

Electron Transfer at Electrodes through Conjugated “Molecular Wire” Bridges

Stephen Creager,*[†] C. J. Yu, Cindy Bamdad, Steve O'Connor, Tanya MacLean, Eric Lam, Yoochul Chong, Gary T. Olsen, Jiye Luo, Michael Gozin, and Jon Faiz Kayyem

Contribution from Clinical Micro Sensors Inc., 126 W. Del Mar Blvd., Pasadena, California 91101

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Abstract: Electron-transfer rates and electronic coupling factors for ferrocene groups attached to gold electrodes via oligo(phenylethynyl) “molecular wire” bridges of variable length and structure are reported. Attachment to gold was achieved via thiol groups at the end of the bridge opposite the ferrocene. Bridge structures were designed to promote strong coupling between gold and ferrocene, thereby promoting rapid electron transport over long distances. The effects of bridge length and of substituents on the phenyl rings in the bridge were addressed. Bridges containing between three and six phenylethynyl units were studied, and a “beta” value of 0.36 \AA^{-1} describing the exponential distance dependence of bridge-mediated electron-transfer rates was obtained. The effect on the rates of adding two propoxy groups onto one of the phenyl rings in the bridge was examined and found to be minimal. The standard electron-transfer rate constant of 350 s^{-1} obtained for the adsorbate with the longest bridge (six phenylethynyl units, corresponding to an electron-transfer distance of approximately 43 \AA) corresponds to an electronic coupling factor between ferrocene and gold of approximately 0.7 cm^{-1} . The extrapolated rate constants at very short distances were nearly the same for the conjugated bridge series and for a related monolayer series in which ferrocene groups were linked to gold via aliphatic bridges. The extrapolated rate constants at short distance also agree with a calculated rate constant for the limiting case of adiabatic electron transfer at an electrode.

Introduction

Electronic conduction through molecular-scale “wires” is a critical phenomenon in the developing field of molecular electronics.^{1,2} There is general agreement that a molecular “wire” should consist of a molecular chain with extended electronic conjugation that would promote strong coupling between the two groups (molecules, electrodes, or other entities) attached to the chain ends. Several theoretical descriptions of electronic conduction through such molecular-scale wires have appeared,^{3–6} and several groups have recently demonstrated direct electronic conduction through small ensembles of molecules^{7–9} and even through single molecules^{10–13} using proximal probe techniques.

Much of the present work on electronic conduction in molecular wires is based on insights gained over the last 40 years from work on electron transfer in bridged donor–acceptor molecules.¹⁴ It has long been recognized that the electronic coupling through a chain linking an electron donor to an acceptor can control the rate of electron transfer between the groups on the two chain ends.¹⁵ This same type of bridge-mediated electronic coupling is now recognized as a critical factor controlling long-range electron transfer in many biological structures (e.g., redox proteins,¹⁶ photosynthetic reaction centers,^{17,18} and nucleic acids^{19–22}), electron conduction across molecular layers in STM,^{10,11,13,23} electron emission in certain

* Author to whom correspondence should be addressed at Clemson University.

[†] Permanent Address: Department of Chemistry, Clemson University, Clemson, SC 29634.

(1) Goldhaber-Gordon, D.; Montemero, M. S.; Love, J. C.; Opitek, G. J.; Ellenbogen, J. C. *Proc. IEEE* **1997**, *85*, 521.

(2) *An Introduction to Molecular Electronics*; Petty, M. C., Bryce, M. R., Bloor, D., Eds.; Oxford University Press: New York, 1995.

(3) Samanta, M. P.; Tian, W.; Datta, S.; Henderson, J. I.; Kubiak, C. P. *Phys. Rev. B* **1996**, *53*, R7626–R7629.

(4) Magoga, M.; Joachim, C. *Phys. Rev. B* **1998**, *57*, 1820–1823.

(5) Magoga, M.; Joachim, C. *Phys. Rev. B* **1997**, *56*, 4722–4729.

(6) Kemp, M.; Roitberg, A.; Mujica, V.; Wanta, T.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 8349–8355.

(7) Dorogi, M.; Gomez, J.; Osifichin, R.; Andres, R. P.; Reifengerger, R. *Phys. Rev. B* **1995**, *52*, 9071–9077.

(8) Andres, R. P.; Bein, T.; Dorogi, M.; Feng, S.; Henderson, J. I.; Kubiak, C. P.; Mahoney, W.; Osifichin, R. G.; Reifengerger, R. *Science* **1996**, *272*, 1323.

(9) Zhou, C.; Deshpande, M. R.; Reed, M. A.; II, L. J.; Tour, J. M. *Appl. Phys. Lett.* **1997**, *71*, 611–613.

(10) Datta, S.; Tian, W.; Hong, S.; Reifengerger, R.; Henderson, J. I.; Kubiak, C. P. *Phys. Rev. Lett.* **1997**, *79*, 2530–2533.

(11) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705.

(12) Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P.; Tour, J. M. *Science* **1997**, *278*, 252–254.

(13) Dhirani, A.-A.; Zehner, R. W.; Hsung, R. P.; Guyot-Sionnest, P.; Sita, L. R. *J. Am. Chem. Soc.* **1996**, *118*, 3319–3320.

(14) Barbara, P. F.; Meyer, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 13148.

(15) McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508–515.

(16) Gray, H. B.; Winkler, J. R. *Annu. Rev. Biochem.* **1996**, *65*, 537–561.

(17) Moser, C. C.; Page, C. C.; Farid, R.; Dutton, P. L. *J. Bioenerg. and Biomembr.* **1995**, *27*, 263–274.

