Topological Effects in Bridge-Mediated Electron Transfer Between Redox Molecules and Metal Electrodes

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Abstract: Electron-transfer rates between ferrocene and gold were measured for a series of alkanethiolate-based monolayers in which ferrocene groups were linked to gold via bridges that included phenyl rings with varying isomeric substitution patterns attached directly to one of the cyclopentadiene rings on ferrocene. Electron transfer was substantially faster (factor of 10) in monolayers with a 1,4-substituted phenyl ring in the bridge relative to that in monolayers with a 1,3-substituted ring in the bridge. The ferrocene/gold electronic coupling is, therefore, much stronger in the former case, despite the fact that the directly bonded pathway between ferrocene and gold is shorter in the latter case. This finding provides definitive evidence for a topological effect (meaning an effect relating to the position of substitution on a bridge component) on the rate of bridge-mediated electron transfer between a redox molecule and a metal electrode for a bridge that includes both aromatic and aliphatic subunits linked together. The effect is somewhat moderated when the chain length of the (non-ferrocene-containing) alkanethiol coadsorbate is changed. It is thought that in such cases the bridge no longer adopts a fully extended conformation and that the electronic coupling then includes contributions from nonbonded pathways involving alkanethiolate chains adjacent to the ferrocene group in the monolayers.

Introduction

The term “molecular wire” has been used for decades to describe the behavior of structures that promote strong electronic coupling and rapid electron transport over long distances. Such structures play a central role in many supramolecular assemblies being proposed for use in molecular-scale electronic devices and technologies.[1−4] Examples of “molecular wire” structures that have been studied both theoretically and experimentally include simple polyenes;[5−11] poly-*p*-phenylenes, phenylenevinylenes, and phenylacetylenes;[12−18] fused aromatic ring systems;[19,20] oligomers of organic heterocycles;[21,22] oligoporphyrins;[23] and, more recently, carbon nanotubes.[24−28] The strong long-range electronic coupling that is promoted by such structures is now recognized to be a common feature of many physical phenomena and devices, including thermal and photoinduced electron transfer in bridged donor−acceptor molecules,[7−17,19−21,29,30] long-range electron transfer in monolayers on electrodes,[31−38] electronic conduction through mo-

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lecular bridges as studied using proximal probe and/or nanolithographically defined contacts,[39−48] and field emission from chemically modified field emitter tips.[49]

The importance of extended electronic conjugation in promoting long-range electronic coupling is widely recognized. However, the importance of the topological connectivity pattern among conjugated groups in molecular bridges, particularly bridges that include multiple discrete subunits, is less widely recognized and is not yet well-understood. The effects of subunit connectivity in supramolecular assemblies are likely to be important in several areas in molecular electronic technology, particularly in molecular switching structures in which one seeks to exercise active control of the coupling across multicomponent bridges via manipulation of the structure and/or properties of a particular bridge subunit. There is evidence that direct linkages across the 1,3 positions of benzene rings are less effective than linkages across the 1,4 positions in promoting long-range electronic coupling, despite that fact that the 1,3 linkage is shorter.[29,50,51] Similar effects have been noted in pyridyl rings,[52] larger fused ring systems,[53] and even in certain nonconjugated fused-ring systems;[54,55] however, a firm understanding of how the connectivity pattern among bridge subunits will affect coupling across longer bridges or bridges that include multiple subunits, some of which may be aromatic and some of which may be aliphatic, is not in place. Additionally, it is not clear how such effects in bridge-mediated electronic coupling between redox molecules will be manifested when one of the redox molecules is replaced by a metal electrode. It has been suggested that making such a replacement has only minor effects on electronic coupling mediated by aliphatic bridges;[33,37] however, quantitative comparisons are lacking for conjugated bridges. A firm understanding of these effects would greatly facilitate the development of molecular electronic technologies.

