

Electron Transfer through Surface-Grown, Ferrocene-Capped Oligophenylene Molecular Wires (5–50 Å) on *n*-Si(111) Photoelectrodes

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S Supporting Information

ABSTRACT: We report the surface growth of oligophenylene molecular wires on Si(111) substrates and their electron-transfer (ET) properties. Iterative wire growth of biphenylene was achieved via Pd-catalyzed Negishi reactions for lengths of $n_{\text{phenyl}} = 1, 2, 4, 6, 8,$ and 12 ($d \approx 5\text{--}50$ Å). The triflate-capped wires were functionalized with vinylferrocene for potentiometric studies. For the oligophenylenes of $n_{\text{phenyl}} = 1, 2,$ and 4 (wire length $d \approx 5\text{--}20$ Å), there was a strong distance dependence ($k_{\text{app}} = 22.6, 16.0, 8.40$ s⁻¹, respectively), correlated to $\beta = 0.07$ Å⁻¹. In contrast, longer oligophenylenes for $n_{\text{phenyl}} = 4\text{--}12$ ($d \approx 20\text{--}50$ Å) displayed a negligible distance dependence with an ET rate of $k_{\text{app}} \approx 10.0 \pm 1.6$ s⁻¹. These data suggest a distance-dependent tunneling mechanism at short lengths ($d < 20$ Å) and a distance-independent ET at longer lengths ($d > 20$ Å).



INTRODUCTION

A comprehensive understanding of electron-transport processes is vital for future development in many fields of technology and science, ranging from the design of molecular electronics to the understanding of biological enzymes. For example, molecular and nanosized constructs of “wires” have been used to study electron-transport efficiency and kinetics over long distances.^{1,2} Indeed, molecular wires provide a unique opportunity to study electron transport in one dimension (along the axis of the wire) and in two dimensions (2D arrays of wires on substrate surfaces) and may comprise an integral component in promising materials for applications such as optoelectronics, energy-storage devices, logic circuits, and sensors.^{3–8} Many studies have investigated the electron-transport ability of molecular wires such as alkyl chains,^{9,10} π -conjugated molecules,^{11,12} DNA,^{13–15} and polypeptides.^{16–18} Among these options, electron-transport phenomena through long, π -conjugated molecules has been the focus of the most extensive research in an effort to utilize these molecules as components in the construction of nanoscale circuits.^{19,20}

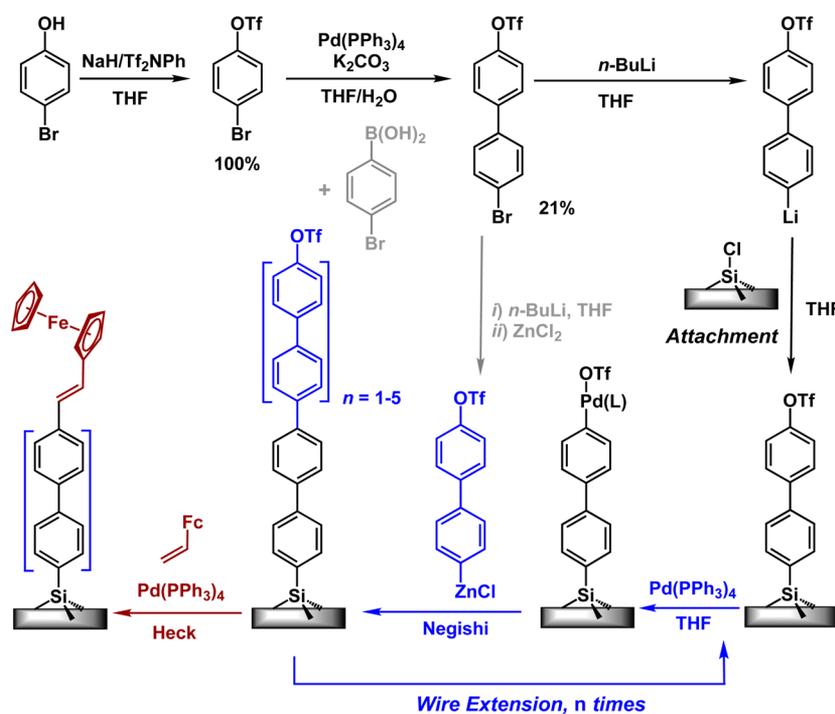
Providing an efficient and reliable molecular/electrode junction is one critical factor for the integration of molecules into circuits in the future.²¹ To date, gold has widely been used as the electrode of choice due to its noble metal character, stability, and ease of surface modification (thiol SAM assembly). Using conjugated Schiff base linkers of varying length on a gold electrode, Frisbie et al. described a transition from a short-range tunneling charge-transport mechanism to a long-range “hopping” mechanism by determining the variation in electrical resistance as a function of the length of the conjugated molecular wire (from 1 to 7 nm). The measurement