(18) Franzen, S.; Goldstein, R. F.; Boxer, S. G. *J. Phys. Chem.* **1993**, *97*, 3040–3053.

(19) Meade, T. J. In *Interactions of Metal Ions with Nucleotides, Nucleic Acids, and their Constituents*; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 1996; Vol. 32, Metal Ions in Biological Systems, pp 453–478.

(20) Holmlin, R. E.; Danliker, P. J.; Barton, J. K. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2714–2730.

(21) Meade, T. J.; Kayyem, J. F. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 352–354.

(22) Stemp, E. D. A.; Barton, J. K. In *Probing of Nucleic Acids by Metal Ion Complexes of Small Molecules*; Sigel, A., Sigel, H., Eds.; Marcel Dekker: New York, 1997; Vol. 33, Metal Ions in Biological Systems, pp 325–366.

(23) Cygan, M. T.; Dunbar, T. D.; Arnold, J. J.; Bumm, L. A.; Shedlock, N. F.; Burgin, T. P.; II, L. J.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *J. Am. Chem. Soc.* **1998**, *120*, 2721–2732.

classes of field emitters,²⁴ electron transfer in certain electrochemical systems,^{25–27} and electronic conduction through molecular wires.

Electrochemical techniques are particularly well suited to studies of long-range electronic coupling and electron transfer between metal electrodes and attached redox molecules.²⁸ Recent work on the electrochemistry of organized monolayers on electrodes provides a general route to creating surface structures in which redox-active molecules are linked to electrodes via well-defined molecular bridges, the structures of which can be systematically varied.²⁵ These monolayer-based structures can serve as excellent model systems for studying bridge-mediated electron transfer, due in part to the inherently electrical nature of the signal (usually a current) that is generated as a result of electron transfer. The electrical nature of the signal from electron transfer is also an advantage in applications that are envisioned for such structures in molecular-scale analytical devices, for example in metal-ion sensors,²⁹ enzyme-based biosensors, immunosensors,^{30,31} and DNA hybridization sensors.^{32–34}

The present work examines the electron-transfer kinetics of ferrocene groups that are attached to gold electrodes via conjugated oligo(phenylethynyl)-based “molecular wire” bridges of variable length and structure. Attachment to the gold is achieved via aryl thiol groups at the end of the bridge opposite the ferrocene.^{35,36} The bridge structures were designed to promote strong electronic coupling between the chain ends, thereby promoting rapid electron transfer over long distances. Electron-transfer rates were measured using a recently described ac voltammetry technique that is particularly well suited to studies of redox kinetics in small populations of redox molecules immobilized on electrodes.³⁷ A comparison is made with a recent electrochemical study by Sachs and co-workers on a similar ferrocene-based monolayer system involving oligo(phenylethynyl) bridges containing two and three phenylethynyl units,³⁸ and also with data from Weber and co-workers on a ferrocene-based monolayer system involving aliphatic bridges.²⁶

Experimental Section

Materials. Gold wire for electrodes was from Alfa (0.127 and 0.050 mm diameter, Premion grade, >99.99% pure) or SPM (0.127 mm diameter, 99.99%). Ethanol (95%, denatured), triethylamine (>98%), and tetrahydrofuran (distilled) from EM science were used as received. Water was purified with a MilliQ system to a resistivity of at least 15

(24) Purcell, S. T.; Garcia, N.; Binh, V. T.; II, L. J.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11985–11989.

(25) Finklea, H. O. in *Electroanalytical Chemistry*; Bard, A. J., Rubinstein, I., Eds.; Marcel Dekker: New York, 1996; Vol. 19, pp 109–335.

(26) Weber, K.; Hockett, L.; Creager, S. E. *J. Phys. Chem. B* **1997**, *101*, 8286–8291.

(27) Hsu, C. P.; Marcus, R. A. *J. Chem. Phys.* **1997**, *106*, 584–598.

(28) Bard, A. J.; Abruna, H. D.; Chidsey, C. E.; Faulkner, L. R.; Feldberg, S. W.; Itaya, K.; Majda, M.; Melroy, O.; Murray, R. W.; Porter, M. D.; Soriaga, M. P.; White, H. S. *J. Phys. Chem.* **1993**, *97*, 7147–7173.

(29) Mandler, D.; Turyan, I. *Electroanalysis* **1996**, *8*, 207–213.

(30) Ghindilis, A. L.; Atanasov, P.; Wilkins, M.; Wilkins, E. *Biosens. Bioelectr.* **1998**, *13*, 113–131.

(31) Skladal, P. *Electroanalysis* **1997**, *9*, 737–745.

(32) Mikkelsen, S. R. *Analyst* **1996**, *8*, 15–19.

(33) Yang, M.; McGovern, M. E.; Thompson, M. *Anal. Chim. Acta* **1997**, *346*, 259–275.

(34) Wilson, E. K. *Chem. Eng. News* **1998**, May 25, 47–49.

(35) Tour, J. M.; Jones, L.; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J. Am. Chem. Soc.* **1995**, *117*, 9529.

(36) Zehner, R. W.; Sita, L. R. *Langmuir* **1997**, *13*, 2973–2979.

(37) Creager, S. E.; Wooster, T. T. *Anal. Chem.* **1998**, *70*, 4257–4263.

(38) 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. *J. Am. Chem. Soc.* **1997**, *119*, 10563–10564.

