Importance of Direct Metal–π Coupling in Electronic Transport Through Conjugated Single-Molecule Junctions

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Supporting Information

ABSTRACT: We study the effects of molecular structure on the electronic transport and mechanical stability of single-molecule junctions formed with Au point contacts. Two types of linear conjugated molecular wires are compared: those functionalized with methythiol or amine aurophilic groups at (1) both or (2) only one of its phenyl termini. Using scanning tunneling and atomic force microscope break-junction techniques, the conductance of mono- and difunctionalized molecular wires and its dependence on junction elongation and rupture forces were studied. Charge transport through monofunctionalized wires is observed when the molecular bridge is coupled through a S–Au donor–acceptor bond on one end and a relatively weak Au–π interaction on the other end. For monofunctionalized molecular wires, junctions can be mechanically stabilized by installing a second aurophilic group at the meta position that, however, does not in itself contribute to a new conduction pathway. These results reveal the important interplay between electronic coupling through metal–π interactions and quantum mechanical effects introduced by chemical substitution on the conjugated system. This study affords a strategy to deterministically tune the electrical and mechanical properties through molecular wires.

INTRODUCTION

This study describes the mechanism of conduction through asymmetric molecular junctions containing conjugated molecules having only one electrode-binding “linker” group.1 Linker groups are aurophilic functional groups that bind the molecule between Au electrodes, such as thiols (−SH), primary amines (−NH₂), and methythiolides (−SMe).2 Typical molecules employed in single-molecule electronics are conjugated or short aliphatic molecules that are functionalized at each end with linker groups. Here, conjugated olefins of varying lengths are end-functionalized with methythiolide and amine linkers at one or both terminal phenyl rings. To explore quantum mechanical effects3 we vary the position of these linkers between the meta or para positions. The conductance and rupture forces of single-molecule junctions formed from these molecules are measured using the break-junction (BJ) technique with a scanning tunneling microscope (STM)2a and an atomic force microscope (AFM).4 We find that for measurable conductivity to occur at least one of the rings must have a linker para to the olefin providing strong electronic coupling to the electrode. We measure both the highest conductivity and the narrowest distribution of conductance for olefins with two para linkers. When one of these para linkers is replaced with a meta linker, the conductance decreases by almost an order of magnitude, due to a reduction in the Au–molecule–Au coupling. If this mechanical contact, the meta linker, is removed leaving only a single para linker, the conductance decreases even further. We show that the conductance of our molecular wires that have at least one para linker decays exponentially with increasing oligomeric length and that they have step lengths corresponding to their molecular length. Both of these results indicate that we are probing the conductance of single-molecule junctions, as opposed to junctions formed by overlapping or interdigitated molecular dyads. That is, these measurements allow us to conclude that monofunctionalized stilbene molecules do not readily form junctions where molecules conduct via intermolecular carrier transfer (i.e., π–π-stacking interactions).5

EXPERIMENTAL METHODS

Syntheses. For this study, we synthesized three different vinylogous series of methythiol-functionalized trans-α,ω-diphenyl-oligoenes as well as 3-(methylthio)stilbene. Each series ranges in length from the stilbene (n = 1) to the triene (n = 3) and is displayed in Figure 1A and 1B. A convenient shorthand is used to name these compounds (PPn, PMn, Pn, and M1), which includes the linker substitution (P = para, M = meta) and the length of the oligomer (n). As examples, PP2 denotes para-para-dithiomethyl-diphenylbutadiene and PM3 denotes para-meta-dithiomethyl-diphenylhexatriene. Both difunctionalized (PPn and PMn) and monofunctionalized (Pn
and M1) molecules were synthesized through Wittig\(^6\) and Horner–Wadsworth–Emmons reactions (see the Supporting Information for synthetic details and characterization).\(^7\)

A set of three additional stilbene derivatives bearing amine linkers were synthesized to deconvolute the electronic and mechanical contributions in molecular junctions: (E)-3,4′-diaminostilbene (PM1A) and (E)-4-aminostilbene (P1A) as analogous compounds to the conducting (E)-(methylthio)stilbenes above, as well as (E)-3-dimethylamino-4′-aminostilbene (PM1TA), where A = amine and TA = tertiary amine.