involved a specialized AFM conductivity instrument, which provided the resistance values from the top of the wire to the bottom of the Au electrode.²² Because of the cost and limited accessibility of such instrumentation to many researchers, it would be desirable to implement a more approachable, potentiostatic means to determine similar electron-transport parameters.

Because of its nearly ubiquitous use in the semiconductor fabrication and solar energy sectors, it is likely that silicon will provide the real-world entry technology of such molecular/electrode contacts. Many recent reports of its utility in solar fuel devices ($2\text{H}_2\text{O} + h\nu \rightarrow 2\text{H}_2 + \text{O}_2$) provide yet another avenue for the development of light-responsive silicon devices that might incorporate electron-transfer designs. As a main component for the development of computing platforms, photovoltaics, and nanoscale devices, it is necessary for silicon substrates to undergo surface modifications with organic molecules to optimize performance and longevity. Additionally, the stabilization of the Si-semiconductor/liquid junction has a particular requirement to resist surface corrosion in air and in an aqueous redox electrolyte without any increase in the surface carrier recombination velocity (SRV). And although the surface modification and characterization by various methods have been investigated extensively and systematically, the lack of examples of surfaces modified with highly conductive organic molecules presents one important hurdle that prevents efficient, interfacial electron transport. The thickness of the molecular

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Scheme 1. Schematic for the in Situ Preparation of Si(111) Electrodes Functionalized with Discrete Lengths of π -Conjugated Molecular Wires^a

^aEach wire was capped with a vinylferrocene unit for the determination of electron-transfer parameters.

layers—or the length of the molecular wires—on the surface will have a significant impact on the electron-transport mechanism.

In principle, the π -conjugation between a redox tag and the surface can be maintained when the grafting is conducted directly from an π -electron molecular precursor and an oxide-free hydrogen-terminated silicon surfaces due to the contiguous chain of sp^2 -hybridized carbon centers.^{23,24} This letter reports the effects of molecular wire length on the heterogeneous electron-transport mechanism through π -conjugated organic molecules covalently anchored onto passivated Si(111) electrodes (Scheme 1).

EXPERIMENTAL SECTION

Wafer Preparation. *n*-type Si(111)-oriented wafers (Cz grown, single-side polished, 350 μm thickness, 1–10 $\Omega\text{-cm}$) were purchased from Virginia Semiconductor. Etching procedures were performed using buffered HF(aq) and 11 M NH_4F (aq) (semiconductor grade, Transene). All solvents were purchased as HPLC grade and purified over alumina with a Pure Process Technology solvent-purification system. Nanopure deionized water having a resistivity of 18 $\text{M}\Omega\text{-cm}$ or higher (Barnstead Nanopure Systems) was used in all procedures involving wafer surfaces. Detailed synthesis procedures are given in Supporting Information. Si(111) wafers were HF etched and chlorinated to prepare Si(111)–Cl as documented previously²⁶ and in the Supporting Information.