MΩ cm. Ferrocene aryl thiols and mercapto alcohols used to prepare monolayers were synthesized as described separately.³⁹

Ferrocene aryl thiols in which the terminal thiol group was protected using 4-ethyl-*N*-methylpyridinium iodide chemistry were deprotected in a 9:1 ethanol:triethylamine solution (approximately 0.2 mM in ferrocene thiol) for 10 min at room temperature. Ferrocene aryl thiols in which the terminal thiol was protected using ethyltrialkylsilane chemistry were deprotected as 0.2 mM ferrocene thiol solutions in tetrahydrofuran that were also 0.1 M in tetrabutylammonium fluoride, for 1 h at 37 °C. All solutions of deprotected ferrocene aryl thiols were then stored as stock solutions (from which coating solutions for preparing monolayer-coated electrodes were made) in capped polypropylene vials in a freezer.

Electrode and Monolayer Preparation. Gold electrodes for monolayer coating were prepared by melting the end of a clean gold wire into a small spherical ball in a gas–air flame. The diameter of the spherical ball varied from one electrode to another but was typically in the range of 0.4–0.7 mm for 0.127 mm diameter wire and 0.2–0.4 mm for 0.050 mm diameter wire. Coating solutions were prepared in ethanol by dilution of stock solutions of deprotected ferrocene aryl thiols prepared as described above. A typical coating solution contained approximately 2.5×10^{-6} M ferrocene aryl thiol and 5.0×10^{-4} M of 16-mercaptohexadecanol in ethanol, except as otherwise indicated. Monolayers were prepared by immersing a freshly melted gold ball electrode in a coating solution containing ferrocene aryl thiol and mercapto alcohol for approximately 10 min at room temperature, after which the electrode was briefly rinsed with ethanol and then immersed in a 1 mM mercapto alcohol solution in ethanol for at least 4 h (typically overnight) at room temperature.

Electrochemical Characterization. After a brief rinse with ethanol followed by water, the coated electrodes were characterized using a recently described ac voltammetry method³⁷ to obtain standard electron-transfer rate constants for the immobilized ferrocene groups. In some cases, dc cyclic voltammetry was also used to characterize the monolayers. Two different instrument configurations were used. For frequencies between 1 and 10 000 Hz, a computer-based CH Instruments model 660 electrochemical workstation was used. This instrument was also used to acquire dc cyclic voltammetry data. For frequencies between 1000 and 100 000 Hz, an analogue instrument consisting of a Stanford Research model SR830 DSP lock-in amplifier, a locally constructed three-electrode adder potentiostat,⁴⁰ a Cypress Systems Omni 90 potentiostat (to generate a slow dc ramp that was summed with the perturbing ac voltage), and an XY recorder was used. The estimated potentiostat bandwidth was in excess of 1 MHz, as determined by calibration with a sinusoidal waveform and a dummy cell resistor in two-electrode mode. Both instrument configurations produced the same ac voltammetry response in the frequency range in which they overlap.

Electrochemical experiments were performed in a three-electrode configuration using an aqueous 1.0 M sodium perchlorate electrolyte. A Ag/AgCl/3 M KCl reference electrode (Bioanalytical Systems) and a platinum wire auxiliary electrode were used. The working electrode was positioned such that the gold ball was immersed just below the surface of the electrolyte, with as little of the thin gold wire as possible exposed to the solution. Electrical connection was made to the other end of the gold wire.

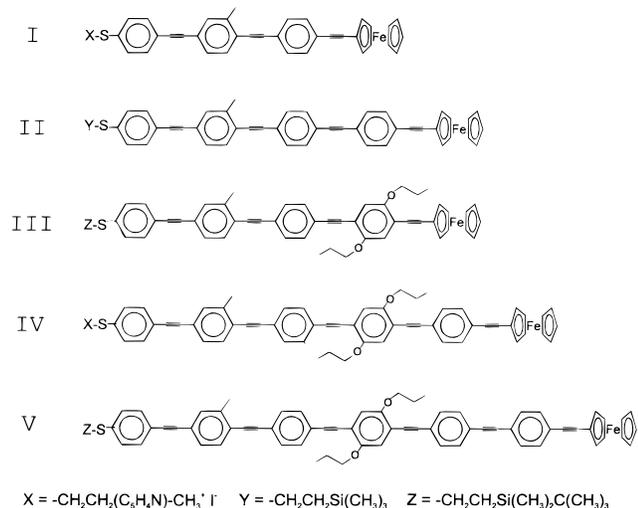
Results

Chart 1 presents the structures of the ferrocene “molecular wire” adsorbates that were studied in this work. The properties of these molecules and the synthetic methods used to prepare them are described separately.³⁹ The molecules differ regarding the number of phenylethynyl units in the bridges, the substituents on the individual phenyl rings, and the chemistry used to protect the terminal thiol groups. Monolayer preparation was always accomplished from dilute ethanol solutions after thiol deprotection, such that the monolayer properties should be indepen-

(39) Yu, C. J. et al. Manuscript in preparation.

(40) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; John Wiley & Sons: New York, 1980.

Chart 1



dent of the thiol protection chemistry. The general features of the ac voltammograms (peak potential, size and shape) were found to be similar for all of the molecules presented in Chart 1, irrespective of the protection chemistry of the thiol, which supports the postulate that the thiol protection chemistry has little or no effect on the properties of the monolayers that are ultimately formed.