We present here an experimental study of topological effects (meaning effects relating to the connectivity pattern among bridge components) in bridge-mediated electron transfer between redox molecules and metal electrodes. The work is based upon a large body of prior work using electrochemical techniques to study long-range electron transfer in organized monolayer structures on electrode surfaces.[34] In the present case, ferrocene groups are used as model redox molecules, and the monolayers are formed using the well-studied gold-alkanethiolate self-assembly techniques.[33,35−37,56−62] A unique feature of the present monolayers is that the bridge linking ferrocene to gold includes a phenyl ring that is attached directly to one of the cyclopentadiene rings on ferrocene. Two different structures were studied, one in which the phenyl ring is substituted at the 1 and 4 positions (monolayer type A) and another in which it is substituted at the 1 and 3 positions (monolayer type B). In both cases, the distal position on the phenyl ring is linked to a 9-mercaptononyloxy chain via the oxygen atom. Figure 1 presents an illustration of the structures envisioned for the two monolayer types. The monolayers were studied using a variant of the ac voltammetry technique.[63] This technique is well-suited to studying redox kinetics in monolayers because one can study processes over a wide time scale simply by manipulating the frequency of the applied voltage. The voltammetric behavior is readily interpreted in terms of a simple equivalent circuit model from which a value for the standard electron-transfer rate constant can be easily obtained. The standard rate constant is the quantitative indicator of the intrinsic electron-transfer rate, which is proportional to the strength of electronic coupling for systems with a fixed reorganization energy.

The central finding of the present work is that electron-transfer rates are substantially higher (factor of 10) in monolayers that include a 1,4-substituted phenyl ring in the bridge relative to that in monolayers that include a 1,3-substituted ring. This finding is, to our knowledge, the first definitive demonstration of a topological effect on the rate of electron-transfer between a redox molecule and a metal electrode. The result is consistent with prior work on intervalence charge-transfer in similarly substituted bis(ferrocene) and bis(ruthenium) complexes, albeit in a system in which one of the redox molecules is replaced by an electrode. The effect is somewhat moderated when the overall monolayer structure is changed by changing the chain length of the (non-ferrocene-containing) alkanethiol coadsorbate that

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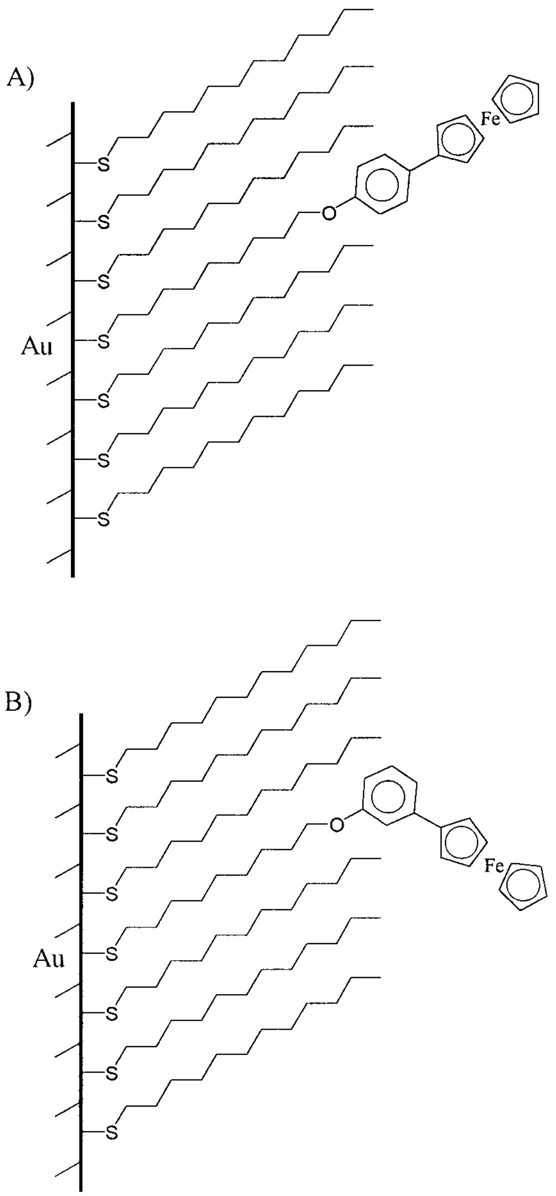