Linker Attachment. A batch of 32 mg (0.084 mmol) of 2Ltf in dry THF was cooled to -80°C in a dry ice/acetone bath, and 50 μL of 1.6 M *n*-BuLi (0.08 mmol) was added; the substrate was allowed to lithiate for 30 min. The chlorinated wafers in a glovebox were rinsed with chlorobenzene and then THF; next they were transferred out of the flush box and into the solution with the lithiated wires, and the attachment reaction was slowly warmed to room temperature over 2.5 h. To passivate the remaining chlorine-terminated sites with methyl groups, the wafers were transferred back into a flushbox and rinsed with THF. The wafers were submerged in a 1:1 mixture of (THF)/

(1.0 M CH_3MgCl) in a sealed pressure vessel at 60°C for 3 h. The wafers were then exposed to air and sonicated in THF, methanol, and water for 10 min each and then dried with a stream of N_2 gas.

Surface Wire Growth. The wires were grown on the surface using Negishi coupling: 1 equiv of the 2Ltf wire was dissolved in dry THF and cooled to -80°C in an acetone/dry ice bath, to which 1 equiv of 1.6 M *n*-BuLi and subsequently 1.5 equiv of ZnCl_2 were added; this was stirred for 30 min. The reaction was then allowed to warm to room temperature, and the solution was allowed to react for 1 h. At the same time, the silicon surface with *n* phenylenes attached (i.e., 2Lfc, 4Lfc, etc.) was immersed in a solution of $[\text{Pd}(\text{PPh}_3)_4]$ in THF in a glovebox to activate the triflate group. This reaction was protected from light and was allowed to react for 3 h. The surface was then transferred into the solution with the 2Ltf wire and was reacted overnight at room temperature. The wafers were then exposed to air and sonicated in THF, methanol, and water for 10 min each and then dried with a stream of N_2 gas.

Ferrocene Attachment. To convert the triflate-functionalized wires to ferrocene-functionalized wires, a Heck coupling reaction was performed in a drybox. First the wafers were submerged in a solution of 5 mg/mL $[\text{Pd}(\text{PPh}_3)_4]$ in toluene for 3 h that was kept in the dark. The wafers were rinsed with toluene and then DMF. They were then submerged in a solution of 10 mM vinylferrocene in DMF in a sealed pressure vessel, heated to 100°C , and allowed to react overnight to obtain ferrocene-functionalized wires (2Lfc). Finally, the wafers were exposed to air and sonicated in water, methanol, and acetone for 10 min each.

Surface Characterization. X-ray photoelectron spectroscopy data was acquired using a Kratos Axis Ultra XPS fitted with an Al $K\alpha$ X-ray source. The pressure in the acquisition chamber was on the order of 10^{-9} Torr, and photoelectrons were collected perpendicular to the surface. Region scans were taken in one spot for carbon, silicon, and iron on each surface. Electrochemical measurements were carried out using a functionalized Si(111) substrate as the working electrode (electrode area 0.44 cm^2 , defined by the O-ring between the working electrode and electrolyte), a Pt wire counter electrode, and a Ag wire reference electrode; degassed (N_2) 1 M $\text{LiClO}_4/\text{CH}_3\text{CN}$ electrolyte solution was used in a one-compartment cell. Substrates were

illuminated with an Oriel 150 W light source fitted with an AM 1.5 filter with an intensity at the sample of 100 mW/cm² (1 sun). Dark measurements were performed as a control for each substrate (<1 μA dark current). Cyclic voltammetry data was obtained using a Pine Wavenow potentiostat controlled by AfterMath software v1.2.5033.