AC voltammetry has proven useful for studying redox kinetics in monolayers on electrodes,^{41–45} particularly when the amount of redox-active material on the electrode is small.³⁷ Figure 1 presents two representative ac voltammograms which illustrate this for a monolayer in which a small quantity of molecule IV (ferrocene attached to a bridge containing five phenylethynyl units) is coadsorbed with an insulating mercapto alcohol. At a relatively low frequency of 100 Hz for the applied ac potential, a feature in the voltammogram corresponding to ferrocene oxidation/reduction is clearly evident with a peak potential near +0.274 V and an ac peak current of approximately 95 nA above baseline. As the frequency is increased this peak gradually disappears, until at 10 000 Hz it is nearly gone. In qualitative terms, this happens because the ferrocene oxidation–reduction reaction can no longer occur rapidly enough to keep up with the changing potential at high frequency. Note that the baseline current still scales nearly linearly with frequency in this range (e.g., the ac current at +0.10 V increases from 288 nA to 26.8 μA as frequency is increased from 100 to 10 000 Hz), indicating that the cell time constant is small enough to enable rapid charging of the electrical double-layer at both frequencies. This nearly proportional relationship between background current and frequency was confirmed up to 100 000 Hz, the highest frequency used in this work.

A recent publication describes a method whereby the diminution in ac peak current relative to baseline in a series of ac voltammograms acquired at different frequencies may be analyzed to yield a standard electron-transfer rate constant, k_o , for oxidation/reduction of an immobilized redox molecule.³⁷ Figure 2 presents a series of plots of $i_{\text{peak}}/i_{\text{background}}$ vs $\log(\text{frequency})$ that illustrate this for several representative monolayer films in which the number of phenylethynyl units in the

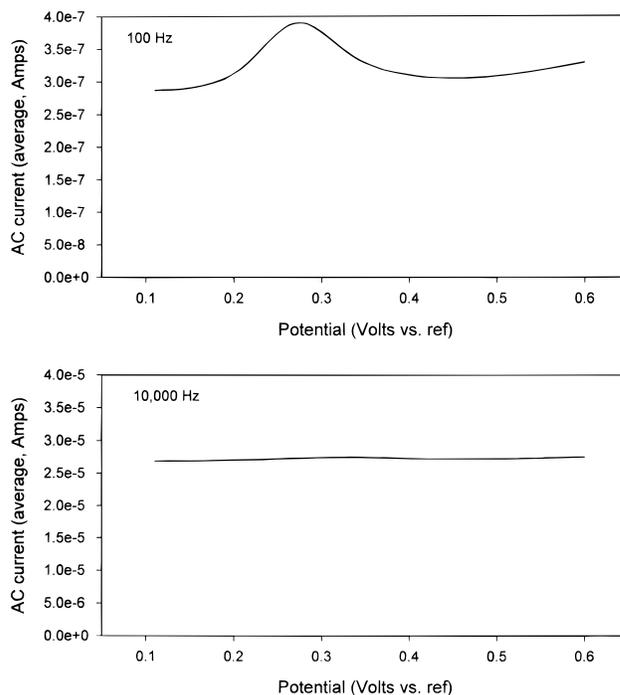


Figure 1. AC voltammograms of a gold ball electrode (from 0.127-mm diameter wire) coated with monolayer of molecule IV with mercaptohexadecanol. Data were acquired using the CHI-660 instrument. Peak amplitude of applied voltage was 25 mV (50 mV peak-to-peak), sampling period was 1 s, sampling interval was 10 mV. Frequency: top, 100 Hz; bottom, 10 000 Hz.

bridge linking a ferrocene group to an electrode is systematically varied. The plots also list values for k_o for each monolayer obtained from fits to the data achieved using the Randles equivalent circuit model as previously described.³⁷ These values are also listed in Table 1, along with other parameters used to achieve the fits. The quality of the fits is generally good over a broad frequency range, which indicates that the systems are all well described by a single rate constant and not a broad distribution of rate constants.³⁷ As expected, the k_o values decrease as the number of phenylethynyl units in the bridge linking the ferrocene to the electrode increases. This reflects the expected diminution in electronic coupling between ferrocene and gold as the length of the molecular bridge between them increases.

Figure 3 presents the standard rate constants from Table 1 as a plot of $\ln(k_o)$ vs distance (a “beta plot”) to illustrate the exponential dependence of rate on distance. Distances are taken from the terminal sulfur at the gold electrode to the carbon in the ferrocene cyclopentadienyl ring attached to the bridge, using average crystallographically determined distances (in related molecules) of 1.79 Å for the carbon–sulfur bond, 1.43 Å for the C–C single bonds, 1.19 Å for the carbon–carbon triple bonds, and 6.84 Å per complete phenylethynyl repeat unit.^{46,47} (Thus, the distance is taken along the main axis of the bridge, without consideration of any tilt in the adsorbate layer.) The slope of this plot (i.e., the beta value which describes the exponential dependence of rate on distance, $\text{rate} \propto \exp[-\beta d]$) is -0.36 \AA^{-1} . Also included on the plot are some previously published data on standard electron-transfer rate constants for a series of ferrocene carboxamide derivatives linked to gold electrodes by alkanethiol chains of variable length.²⁶ Distances

(41) Laviron, E. *J. Electroanal. Chem.* **1979**, *105*, 35–42.

(42) Laviron, E. *J. Electroanal. Chem.* **1979**, *97*, 135–149.

(43) Kakutani, T.; Senda, M. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 3236–3241.

(44) Finklea, H. O.; Ravenscroft, M. S.; Snider, D. A. *Langmuir* **1993**, *9*, 223–227.

(45) Nahir, T. M.; Bowden, E. F. *J. Electroanal. Chem.* **1996**, *410*, 9.

(46) Adams, R. D.; Barnard, T.; Rawlett, A.; Tour, J. M. *Eur. J. Inorg. Chem.* **1998**, *1998*, 429–431.

(47) Hsung, R. P.; Chidsay, C. E. D.; Sita, L. R. *Organometallics* **1995**, *14*, 4808–4815.