Figure 1. Illustrative structures of monolayers studied in this work. Top, mixed monolayers of 1,4-Fc$-$C$_6$H$_4$$-O-C_9H_{18}$$-SH/C_{12}H_{25}$$-$SH (type A); bottom, monolayers of 1,3-Fc$-$C$_6$H$_4$$-O-C_9H_{18}$$-SH/C_{12}H_{25}$$-$SH (type B).

comprises the majority of the monolayer. It is thought that insuch cases the bridge linking ferrocene directly to gold no longer adopts a fully extended conformation and that the electronic coupling includes contributions from pathways involving the alkanethiolate chains adjacent to the ferrocene group in the monolayers.

Experimental Methods

Materials. Gold wire for electrodes (0.127 mm diameter, Premion grade, >99.99% pure) was obtained from Alfa Aesar. Ethanol (100%) was from AAPER Alcohol and Chemical Company. Perchloric acid (70% in water, reagent ACS grade) was obtained from Acros. Water was purified with a NANOpure system (Barnstead) to a resistivity of at least 12 MΩ cm. Alkanthiols 1-mercaptononane, 1-mercaptodecane, 1-mercaptoundecane, 1-mercaptododecane, and 1-mercaptotetradecane (>98% pure) were obtained from Aldrich. 1-Mercaptotridecane, mercapto alcohols 10-mercaptodecanol and 9-mercaptononanol, and the two phenylferrocene-containing alkanethiol derivatives were prepared as described in the Supporting Information.

Electrode and Monolayer Preparation. Gold electrodes were prepared by first melting the tip of a gold wire in a Bunsen burner flame to form a small sphere with a diameter of approximately 0.50 mm. The spheres were then etched in dilute aqua regia (4:3:1 H_2O:HCl:HNO_3) for one minute, after which mixed monolayers were formed on the electrode surfaces by immersing the electrodes in a coating solution of thiols in ethanol. The coating solutions were typically 1mM total thiol concentration at a 1:1 ratio of ferrocenyl-thiol to nonelectroactive coadsorbate thiol. Electrodes were exposed to the coating solution for 10 minutes, then they were rinsed with water, followed by 2-propanol, and were placed in a 500-μM ethanolic solution of the coadsorbate thiol at ~45 °C for at least thirty minutes. The heat treatment step in coadsorbate thiol is used to displace weakly bound adsorbates, thereby filling defect sites and creating well-ordered self-assembled monolayers in which the ferrocene-containing adsorbate is the minority constituent. The electrodes were then cooled slowly (over two or more hours) to room temperature on the benchtop prior to electrochemical characterization.

Electrochemical Characterization. After rinsing with 2-propanol and then with water, the monolayer-coated electrodes were placed in a three-electrode cell containing an aqueous 1.0 M perchloric acid electrolyte and a silver/silver chloride/saturated potassium chloride reference electrode and platinum wire counter electrode. The working electrode was positioned so that the gold sphere was held just below the surface of the electrolyte with as little of the wire exposed to the solution as possible. An electrical connection was made at the end of the wire that was opposite to the sphere. Coated electrodes were characterized using a recently described ac voltammetry method.[63] The ac voltammograms were collected on a Solartron SI 1260 impedance/gain phase analyzer connected to a Solartron SI 1287 electrochemical interface.

Results

Figure 2 presents a pair of ac voltammograms acquired at two monolayer-coated gold electrodes, one in which a ferrocene group was linked to gold by a bridge system that included a 1,4-substituted phenyl ring that was linked to one of the cyclopentadienyl rings on ferrocene (monolayer type A), and another in which the bridge system was similar except that it utilized the 1,3-substituted regioisomer (monolayer type B). Both voltammograms exhibit the expected feature near +0.4 V that corresponds to ferrocene oxidation/reduction. The peak potential is nearly the same in both voltammograms, which suggests that the ferrocene groups experience similar local microenvironments in each case. Both voltammograms are also relatively noisy, which probably reflects instrumental and/or environmental noise at these lower frequencies. The noise was greatly diminished at higher frequencies.