RESULTS AND DISCUSSION

To minimize the synthetic effort (compared to generating each discrete-length wire in solution prior to attachment), a “solid-phase” wire growth method on Si(111) was designed. The biphenyl linker 4'-bromo-(1,1'-biphenyl)-4-yl-triflate was synthesized in two steps from *p*-bromophenol and PhNTf₂, followed by Suzuki coupling to *p*-bromophenyl boronic acid. This useful synthon provided the entry to two procedures: (i) the direct attachment of the corresponding “2-phenyl” lithiate to the silicon surface (Scheme 1, top) and (ii) conversion of the bromo 2-phenyl linker to its corresponding Negishi reagent for coupling to the Pd-activated surface triflate moiety (with ZnCl₂; Scheme 1, bottom). As such, the surface wires could be extended by 2-phenyl increments indefinitely by the attach → activate → couple strategy illustrated in Scheme 1. By this method, π-conjugated organic molecular wires with systematically varying numbers of phenyl units (*n* = 1, 2, 4, 6, 8, 12) were prepared. Note that after the attachment of the first 2-phenyl linker, the surface was passivated with CH₃MgBr to back-fill any unpassivated Si–Cl sites.^{25,26}

Finally, to avoid the need for specialized AFM or conductivity measurements, a ferrocene redox marker was coupled to the terminal triflate moiety via a Pd-catalyzed Heck coupling reaction with vinylferrocene. This resulting wire/ferrocene moiety retains π-conjugation from the bulk Si to the iron center, thus permitting direct electrochemical measurements of electron transfer from Fc to the *n*-Si(111) electrode surface. Photoelectrochemical cyclic voltammetry (PEC–CV) measurements on the Silwire devices were performed using the functionalized *n*-Si(111) substrate as the working electrode (electrode area 0.44 cm², defined by the O-ring interface between the working electrode and electrolyte), a Pt wire counter electrode, and a Ag wire reference electrode. Substrates were illuminated with an Oriel 150 W light source fitted with an AM 1.5 filter, with an intensity at the sample of 100 mW/cm² (1 sun). Dark measurements were performed as a control for each substrate (<1 μA dark current) as reported previously.^{26,27}

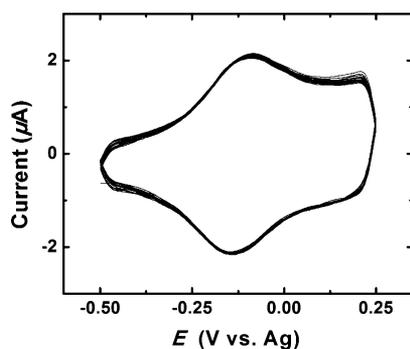


Figure 1. Stability Test: Successive cyclic voltammograms obtained for the 2-Ph-Fc-modified surfaces after Heck coupling with vinyl ferrocene. Experiment conditions: 30 consecutive scans were performed at 250 mV s⁻¹ in 1 M LiClO₄ in CH₃CN solution at room temperature (ca. 20 °C).

The stability of the Silwire device was tested by successive PEC–CV sweeps under 1 sun illumination (AM1.5, 100 mW cm⁻²). After the attachment of the first 2-phenyl linker (2-Ph-Fc), passivation by methylation, and then wire extension according to Scheme 1, the oligo *p*-phenylene-Fc substrates were subjected to 30 redox cycles at 250 mV/s. An anodic response was observed near 0 V vs Ag, followed by a cathodic response centered near -0.13 V vs Ag. The Δ*E*_p value remains constant despite the applied anodic (and cathodic) potentials, which indicates that the surface of the Si working electrode remains unchanged during the measurement period. The change in the observed peak currents and *E*_p values is negligible during the 30 CV cycles, indicating the stability of the Si(111) surface.

To determine the diffusivity (or lack thereof) of the ferrocene redox marker, the scan-rate dependence was determined for each sample. The resulting data for the 2-Ph-Fc construct (scan rates (*v*) ranging from 100 to 2000 mV s⁻¹) construct is shown in Figure 2 (left). The observed quasi-reversible process is attributed to the Fe(II/III) redox cycle of the Heck-coupled ferrocene moiety as reported previously,^{26,27} as well as other examples of attached ferrocene.^{28–31} Quantitative analysis of the total number of redox-active ferrocene units was performed by analyzing the baseline-corrected peak heights at the varying scan rates. The relationship between the anodic peak current (*i*_p) of Heck-coupling surfaces as a function of scan rate (*v*) is shown in Figure 2 (right). The linear relationship shown in Figure 2 (right) is consistent with the ferrocene unit being nondiffusive and covalently attached. The electrochemical coverage (Γ) of the 2-Ph-Fc covalently functionalized ferrocene surface was 1.1 × 10⁻¹¹ mol cm⁻², which can be converted to indicate that ~1% of atop sites on Si(111) were covalently modified by the 2-Ph-Fc unit on the surface. Importantly, the other surfaces modified with multiple *p*-phenylene units (*n*_{ph} = 1, 2, 4, 6, 8, 12) exhibited similar electrochemical surface coverages (Table 1), thus indicating a ~1:1 conversion during the extension of the wires by iterative Negishi coupling methodology on the surface.