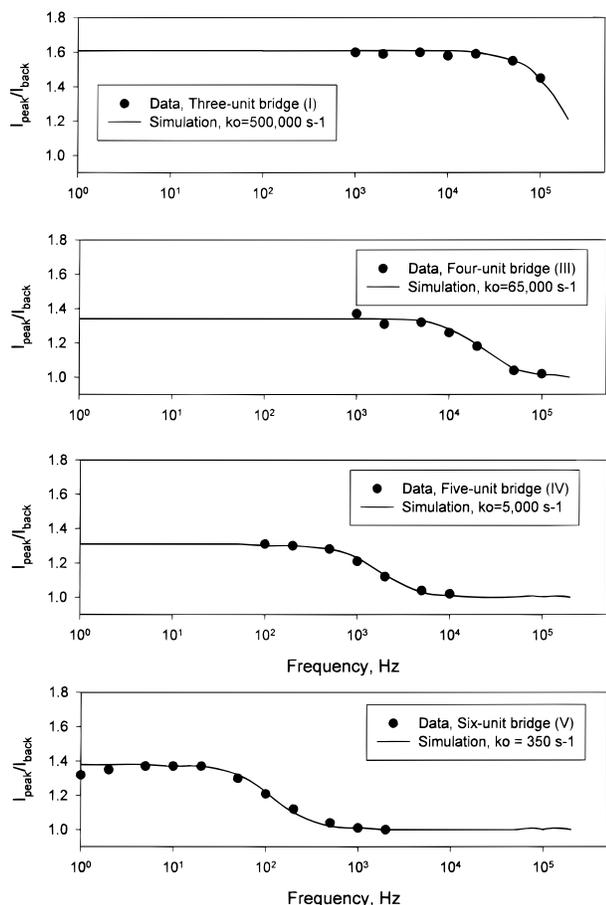


Figure 2. Data analysis to obtain electron-transfer rate constants for ferrocene groups linked to gold electrodes by oligo(phenylethynyl) bridges of differing lengths. See ref 37 for details of the data analysis, and Table 1 for summary of parameters used to fit the data. Top, molecule I, three phenylethynyl groups; next, molecule III, four phenylethynyl groups; next, molecule IV, five phenylethynyl groups; bottom, molecule V, six phenylethynyl groups. Top two data sets were for gold balls from 0.05-mm diameter wire, data acquired using the analogue instrument configuration; bottom two data sets were for gold balls from 0.127 mm diameter wire, data acquired using the CH-660 instrument.

Table 1. Redox Properties from ac Voltammetry of Ferrocene Monolayers^a

monolayer	k_0 (s ⁻¹) ^b	Γ (mol cm ⁻²)	$ V_{ab} $ (cm ⁻¹) ^c
(I) + HO-(CH ₂) ₁₆ -SH	5×10^5	6.5×10^{-13}	26
(II) + HO-(CH ₂) ₁₆ -SH	6×10^4	3.5×10^{-13}	9
(III) + HO-(CH ₂) ₁₆ -SH	6.5×10^4	3.5×10^{-13}	9
(IV) + HO-(CH ₂) ₁₆ -SH	5×10^3	3.2×10^{-13}	2.6
(IV) + HO-(CH ₂) ₁₂ -SH ^d	4×10^3	1.1×10^{-13}	2.3
(V) + HO-(CH ₂) ₁₆ -SH	3.5×10^2	4.0×10^{-13}	0.7

^a Other fitting parameters were as follows: $C_{dl} = 1.0 \times 10^{-6}$ F cm⁻²; solution resistivity = 5 ohm cm; electrode radius = 0.2 mm for balls from 0.05-mm diameter wire (molecules I, II, and III) and 0.4 mm for gold balls from 0.127-mm diameter wire (molecules IV and V). ^b Each k_0 measurement was reproduced at least one time, and in most cases several times, on a freshly prepared monolayer. The values listed are precise to within at least $\pm 20\%$. ^c Calculated using eq 2 as described in the text. ^d Monolayer was prepared from a solution containing 25 μ M of deprotected molecule IV and 500 μ M of mercaptododecanol.

in this case are again taken from the sulfur to the ferrocene cyclopentadiene ring, assuming a carbon-carbon distance of 1.27 Å (appropriate for a fully extended all-trans polymethylene chain⁴⁸) and taking the amide as equivalent to two methylene units. (Preliminary work comparing electron-transfer rates in alkylferrocene and *N*-alkylferrocenecarboxamide monolayers

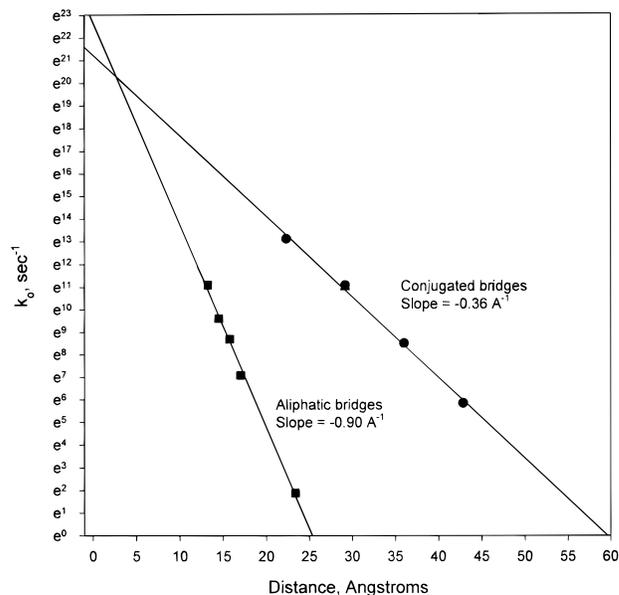


Figure 3. Beta plots ($\ln(k_0)$ vs distance) for ferrocene monolayers with conjugated bridging groups (circles) and aliphatic bridging groups (squares). Data for conjugated bridging groups are in Table 1 and that for aliphatic bridging groups are in ref 26.

suggests that the contribution to the electronic coupling of an amide group is almost indistinguishable from that of two methylene groups.⁴⁹) These data will be discussed further below.