**STM and AFM-BJ Measurements.** STM-BJ measurements\(^2a,b\) were performed in dilute solutions (1 ± 0.1 mM in 1,2,4-trichlorobenzene) of molecular wires using a gold-on-mica substrate and a gold STM tip (cut Au wire, 0.25 mm diameter, 99.998%, Alfa Aesar). Gold atomic point contacts were repeatedly formed and broken in the solution of molecules under a 500 mV voltage applied to the junction with a 100 kΩ resistor in series. As the point contacts are broken, one or a few molecules may bind to bridge the gap between the broken Au contact, thereby forming molecular junctions. The electrodes are then pulled farther apart until the junction is broken. Conductance (current/voltage) is measured as a function of piezo displacement yielding individual conductance traces. In doing so, our STM-BJ method does not take consecutive measurements on a single junction. Instead, at the end of each measurement the junction is destroyed. Then, before forming a new junction, the tip and substrate are smashed together and pulled apart, forming fresh electrodes and thus a new junction. For each molecule, over 5000 traces are collected and analyzed by creating one-dimensional (1D) conductance and two-dimensional (2D) conductance-displacement histograms\(^2d,8\) that reveal statistically relevant information on junction conductance, as well its evolution under junction elongation.

Molecular conductance step lengths\(^9\) and the slopes of the conductance features (\(\beta_\text{s}\)) in the 2D histograms were determined by fitting the average conductance profile; both procedures are outlined in detail in the Supporting Information.

Simultaneous conductance and force measurements were obtained using a custom-built conducting AFM setup.\(^14\) Single-molecule junctions were formed between a gold-coated commercial AFM cantilever (NanoAndMore, Inc.) and a gold-on-mica substrate. Conductance is measured across the tip/sample junction at a bias of 75 mV. The force is measured simultaneously by monitoring the deflection of a laser focused on the back of the cantilever. AFM-BJ measurements are carried out on PP1, PM1, and P1. In each case, 2D force-displacement histograms are constructed from measurements on over 8000 junctions.

**Theoretical Methods.** Density functional theory (DFT) electronic structure calculations examined shape and energy differences among the most relevant molecular orbitals (MOs) for molecular conductance. All calculations were performed using Jaguar\(^10\) with the B3LYP hybrid functional and the 6-31G** basis sets. The molecular geometries were fully optimized. The final geometries, total energies, and MO energies for each molecule in this study are given in the Supporting Information.

**RESULTS AND DISCUSSION**

We begin by comparing the conductance and rupture forces of molecular junctions of four stilbene derivatives having either one or two methysulphide linkers in either the meta or para positions (PP1, PM1, P1, and M1). Their 1D logarithmically binned conductance histograms are obtained from STM-BJ measurements and are compared in Figure 2A. The histogram for PP1 shows a clear molecular conductance peak, indicating that reproducible single-molecule junctions are formed throughout thousands of measurements. The sharpest peak at 10⁻³ \(G_0\) is characteristic of a conjugated stilbene having two para linkers, as has been shown before.\(^3d,11\) A characteristic conductance signature (peak in the histogram) appears for P1 even though it contains only one linker. The peak conductance for P1 is almost 2 orders of magnitude lower than that for PP1; therefore, electronic coupling across the P1 junction is weaker than with PP1. From the width of the peak, we conclude that the junction conductance varies significantly more than in the case of PP1, which has two linkers. We quantify the peak width for all junctions in Table 1 using the half-width at half-maximum. We next compare P1 with M1, which also has only one linker, but now at the meta-position, we see no peak in this histogram indicating that junctions with a conductance above our instrument noise (∼10⁻⁷ \(G_0\)) are not formed with M1. This trend is expected since meta linkers do not provide strong electronic coupling into the \(\pi\)-system.\(^3a\) Nonetheless, they do provide a mechanical link as we have previously shown.\(^3d\) Indeed, we see with PM1 that the additional mechanical stability provided by the meta linker yields both a higher conductance and a narrower distribution compared with P1. Conductance values for each compound are given in Table 1.