Peak currents in reversible ac voltammograms may be used to estimate the amount of redox species immobilized on an electrode surface using eq 1, where $I_{\mathrm{avg}}(E_{\mathrm{o}})$ is the average ac peak current in the voltammogram; n is the number of electrons transferred per redox event; F is the Faraday constant; R is the universal gas constant; T is the temperature; and E_{ac} is the amplitude and f, the frequency, of the applied ac voltage perturbation.[64] The equation may be solved for N_{tot}, the total number of moles of redox-active species giving rise to the peak.

$$I_{\mathrm{avg}}(E_{\mathrm{o}}) = 2nfFN_{\mathrm{tot}}\frac{\sinh(nFE_{\mathrm{ac}}/RT)}{\cosh(nFE_{\mathrm{ac}}/RT) + 1} \qquad (1)$$

Thus, the peak in Figure 2a for monolayer A corresponds to approximately 3.7×10^{-14} moles of ferrocene and the peak in Figure 2b for monolayer B, to 1.5×10^{-14} moles of ferrocene. These values may be expressed as surface coverages by

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[64] O'Connor, S. D.; Olsen, G. T.; Creager, S. E. *J. Electroanal. Chem.* **1999**, *466*, 197−202.

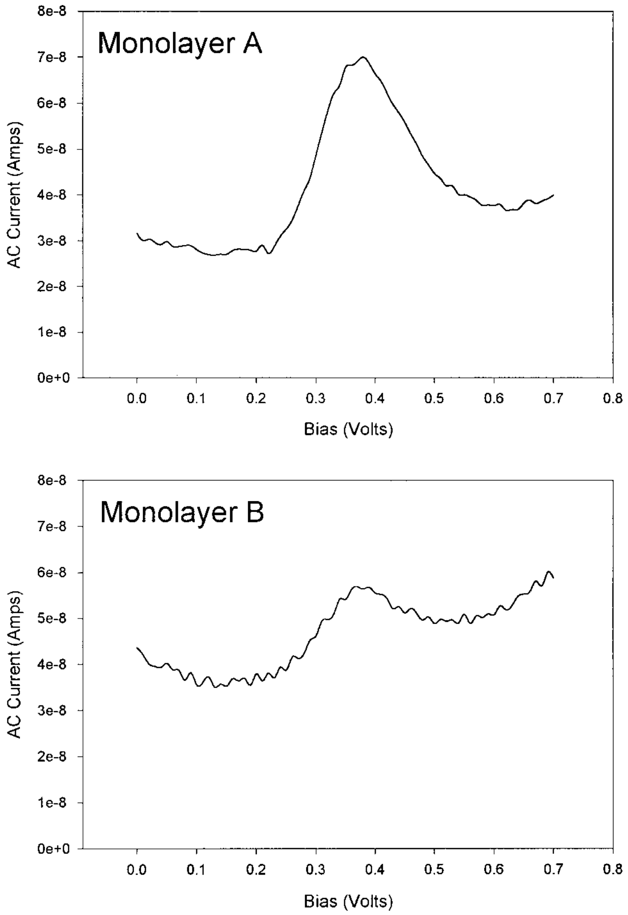

Figure 2. Comparison of ac voltammograms at 10 Hz of mixed monolayers of 1,4-Fc$-C_6H_4-O-C_9H_{18}-$SH (type A) and 1,3-Fc$-C_6H_4-O-C_9H_{18}-$SH (type B) with dodecanethiol. Surface coverages of the redox-active species are approximately 4.7×10^{-12} mol cm^{-2} and 1.9×10^{-12} mol cm^{-2}, respectively.

normalizing to the estimated electrode area of approximately 0.008 cm^2 (obtained by a measurement of the diameter of the ball with a micrometer and assuming the ball is a sphere). Thus, the estimated ferrocene surface coverage for monolayer A is 5×10^{-12} moles cm^{-2}, and that for monolayer B is 2×10^{-12} moles cm^{-2}. Both of these values are less than one percent of that corresponding to a close-packed ferrocene monolayer.[56,57] The ferrocene-containing adsorbate is, therefore, present as a minority constituent in a monolayer for which the overall structure is probably dominated by the majority constituent, in this case, dodecanethiol.

