peak near the end of the step. $\Delta x$ the extension of the step. The values of $\Delta x$ should not be over-interpreted in a quantitative manner because $\Delta x$ is notably affected by the ill-defined microscopic structure at the molecule junction.

Fig. 2 Traces of conductance versus STM tip stretching and histograms measured by STM break junction. (a)–(d) II–V. (e) octanedithiol, (f) [Co$_2$(1,2-dpa)$_2$(NCS)$_2$]$^{20}$ dpa$^-$, dipyridylamido anion; NCS, isothiocyanate. $G_0 = 2e^2/h \sim 77.4 \, \mu\text{s}, \text{the fundamental conductance unit,}^{30}$ where $e$ is the electron charge and $h$ is the Planck’s constant.
the intercept for II-V represents an identical structure to that of I (see Fig. 1), it would seem that the contact resistance of the oligoaryls should be the same as the single-molecule junction resistance of I. Interestingly, the contact resistance of II-V is 38.7 ± 1.1 MΩ, almost two times the resistance of I (20.9 ± 2.9 MΩ). This discrepancy shows that the meta-molecule contact strength is, rather than a constant, weakened by the hybridization of the benzenedimethanethiol headgroup with the π-conjugated backbone.

In summary, with the relatively flexible benzene–furan oligoaryls, we demonstrate the effect of molecular conformation on the conductance of π-conjugated molecules. Upon the tip stretching, the conformations at Gpeak develop a smaller β than those of the most probable G. The fact that the contact resistance of II-V is larger than the single-molecule resistance of I shows the importance of molecular backbone-headgroup interactions on the electron transmission probability through the headgroup.

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Notes and references