We confirm the mechanical enhancement provided by the meta linker by measuring force in AFM-BJs of PP1, PM1, and P1. The rupture forces are measured by pulling the junction apart until it breaks and (to a first-order approximation) establish an upper limit on the strength of the weakest Au–molecule interaction. Stilbenes with two methysulphide linkers (regardless of their position on the phenyl rings) are stabilized in the junction and give rupture forces of 0.5 nN, as is the case with PP1\(^5d\) and PM1 (Figure 2C). In contrast, we found that the rupture force for P1 is smaller than 0.3 nN (twice the instrumental noise). Our rupture force results for each stilbene

**Figure 1.** Chemical structures of trans-stilbene and all-trans-oligoene molecular wires: (A) difunctionalized series, having only para-positioned linker groups (PPn) or a mixture of para and meta linkers (PMn); (B) monofunctionalized wires Pn and M1 contain either one meta or one para linker. (C) Stilbene derivatives end-functionalized with primary and tertiary amines.
BJ Measurements

Table 1. Tabulation of Conductance Parameters from STM-

<table>
<thead>
<tr>
<th>Molecule</th>
<th>1D Conductance Peak (G_0)</th>
<th>Conductance Peak Width (Å^-1)</th>
<th>Slope [I]</th>
<th>Step Length (nm)</th>
<th>Molecule Length (nm)</th>
</tr>
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<tbody>
<tr>
<td>PP1</td>
<td>1.2×10^-3</td>
<td>0.42</td>
<td>0.18</td>
<td>0.57</td>
<td>1.31^-t</td>
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<td>PP2</td>
<td>6.2×10^-4</td>
<td>0.44</td>
<td>0.12</td>
<td>0.73</td>
<td>1.50^-t</td>
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<tr>
<td>PP3</td>
<td>3.8×10^-4</td>
<td>0.44</td>
<td>0.12</td>
<td>0.82</td>
<td>1.70^-t</td>
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<tr>
<td>PM1</td>
<td>2.9×10^-4</td>
<td>0.63</td>
<td>0.58</td>
<td>0.66</td>
<td>1.20^-t</td>
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<tr>
<td>PM2</td>
<td>1.0×10^-4</td>
<td>0.69</td>
<td>0.35</td>
<td>0.70</td>
<td>1.45^-t</td>
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<tr>
<td>PM3</td>
<td>7.2×10^-6</td>
<td>0.74</td>
<td>0.35</td>
<td>0.87</td>
<td>1.70^-t</td>
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<tr>
<td>P1</td>
<td>2.1×10^-6</td>
<td>0.90</td>
<td>0.67</td>
<td>0.61</td>
<td>1.13^-t</td>
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<td>P2</td>
<td>2.6×10^-6</td>
<td>0.94</td>
<td>0.54</td>
<td>0.75</td>
<td>1.37^-t</td>
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<td>P3</td>
<td>1.7×10^-6</td>
<td>1.02</td>
<td>0.46</td>
<td>0.66</td>
<td>1.61^-t</td>
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<td>M1</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>n/a</td>
<td>1.00^-t</td>
</tr>
<tr>
<td>PM1A</td>
<td>2.2×10^-5</td>
<td>0.63</td>
<td>0.67</td>
<td>0.63</td>
<td>1.14^-t</td>
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<tr>
<td>P1A</td>
<td>2.8×10^-5</td>
<td>0.98</td>
<td>0.70</td>
<td>0.67</td>
<td>1.09^-t</td>
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<tr>
<td>PM1A</td>
<td>2.8×10^-5</td>
<td>1.03</td>
<td>0.89</td>
<td>0.66</td>
<td>1.09^-t</td>
</tr>
</tbody>
</table>

^tMolecular length is taken from DFT optimized structures. ^tMolecules do not form conductive junctions. ^tLength refers to the through-space distance between terminal linker group heteroatoms. ^tLength refers to the through-space distance from the para-linker group heteroatom to the most distant carbon atom. ^tConductance peak widths are determined using the half-width at half-maximum on the high-conductance side of the peak, since low-conductance half-maxima are sometimes lost in the experimental noise.