Apparent rate constants, *k*_{app}, were calculated for all modified surfaces according to the standard Laviron method expressed as eq 1.^{32,33}

$$k_{\text{app}} = \frac{(1 - \alpha)nFv_a}{RT} \quad (1)$$

The transfer coefficient α (a measure of the energy barrier symmetry) was approximated as 0.5.³⁴ The peak potentials *E*_{p,a} and *E*_{p,c} were plotted versus log(*v*) (Figure 3), and *E*_{p,a} and *E*_{p,c} were plotted separately to determine the convergent intercept of the anodic and cathodic linear regions. The potential of the convergence point (*v*_a in eq 1) was then used in the standard Butler–Volmer theory analysis.

Following Butler–Volmer analysis, the charge-transfer rate constants (*k*_{app}) for the substrates modified with discrete-length multi-*p*-phenylene wires (*n* = number of phenyls) are displayed in Figure 4 and tabulated in Table 1. The results indicate a clear change in the charge-transfer mechanism beyond four phenylene units (~20 Å). For short wires between the electrode and the ferrocene (*n* ≤ 4 phenyl rings), the higher charge-transfer rate constant (*k*_{app} = 25 → 10 s⁻¹) decreases linearly with increasing *n*, which is consistent with a tunneling mechanism. However, for surfaces with longer wires (*n* ≥ 4 up to *n* = 12), the charge-transfer rate exhibits a negligible distance depend-

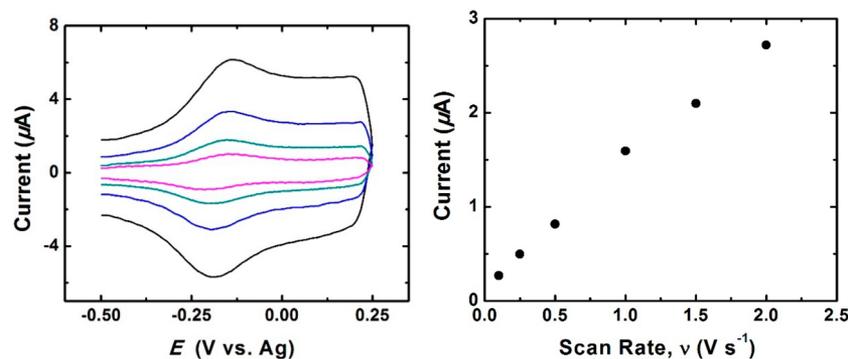


Figure 2. (Left) Cyclic voltammograms obtained for the 2-Ph-Fc molecular wire covalently anchored onto the passivated Si(111) electrode at scan rates of 0.1, 0.5, 1.0, and 2 V s^{-1} . (Right) Corresponding relationship between i_p and ν . Experiment conditions: 1 M LiClO_4 in CH_3CN solution at room temperature (ca. 20 $^\circ\text{C}$).