It is instructive to consider the different responses in ac voltammetry and dc cyclic voltammetry for these electrodes. Figure 4 presents such a comparison for a gold electrode coated with a mixed monolayer of molecule IV with mercaptohexadecanol. The ac voltammogram was acquired at a relatively low frequency (100 Hz) and the dc voltammogram at a low scan rate (20 mV s⁻¹) such that a reversible response should be obtained in both cases. Both voltammograms show the expected feature near +0.28 V corresponding to ferrocene oxidation/reduction.

It is straightforward to estimate the quantity of ferrocene present on this electrode from the currents associated with the peaks in each voltammogram. This is most straightforward in the case of dc voltammetry, since one can simply integrate the charge under the peak and convert it to a number of moles of ferrocene using the Faraday constant. For the voltammogram in Figure 4, this procedure yields approximately 1.3 nC of charge or 14 femtomoles (8×10^9 molecules) of ferrocene.

For the ac voltammogram, the procedure is slightly more complicated since the current depends on the ac amplitude and frequency. Equation 1 presents the expected relationship between the voltammetric peak current and the number of moles of redox-active adsorbate giving rise to the peak, assuming reversible Nernstian behavior and a linear current-voltage relationship.^{41,43} In this equation f is the frequency in hertz, ϵ

$$i_{\text{peak}} = \left(\frac{2}{\pi}\right) \left(\frac{F^2}{4RT}\right) (\text{no. of moles adsorbate}) (2\pi f) \epsilon \quad (1)$$

the peak amplitude of the applied ac voltage, and i_{peak} is the ac peak current (average) in the ac voltammogram. Note that the factor $2/\pi$ is required to present the ac current as an average ac current instead of a peak ac current.

(48) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321.

(49) Sumner, J.; Weber, K.; Creager, S. Manuscript in preparation. 1998.

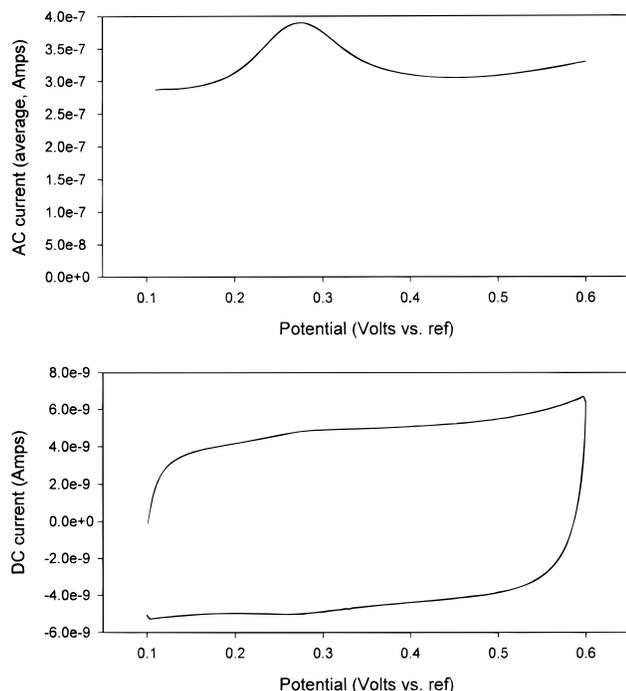


Figure 4. Comparison of ac voltammetry (top) and dc cyclic voltammetry (bottom) of a gold ball electrode (from 0.127-mm diameter wire) coated with a monolayer of molecule IV with mercaptohexadecanol. The ac voltammogram was acquired using the same parameters as those listed in Figure 1; dc cyclic voltammogram was acquired at 20 mV s⁻¹ at a sampling interval of 1 point every mV.

Application of this relation to the ac voltammogram in Figure 4 yields a value of 10 femtomoles (6×10^9 molecules) for the amount of ferrocene giving rise to the peak, in good though not completely quantitative agreement with the value obtained from integration of the peak in the dc voltammogram. Possible causes for the small difference between the values obtained by the two methods include nonideal voltammetric peak shapes associated with interactions among oxidized and reduced species,⁴³ errors associated with the correction for the relatively large background current due to double-layer charging, and errors associated with the use of a relatively large ac voltage amplitude (50 mV peak-to-peak) while assuming a linear current–potential relationship.

Discussion

Distance Dependence. Several aspects of these results warrant further discussion. We first consider the slopes of the beta plots in Figure 3 for monolayers in which ferrocene groups are linked to gold by conjugated (phenylethynyl) and nonconjugated (alkane) bridges. The beta value of 0.36 \AA^{-1} obtained for the conjugated bridge system is much lower than the value of 0.90 \AA^{-1} for the aliphatic system shown in the figure and widely reported for many related aliphatic monolayer systems.^{25,26,50} Another way of thinking about these numbers is that they indicate that rates are diminished by a factor of 3.0 for each methylene unit in the aliphatic bridges, and by a factor of 11.7 for each complete phenylethynyl unit in the conjugated bridges. A shallow distance dependence of electron-transfer rates for conjugated bridges has been observed experimentally in several molecular donor–acceptor systems,^{51–56} and in one case, similar behavior was also seen in a monolayer-based electrochemical system.³⁸ A shallow distance dependence of electron-transfer rates through conjugated spacers is thought to be due

qualitatively to the extended nature of the electronic orbitals in conjugated structures, as compared to aliphatic structures in which the molecular orbitals are for the most part localized to smaller numbers of atoms.