result of a strengthened Au–π interaction, where the tunneling pathway is coupling directly into the π-space of the second ring while the meta linker secures that end to the electrode surface. Similar metal–π (Pt or Ag) interactions have been used to rationalize the conductance mechanism through symmetric metal–benzene–metal junctions at low temperature, as well as molecular junctions of C_60 and stacked oligomers of paracyclophane using Au electrodes at room temperature. To understand the conduction mechanism in greater detail, it is necessary to verify that conduction occurs through the molecular backbone of a single molecule. Therefore, we measured the length dependence of conductance through a series of oligomers PPn, PMn, and Pn, with n = 1, 2, and 3. The peak conductance of each oligomer is given in Table 1. In Figure 2B, we plot the conductance histogram peaks against the molecular length for each series. The para–para bound series, PPn, is especially useful as a control group representing typical linear α,ω-diphenyl-oligoenes. The decay constant (β), which describes the exponential decrease of conductance with increasing molecular length is found to be $β = 0.23 ± 0.02$ Å^-1, in good agreement with published results. For the PMn series, we also find an exponentially decreasing conductance with a decay constant of $β = 0.27 ± 0.08$ Å^-1, which is similar to that of PPn. This indicates that conduction is through the π-system of a single molecule and not by any other mechanism, such as π–π stacking between dimers. When measuring conductance of the Pn series, we found that conductance peak values shifted within half of an order of magnitude over the course of the experiment (thousands of consecutive traces). The experimentally observed variation in conductance is illustrated by the error bars in Figure 2B (see the Supporting Information for details of the variability analysis). The

Figure 2. (A) 1D conductance histograms constructed using logarithmic bins for junctions of PP1 (red), PM1 (blue), P1 (black), and M1 (dashed). M1 does not form conductive junctions. Histograms were generated from over 5000 traces without data selection, using 100 bins/decade. (B) Plot of molecular length vs conductance for para–para series (PPn; red) and para–meta series (PMn; blue). Exponential decay constants were found to be $β = 0.23 ± 0.03$ and $0.27 ± 0.08$ Å^-1, respectively. The effective contact resistance for PPn is 520 kΩ and for PMn is 1820 kΩ. Conductance for Pn (black) is represented with the mean peak conductance (black circles) within a distribution of the inner 50th percentile (black boxes) and the inner 80th percentile (bars). Due to junction-to-junction variations, larger samples sizes were used for Pn (over 30 000 individual conductance traces). (C) The 2D force histogram of PM1 junctions compiled from ~8000 traces. The statistically averaged force profile (overlaid blue trace) shows an abrupt drop at zero-displacement of 0.5 nN corresponding to the average force required to rupture the junction. (Inset) Average force profiles from measurements of PP1 and PM1 junctions, which yield a rupture force of 0.5 nN for both.

are overlaid in Figure 2C (inset). Consequently, the interaction between the Au electrode and unsubstituted phenyl ring does not contribute much to the mechanical stability of the junction at room temperature. Since linkers in the meta position behave as typical mechanical contacts (albeit without providing electrical coupling), we postulate that the conductance modulation found between the PMn and Pn series is the
variability increased with molecular length (P1 < P2 < P3), making it impossible to determine a valid decay constant.\textsuperscript{16} Outside of the monosubstituted Pn series, the variation during and between different experimental runs (changing tip and substrate) caused insignificant variations in the most frequently measured conductance. This is typically the result obtained with methylsulfide linkers.

To further understand junction evolution, we show how the conductance changes during elongation. By constructing 2D conductance-displacement histograms, we can determine the maximal junction length, or step length, as well as trends in the molecule-electrode coupling. Figure 3A displays the 2D histograms\textsuperscript{17} of the stilbenes junctions, PPI, PM1, and P1 (all others are given in the Supporting Information). Their molecular conductance features extend about 0.6 nm. We note that they are ~0.7 nm shorter than the molecular lengths, which is common in STM-BJs due to snapback relaxations at the Au electrodes.\textsuperscript{18} We quantify the step length for each molecule as detailed in the Supporting Information and summarize them in Table 1. For each oligomeric series, the step length increases linearly with molecular backbone length (Figure 3D).\textsuperscript{26} The fact that all three molecular systems scale linearly with molecular wire length, and with similar slopes, indicates that in each case the molecular junctions are formed with only a single molecule. The step lengths of Pn are slightly longer (0.02–0.04 nm) than those of PPn. We attribute the difference to changes in the linker group\textsuperscript{27} (para-SMe vs Au–π) and not the formation of π–π-stacked dimers since significantly larger step lengths would then be expected.