Table 1. Electron-Transfer Parameters for Surface-Grown Oligophenylene Molecular Wires on n -Si(111)

number of phenylenes n	approximate wire length (\AA)	electrochemical coverage Γ (mol cm^{-2})	electrochemical coverage Γ (%)	electron transfer rate k_{app} (s^{-1})	decay constant β (\AA^{-1})
1	4	1.71×10^{-11}	1.32	22.6	0.07
2	9	1.13×10^{-11}	0.87	16.0	0.07
4	17	6.01×10^{-11}	4.63	8.40	0.07
6	26	2.60×10^{-11}	2.00	10.1	
8	34	4.87×10^{-12}	0.375	8.33	
12	52	1.45×10^{-11}	1.12	11.6	

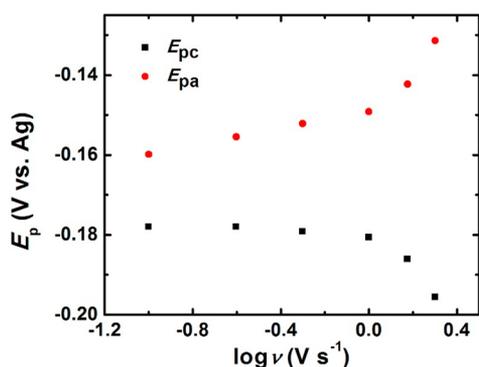


Figure 3. Relationship between E_p values and $\log \nu$ for 2-Ph-Fc. Experiment conditions: 1 M LiClO_4 in CH_3CN solution at room temperature (ca. 20 $^\circ\text{C}$).

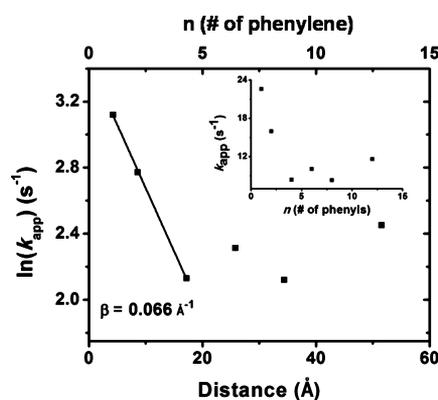


Figure 4. Relationship between k_{app} and n (number of phenylene units) obtained for the π -conjugated organic molecular wires covalently anchored to passivated Si(111) electrodes.

ence, suggesting a long-range or hopping mechanism of charge transfer.

CONCLUSIONS

We have developed a method for the growth of discrete-length oligo-*p*-phenylene ($n_{\text{phenyl}} = 1, 2, 4, 6, 8$ and 12) molecular wires ($d \approx 5\text{--}50$ \AA) on a Si(111) substrate. The wires were systematically extended in situ by an iterative, Pd-catalyzed Negishi coupling methodology. Because of the presence of the capping triflate moiety, vinylferrocene was coupled to the tip of the wire to facilitate the electrochemical interrogation of electron-transfer parameters. This method obviates the need for advanced instrumentation, such as conductive tip AFM or point-by-point resistivity measurements. Photoelectrochemical cyclic voltammetry (PEC-CV) revealed electrochemical coverages of $\Gamma_{\text{avg}} \approx 1.7\%$, indicating an $\sim 1:1$ conversion during the wire-extension procedure. For short wires between the semiconductor substrate and ferrocene ($n_{\text{phenyl}} = 1\text{--}4$; $d < 20$ \AA), a strong distance dependence was observed ($\beta = 0.07$ \AA^{-1}), consistent with a tunneling mechanism. In contrast, longer wires ($n_{\text{phenyl}} = 4\text{--}12$; $d = 20\text{--}50$ \AA) resulted in a distance-independent charge transfer. These results demonstrate that both long and short molecular wires would be suitable for the attachment of catalysts in a solar fuel device, wherein the solar flux (25 mA cm^{-2}) requires $k_{\text{ET}} \approx 10$ s^{-1} at a nominal value of a 10% single-site catalyst coverage.

ASSOCIATED CONTENT

Supporting Information

Materials, synthesis procedures, surface preparation, and details regarding physical and electrochemical measurements. The ^1H , ^{13}C , and ^{19}F NMR of the linkers and mass spectral data. CV traces, stability test, and Laviron analysis may also be found in the SI. The Supporting Information is available free of charge

on the ACS Publications website at DOI: 10.1021/acs.langmuir.5b02121.