Variable-frequency ac voltammetry is useful for studying redox kinetics in monolayers via the frequency dependence of the peak and background currents.[38,59,63] Qualitatively, as the frequency increases, the peak current will diminish relative to the background, reflecting the fact that the time scale of the fluctuating potential is becoming fast relative to that for electron transfer. Figure 3 presents four representative ac voltammograms which illustrate this behavior for a monolayer of type A over a frequency range between 10 and 10 000 Hz. At 100 Hz and below, the peak size is fixed relative to background, which indicates that electron transfer is fast on the experimental time scale in this regime. At 1000 Hz, the peak is clearly diminished relative to the background, and at 10 000 Hz it is nearly indistinguishable from background. This behavior is indicative of the fact that electron transfer can no longer keep up with the oscillating potential at higher frequencies.

The phenomenon of diminishing peak size with increasing frequency may be treated quantitatively by using a Randles equivalent circuit model to fit a plot of the ratio of the peak current to the background current versus log(frequency).[38,59,63] The primary fitting parameters are the standard electron-transfer rate constant, the specific capacitance of the electrode−solution interface, and the surface coverage of the redox species. Figure 4 presents data plots and fitted curves for representative monolayers of types A and B. The best-fit standard rate constant is approximately 3000 sec^{-1} for monolayer A, and approximately 300 s^{-1} for monolayer B. It is remarkable and significant that these rate constants differ by so much (factor of 10) for structures that differ only in the substitution pattern of a single aromatic ring embedded within the bridging group. This aspect of the results will be considered in greater depth in the discussion section.

Table 1 presents the results of a series of measurements of electron-transfer rates on monolayers similar to those in Figure 1, except that the length of the nonelectroactive alkanethiols that comprise the majority of the monolayer were systematically varied. The data fall naturally into two groups: one in which the alkanethiol chain is long (11 or more methylene units) and another in which it is short (10 or fewer methylene units). When the chain is long, the rate constants for the two monolayer types consistently differ by a factor of approximately 10 and are relatively insensitive to the chain length of the coadsorbate alkanethiol. This behavior is consistent with the monolayers' adopting a conformation in which the bridging groups are fully extended, such that the electronic coupling is dominated by the direct through-bond pathway of the bridge that includes the phenyl ring. In contrast, when the alkanethiol chains become shorter than 11 methylene units, the electron-transfer rate constants for both monolayers increase dramatically (10−30 times), and the difference in rates between the two monolayer types is diminished. This behavior is consistent with the bridging groups' adopting a conformation whereby the phenylferrocene units are able to "bend over" at the aryl ether linkage and contact the monolayer surface. In this conformation, the electronic coupling may be dominated by contributions from the surrounding alkanethiol monolayer, and the effect of the benzene ring on the electronic coupling is diminished. In fact, the standard electron-transfer rate constants of approximately 25 000 s^{-1} and 13 000 s^{-1} obtained for monolayers of types A and B using decanethiol as coadsorbate are not greatly different from the rate constant of 27 500 s^{-1} that were reported in a related study for a monolayer in which ferrocene was directly linked to a gold electrode by a decanethiol chain.[59] This result supports the hypothesis (previously put forth by Finklea and co-workers for a related system[65]) that electronic coupling in alkane-based monolayers in which the adsorbate is not fully extended may be dominated by contributions from the adjacent coadsorbate species.