The 2D histograms also show that the slope of the conductance-versus-displacement curves changes significantly between each series in the order, PPn > PMn > Pn. The white lines overlaid in Figure 3A–C represent the statistically averaged decreasing conductance, whose slopes are tabulated in Table 1 for all our molecules. Steeper slopes correspond to junctions whose conductance decreases with elongation due to weaker metal–molecule coupling. For PMn and Pn series, where conduction occurs through π–metal overlap, the conductance should depend sensitively on junction geometry, and specifically, conductance should decrease as the area of overlap between the electrode and the molecular backbone is decreased with increasing elongation.

Since the conductance of the PPn series is systematically higher than the corresponding PMn series, and since meta-substitution appears to be nonconductive, our data suggest that conduction in PMn junctions occurs through the combination of a Au–S interaction in the para-substituted ring and a direct Au–π interaction in the meta-substituted ring. To verify this hypothesis, and to distinguish the role of the linker at the meta position from its electronic influence into the π-system, we employed a series of amine-terminated stilbenes where, in contrast to the methylsulfide stilbenes, we are able to retain electronic effects while disrupting the mechanical coupling at the meta-linker (PM1A and PM1TA from Figure 1C). Molecules terminated with primary amines (RNH\textsubscript{2}) bind to the Au electrodes, forming molecular junctions in the STM-BJ setup. However, when primary amines are methylated to form tertiary amines (RNMe\textsubscript{2}), they do not bind to Au.\textsuperscript{28} In this way, the linker group’s electron-donating contributions to the MOs are preserved while arresting additional mechanical stabilization.

Conductance histograms of PM1A, P1A, and PM1TA junctions are compared in Figure 4. The conductance peak for the para–meta bound junction (PM1A) is almost an order of magnitude higher than that of the para–π bound junction (P1A), similar to what was observed for the methylsulfide analogues (PM1 vs P1). However, when the meta-NH\textsubscript{2} of PM1A is replaced by meta-NMe\textsubscript{2}, the conductance of the resulting PM1TA drops by an order of magnitude, overlapping the conductance of monofunctionalized P1A. With these direct structural comparisons, we conclude that the electrical pathway in the para–meta bound series is through a Au–π interaction and that the meta linker serves as a mechanical stabilizer that enhances the electronic coupling between the terminal phenyl group and the Au electrode.

**Theoretical Analysis.** To gain insight into the electronic structure of our molecular junctions, DFT calculations were carried out to examine the shape of MOs. The methylsulfide-functionalized stilbenes (PPI, PM1, and P1) are considered. The most relevant MOs are those nearest to the Fermi level of the electrodes. Since these junctions are generally highest-

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**Figure 3.** 2D conductance-displacement histograms are generated from over 5000 individual measurements on (A) PPI, (B) PM1, and (C) P1 single-molecule junctions. Colored contour represents the number of counts × 1000. Step lengths are marked by black arrows, representing the 90th percentile of conductance, at 0.57, 0.56, and 0.61 nm, respectively. (D) Plot of the step lengths vs molecular wire lengths of PPn (red), PMn (blue), and Pn (black) series, with slopes of 0.52, 0.62, and 0.52, respectively. Molecular wire lengths were determined by DFT calculations.
systems and SLP are strongly coupled to one another. Due to conductance pathway.

PM1 inspection we both sulfur lone pairs (SLP). In contrast, the two SLP’s in the strongly coupled across the molecular backbone and include which are shown in Figure 5A. We see that the orbitals are experimentally distinguishable in PP1 however, since it is expected to be more resistive, it may not be para pathway. This secondary path is also predicted to exist in para; Figure 5B) are decoupled. In fact, the energy cost to mix these orbitals and establish a conduction pathway (through each SLP) is roughly equal to the energetic cost (∼0.85 eV) required to disrupt that in the previous case (PP1). In light of this, it would be reasonable to expect PM1 to not conduct at all. However, upon deeper inspection we find density located on the phenyl ring opposite the para linker and purpose this as an alternative conduction pathway. This secondary path is also predicted to exist in PP1; however, since it is expected to be more resistive, it may not be experimentally distinguishable in PP1. In the special case of PM1, the secondary path may be the only available conductance pathway.

For the para–π bound molecule (P1; Figure 5) the ring systems and SLP’s are strongly coupled to one another. Due to the lack of a second linker, a single conductance pathway exists in P1, which closely resembles that of the secondary path found in PM1, leading to conducting junctions, despite lacking in the mechanical stability provided by a second linker. This MO interpretation helps to identify relationships linking the intrinsic properties of the bridging molecule with the conductance mechanism and overall device performance. Further studies that include the mapping of the density of states and couplings of the Au electrodes are beyond the scope of this study. Our theoretical results agree with our experimental findings and give weight to a dominant secondary pathway in PM1 that is similar to that found in P1.