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Carroll, R. L.; Gorman, C. B. The genesis of molecular electronics (Special Issue). *Angew. Chem., Int. Ed.* **2002**, *41*, 4378.
- (2) Sikes, H. D. Rapid electron tunneling through oligophenylene-vinylene bridges. *Science* **2001**, *291*, 1519.
- (3) Malliaras, G.; Friend, R. An organic electronics primer. *Phys. Today* **2005**, *58*, 53–58.
- (4) Tuccitto, N.; Ferri, V.; Cavazzini, M.; Quici, S.; Zhavnerko, G.; Licciardello, A.; Rampi, M. A. Highly conductive ~40-nm-long molecular wires assembled by stepwise incorporation of metal centres. *Nat. Mater.* **2009**, *8*, 41–46.
- (5) Ho Choi, S.; Kim, B.; Frisbie, C. D. Electrical resistance of long conjugated molecular wires. *Science* **2008**, *320*, 1482–1486.
- (6) Luo, L.; Frisbie, C. D. Length-dependent conductance of conjugated molecular wires synthesized by stepwise “click” chemistry. *J. Am. Chem. Soc.* **2010**, *132*, 8854–8855.
- (7) Søndergaard, R.; Strobel, S.; Bundgaard, E.; Norrman, K.; Hansen, A. G.; Albert, E.; Csaba, G.; Lugli, P.; Tornow, M.; Krebs, F. C. Conjugated 12 nm long oligomers as molecular wires in nanoelectronics. *J. Mater. Chem.* **2009**, *19*, 3899–3908.
- (8) Hu, W.; Jiang, J.; Nakashima, H.; Luo, Y.; Kashimura, Y.; Chen, K.-Q.; Shuai, Z.; Furukawa, K.; Lu, W.; Liu, Y.; Zhu, D.; Torimitsu, K. Electron transport in self-assembled polymer molecular junctions. *Phys. Rev. Lett.* **2006**, *96*, 027801.
- (9) Carter, M. T.; Rowe, G. K.; Richardson, J. N.; Tender, L. M.; Terrill, R. H.; Murray, R. W. Distance dependence of the low-temperature electron transfer kinetics of (ferrocenylcarboxy)-terminated alkanethiol monolayers. *J. Am. Chem. Soc.* **1995**, *117*, 2896–2899.
- (10) Weber, K.; Hockett, L.; Creager, S. Long-range electronic coupling between ferrocene and gold in alkanethiolate-based monolayers on electrodes. *J. Phys. Chem. B* **1997**, *101*, 8286–8291.
- (11) Ramachandran, G. K.; Hopson, T. J.; Rawlett, A. M.; Nagahara, L. A.; Primak, A.; Lindsay, S. M. A bond-fluctuation mechanism for stochastic switching in wired molecules. *Science* **2003**, *300*, 1413–1416.
- (12) Sachs, S. B.; Dudek, S. P.; Hsung, R. P.; Sita, L. R.; Smalley, J. F.; Newton, M. D.; Feldberg, S. W.; Chidsey, C. E. D. Rates of interfacial electron transfer through π -conjugated spacers. *J. Am. Chem. Soc.* **1997**, *119*, 10563–10564.
- (13) Hall, D. B.; Holmlin, R. E.; Barton, J. K. Oxidative DNA damage through long-range electron transfer. *Nature* **1996**, *382*, 731–735.
- (14) Porath, D.; Bezryadin, A.; Vries, S. D.; Dekker, C. Direct measurement of electrical transport through DNA molecules. *Nature* **2000**, *403*, 635–638.
- (15) Fink, H.-W.; Schöneberger, C. Electrical conduction through DNA molecules. *Nature* **1999**, *398*, 407–410.
- (16) Kraatz, H.-B. Interactions of ferrocenyl-peptides in solution and on surfaces. *Macromol. Symp.* **2003**, *196*, 39–44.
- (17) Galka, M. M.; Kraatz, H.-B. Electron transfer studies on self-assembled monolayers of helical ferrocenyl-oligoproline-cystamine bound to gold. *ChemPhysChem* **2002**, *3*, 356–359.