Sachs and co-workers have presented the results of calculations on the distance dependence of electronic coupling across phenylethynyl spacers with radical ions on the two ends.³⁸ The beta value of 0.36 \AA^{-1} from the present work is close to the values of 0.39 and 0.43 \AA^{-1} calculated by Sachs and co-workers for radical cations and anions (respectively) in a conformation in which the phenyl rings in the bridge are nearly coplanar. Magoga and Joachim have also reported the results of calculations on the distance dependence of electronic coupling across phenylethynyl spacers, in this case with metal electrodes attached to the two ends of the bridge.⁵ They report a calculated damping factor (equivalent to a beta value) of approximately 0.28 \AA^{-1} for phenylethynyl spacers (conformation not specified), again in reasonable agreement with the value of 0.36 \AA^{-1} obtained in the present work. Both the electronic coupling and the damping factor (beta value) should depend strongly on the bridge conformation, specifically on the twist angles between adjacent rings.^{38,57} Little is known about the bridge conformation in the present monolayers; however, the torsional barrier in tolane (a related molecule) has been estimated to be between 200 and 300 cm^{-1} ,^{57,58} which should be sufficient to impart a mild preference for a coplanar configuration at room temperature.

The study by Sachs and co-workers reports an experimental beta value of 0.57 \AA^{-1} for phenylethynyl-based bridges from an electrochemical study of redox kinetics for two members of a monolayer-based system that is very similar to that studied in the present work.³⁸ The discrepancy between this value and the value of 0.36 \AA^{-1} obtained in the present work is significant, and the cause of the discrepancy is not certain. We do note that there are significant differences in the monolayers and the methods used in the two studies. For example, Sachs and co-workers worked at ferrocene surface coverages that were typically 10 times higher than those used in the present work. Also, Sachs and co-workers measured electron-transfer rates using a novel laser-based coulometric temperature-jump method⁵⁰ suitable for measuring very fast rates (e.g., rate constants up to $3 \times 10^6 \text{ s}^{-1}$ are reported in reference 38), whereas the present work utilizes an ac voltammetry method that is well suited for measuring less rapid rates (e.g., the maximum rate reported herein is $5 \times 10^5 \text{ s}^{-1}$). The good linearity of the beta plot in the present work over a very wide distance range (four different bridge lengths were studied), combined with the fact that the electron-transfer rates in the present work are all slow enough that limits associated with cell time constants can be ruled out, give us confidence that the beta value obtained in the present work is reliable, particularly for the longer distances.

Electron-transfer rates in monolayers may be interpreted in terms of factors describing the electronic coupling between the

(51) Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198–205.

(52) Woitellier, S.; Launay, J. P.; Spangler, C. W. *Inorg. Chem.* **1989**, *28*, 758–762.

(53) Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40–51.

(54) Helms, A.; Heiler, D.; McLendon, G. *J. Am. Chem. Soc.* **1992**, *114*, 4, 6227–6238.

(55) Osuka, A.; Tanabe, N.; Kawabata, S.; Yamazaki, I.; Nishimura, Y. *J. Org. Chem.* **1995**, *60*, 7177–7185.

(56) Finckh, P.; Heitele, H.; Volk, M.; Michel-Beyerle, M. E. *J. Phys. Chem.* **1988**, *92*, 6584–6590.

(57) Seminario, J. M.; Zacarias, A. G.; Tour, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 3970–3974.

(58) Okuyama, K.; Hasegawa, T.; Ito, M.; Mikami, N. *J. Phys. Chem.* **1984**, *88*, 1711–1716.

(50) Smalley, J. F.; Feldberg, S. W.; Chidsey, C. E. D.; Linford, M. R.; Newton, M. D.; Liu, Y.-P. *J. Phys. Chem.* **1995**, *99*, 13141–13149.

immobilized redox molecule and the underlying electrode.^{26,27} Equation 2 presents an equation for the rate constant of nonadiabatic electron transfer at an electrode in terms of the reorganization energy, λ , for the immobilized redox molecule, the density of electronic states, $\rho(\epsilon)$, of the electrode, and the electronic coupling factor, $|V_{ab}|$, between the redox molecule and the electrode.^{26,59,60}

$k_o =$

$$\rho(\epsilon) |V_{ab}|^2 \left(\frac{2\pi kT}{h} \right) \sqrt{\frac{\pi}{kT}} \int_{-\infty}^{\infty} \exp \left[\frac{-((\epsilon_F - \epsilon) + \lambda)^2}{4\lambda kT} \right] f(\epsilon) \frac{d\epsilon}{kT} \quad (2)$$

By substituting a value of 0.85 eV for the reorganization energy for ferrocene monolayers in water^{59,61} (assumed to be independent of distance)⁵⁰ and a value of 0.3 states eV⁻¹ for the state density of gold near the Fermi energy,^{26,27} and solving the integral in eq 2 numerically, it is possible to solve for the term $|V_{ab}|$ describing the electronic coupling between ferrocene and gold mediated by the molecular wire bridges. The values so obtained for the present oligo(phenylethynyl) monolayers are listed in Table 1. The coupling factors are relatively large considering the very long distances over which they act (over 40 Å in the case of molecule V). Even so, the coupling factors are all small enough that the reactions are rigorously nonadiabatic, as is assumed in the development of eq 2.⁶²