■ CONCLUSION

The mechanism of conductance through monofunctionalized single-molecule wires was determined by measuring the electrical and mechanical properties in single-molecule junctions. By using a combination of rational molecular design, STM- and AFM-BJ techniques, we showed that mono- and difunctionalized molecular wires conduct through the backbone of a single molecule rather than though π–π−stacked dimers. The conductance mechanism differs between the para–para bound (PnP) and para–π bound molecules (Pn, P1A, and P1TA). Since the Pn series is functionalized with only one linker, a mechanically weak, yet electronically coupled, Au–π interaction completes the molecular circuit. The limited strength of this new interaction causes significant variability in junction-to-junction conductance. However, installing a second linker at the meta position stabilizes this interaction by securing the terminal phenyl group to the electrode surface, such as for the para–meta compounds (PMn and PM1A). Meta linkers result in quantum electronic interference effects that suppress the conductance, but the position of the linkers (meta vs para) does not significantly alter their mechanical attachment to the Au electrodes. By exploiting this attribute we strengthen a direct molecule–metal interaction that dominates in the charge transport of monofunctionalized molecular junctions, in turn enabling us to quantify the charge transport properties arising from Au–π interactions. This strategy may prove useful in future molecular-scale device architectures for the positioning of molecules onto electrode surfaces while mediating their electronic couplings, such as is needed for advancement in single-molecule rectification.20

Figure 4. Log-binned conductance histograms of amine-functionalized stilbene molecular wires: para–meta PM1A (blue), para–π P1A (green), and methylated para–meta PM1TA (black) were generated from 5000 individual conductance traces.

Figure 5. DFT calculated isosurfaces of MOs relevant in single-molecule conductance. Geometries of PP1, PM1, and P1 were optimized and MOs calculated at the B3LYP/6-31** level of theory in the gas phase. HOMO energies were normalized to 0 eV for easy comparison. Contour values set at 0.75.
ASSOCIATED CONTENT
1 Supporting Information
Synthetic details and characterization data for all compounds; details of experimental setup and analysis methods; theoretical methods and tabulated results. This material is available free of charge via the Internet at http://pubs.acs.org.

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(5) dππ-stacking in STM-BJs has been previously reported; however, many experimental factors were different from our study, including the structure of their bridging molecules, longer molecular lengths, and different solvent system during their STM-BJ measurements. See: Wu, S. M.; Gonzalez, M. T.; Huber, B.; Grunder, S.; Mayorga, M.; Schonenberger, C.; Calame, M. Nat. Nanotechnol. 2008, 3, 569.
(14) PPn, PMn, and Pn represent the first oligoene series having no main-chain functionalizations to be studied in STM-BJs or other single-molecule methods. Other oligoene systems studied are based on carotenoid or α,ω-diphenyl-µ,µ-dicyano structures, which are decorated with methyl or cyano groups along the conjugated backbone (see ref 15).
(16) Large variability in the junction conductance of the Pn series results in a range in the estimation of the decay constant (0 > β > 0.46 Å⁻¹).
(17) 2D histograms are generated using an automated algorithm with the added requirement that a G0 break is clearly identifiable in the trace (more than 80% of the traces that start with a conductance greater than 1 G0 and successfully break satisfy this requirement). In 2D histograms the conductance is binned logarithmically with 200 bins per decade in conductance (y-axis), while displacement is binned linearly (x-axis).
(18) Immediately after the formation of gold point contact electrodes, surface adatoms quickly reorganize, thus widening the distance between the electrodes. We refer to this as the “snapback” distance. This was first discovered during measurements at 4 K: (a) Yanson, A. I.; Bollinger, G. R.; van den Brom, H. E.; Agraist, N.; van Ruitenbeek, J. J. Phys. Chem. A 1998, 102, 783. For room temperature: (b) Quek, S. Y.; Kamenetska, M.; Steigerwald, M. L.; Choi, H. J.; Louie, S. G.; Hybertsen, M. S.; Neaton, J. B.; Venkataraman, L. Nat. Nanotechnol. 2009, 4, 230.