- (18) Dey, S. K.; Long, Y. T.; Chowdhury, S.; Sutherland, T. C.; Mandal, H. S.; Kraatz, H. B. Study of electron transfer in ferrocene-labeled collagen-like peptides. *Langmuir* **2007**, *23*, 6475–6477.
- (19) Nitzan, A.; Ratner, M. A. Electron transport in molecular wire junctions. *Science* **2003**, *300*, 1384–1389.
- (20) Davis, W. B.; Svec, W. A.; Ratner, M. A.; Wasielewski, M. R. Molecular wire behaviour in *p*-phenylenevinylene oligomers. *Nature* **1998**, *396*, 60–63.
- (21) Lörtscher, E. Wiring molecules into circuits. *Nat. Nanotechnol.* **2013**, *8*, 381–384.
- (22) Ho Choi, S.; Kim, B. S.; Frisbie, C. D. Electrical resistance of long conjugated molecular wires. *Science* **2008**, *320*, 1482.
- (23) Buriak, J. M. Organometallic chemistry on silicon and germanium surfaces. *Chem. Rev.* **2002**, *102*, 1271–1308.
- (24) Scheres, L.; Giesbers, M.; Zuillhof, H. Organic monolayers onto oxide-free silicon with improved surface coverage: Alkynes versus alkenes. *Langmuir* **2010**, *26*, 4790–4795.
- (25) O’Leary, L. E.; Johansson, E.; Brunschwig, B. S.; Lewis, N. S. Synthesis and characterization of mixed methyl/allyl monolayers on Si(111). *J. Phys. Chem. B* **2010**, *114*, 14298–14302.
- (26) Li, F.; Basile, V. M.; Pekarek, R. T.; Rose, M. J. Steric spacing of molecular linkers on passivated Si(111) photoelectrodes. *ACS Appl. Mater. Interfaces* **2014**, *6*, 20557–20568.
- (27) O’Leary, L. E.; Rose, M. J.; Ding, T. X.; Johansson, E.; Brunschwig, B. S.; Lewis, N. S. Heck coupling of olefins to mixed methyl/thienyl monolayers on Si(111) surfaces. *J. Am. Chem. Soc.* **2013**, *135*, 10081–10090.
- (28) Fabre, B. Ferrocene-terminated monolayers covalently bound to hydrogen-terminated silicon surfaces: Toward the development of charge storage and communication devices. *Acc. Chem. Res.* **2010**, *43*, 1509–1518.
- (29) Zigah, D.; Herrier, C.; Scheres, L.; Giesbers, M.; Fabre, B.; Hapiot, P.; Zuillhof, H. Tuning the electronic communication between redox centers bound to insulating surfaces. *Angew. Chem., Int. Ed.* **2010**, *49*, 3157–3160.
- (30) Fabre, B.; Hauquier, F. Single-component and mixed ferrocene-terminated alkyl monolayers covalently bound to Si(111) surfaces. *J. Phys. Chem. B* **2006**, *110*, 6848–6855.
- (31) Bellec, N.; Fauchoux, A.; Hauquier, F.; Lorcy, D.; Fabre, B. Redox-active organic monolayers deposited on silicon surfaces for the fabrication of molecular scale devices. *Int. J. Nanotechnol.* **2008**, *5*, 741–756.
- (32) Laviron, E. J. General expression of the linear potential sweep voltammogram in the case of diffusionless electrochemical systems. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *101*, 19–28.
- (33) Eckermann, A. L.; Feld, D. J.; Shaw, J. A.; Meade, T. J. Electrochemistry of redox-active self-assembled monolayers. *Coord. Chem. Rev.* **2010**, *254*, 1769–1802.
- (34) Klingler, R. J.; Kochi, J. K. Electron-transfer kinetics from cyclic voltammetry: Quantitative description of electrochemical reversibility. *J. Phys. Chem.* **1981**, *85*, 1731.