Another important point regarding Figure 3 is that the electron-transfer rates in both bridge systems extrapolate to the same value (approximately $\exp[20.3]$ or 6.6×10^8 s⁻¹) at a gold-ferrocene distance of between 3 and 4 Å. (Note that the distance estimates in both cases include the terminal carbon-sulfur bond distance but not the sulfur-gold distance.) This rate constant should correspond to the adiabatic limit in which the rate is controlled not by the strength of electronic coupling between ferrocene and gold but rather by the dynamics of nuclear motion (in this case mostly those of solvent molecules) along the reaction coordinate. It is instructive to compare the extrapolated rate constants in Figure 3 to a rate constant calculated using expressions appropriate for adiabatic electron transfer at an electrode. Equation 3 presents a rate equation appropriate for this situation.^{26,59,60,63} In this equation, the term κ_{el} corresponds to the electron transmission coefficient, the term ν_n to the nuclear frequency factor, and the product of these two terms to the barrier crossing frequency.

$$k_o = \kappa_{el} \nu_n \int_{-\infty}^{\infty} \exp \left[\frac{-((\epsilon_F - \epsilon) + \lambda)^2}{4\lambda kT} \right] f(\epsilon) \frac{d\epsilon}{kT} \quad (3)$$

Substituting the reported solvent reorganization energy of 0.85 eV for ferrocene monolayers in water^{59,61} and the reported barrier crossing frequency (the product of κ_{el} and ν_n) of 3.5×10^{11} s⁻¹ for hydroxymethylferrocene in water^{64,65} into eq 3 yields a calculated adiabatic electron-transfer rate constant of 2.4×10^8 s⁻¹, in fairly good agreement (factor of 3) with the extrapolated rate constants for the two monolayer systems at short distances. The good agreement between the extrapolated rate constants and the calculated adiabatic rate constant serves to validate the models that have been used to describe electron-

transfer dynamics in systems of this type. It also places an upper limit on the standard electron-transfer rate constant that can be expected for ferrocene oxidation/reduction at an electrode.

Ring Substituent Effects. An important point regarding molecules II and III in Chart 1 is that, aside from the thiol protection chemistry, they differ only in the substituents on the phenyl rings in the bridge. Molecule II has only hydrogen substituents on the rings, whereas molecule III has two propoxy groups on the ring adjacent to the ferrocene. These groups were added to impart solubility to the higher members of the series. The standard rate constants for ferrocene oxidation/reduction in monolayers containing molecules II and III were found to be similar (Table 1), which suggests that ring substituent effects on electron-transfer rates in this class of "molecular wire" bridging molecules are small. This finding is significant since it suggests that further synthetic modifications to the bridges, for example, to impart solubility or to link other chemically sensitive molecules (e.g., electroactive or photoactive moieties, or molecules with a desired chemical binding affinity) onto the bridge, could be readily made without dramatically affecting the electronic coupling along the bridge. Of course, the use of such chemically modified bridges in monolayer-based systems may also be constrained by structural factors associated with the overall monolayer integrity.

Coadsorbate Effects. The fourth and fifth entries in Table 1 correspond to monolayers in which the ferrocene-containing adsorbate is the same but the mercapto alcohol coadsorbate is changed from one with 16 methylene units to one with 12 methylene units in the chain. If there are contributions to the electronic coupling from pathways through the coadsorbates (as has been observed for some monolayers in which redox molecules are linked to electrodes by aliphatic chains⁶⁶), then there should be a substantial difference in rate for these two cases. In fact, the difference is found to be minimal. This insensitivity to the nature (length) of the coadsorbate probably reflects at least two factors, the first being the relatively strong coupling through the conjugated bridge compared to that expected through alkyl chains, and the second being the rigidity compared to alkanes of the conjugated bridge to which the ferrocene is attached.

Conclusions

AC voltammetry was used to measure standard electron-transfer rate constants for ferrocene linked to electrodes via conjugated phenylethynyl molecular wire bridging groups in self-assembled monolayer films. Bridges containing between three and six phenylethynyl units were studied, corresponding to estimated electron-transfer distances between 22 and 43 Å. A "beta value" of 0.36 Å⁻¹ describing the exponential distance dependence of the bridge-mediated electron-transfer rates between ferrocene and gold was obtained. The extrapolated rate constants at short distance were nearly the same for the conjugated bridges and for a related series of monolayers in which ferrocene groups were linked to gold via aliphatic bridges. The extrapolated rate constants also agreed with a calculated rate constant for the limiting case of adiabatic electron transfer at an electrode. The effects on the electron-transfer rates of adding propoxy groups onto one of the phenyl rings in the bridge, and of varying the length of the mercapto alcohol coadsorbate in the monolayers, were found to be minimal.

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(59) Chidsey, C. E. D. *Science* **1991**, *251*, 919–922.

(60) Zusman, L. D. *Chem. Phys.* **1987**, *112*, 53–59.

(61) Weber, K.; Creager, S. E. *Anal. Chem.* **1994**, *66*, 3164–3172.

(62) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437–480.

(63) Weaver, M. J. *Chem. Rev.* **1992**, *92*, 463–480.

(64) Weaver, M. J.; McManis, G. E. *Acc. Chem. Res.* **1990**, *23*, 294–300.

(65) Nielson, R. M.; McManis, G. E.; Weaver, M. J. *J. Phys. Chem.* **1989**, *93*, 4703–4706.

(66) Finklea, H. O.; Liu, L.; Ravenscroft, M. S.; Punturi, S. *J. Phys. Chem.* **1996**, *100*, 18852–18858.