The table also presents data for two monolayers in which the terminal functional group on the alkanethiol coadsorbate is changed from a hydrogen to a larger and more polar hydroxyl group. The effect on monolayers of type A is minimal, amounting to little more than a shift in the carbon chain length at which the transition from slower rates (extended conformation) to faster rates (bent conformation) occurs. The effect on monolayers of type B is slightly different. The transition from slower to faster rates also is shifted to longer chain lengths; but

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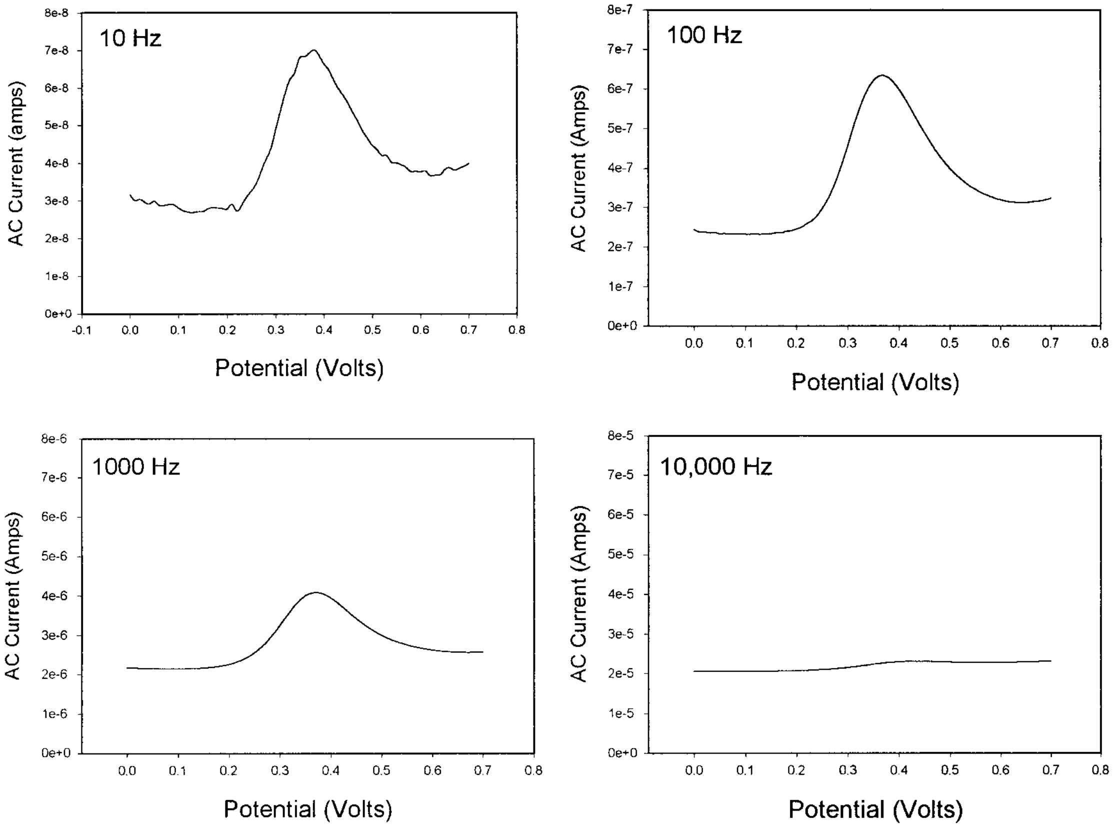

Figure 3. AC voltammograms of a mixed 1,4-Fc$-C_6H_4-O-C_9H_{18}-$SH/$C_{12}H_{25}-$SH (type A) monolayer on a gold electrode at selected frequencies from 10 Hz to 10 000 Hz. As frequency increases, the peak current diminishes relative to the background.

in addition, the faster rate constant obtained with the shorter coadsorbate chains is not so large as it is for the hydrogen-terminated alkanethiol layers of comparable length. This subtle difference in behavior for the two monolayer types may be attributed to a slight difference in phenylferrocene orientation at the monolayer-solution interface; that is, the surface of the hydroxyl-terminated monolayer is polar and may, therefore, enforce a conformation whereby the ferrocene group in monolayers of type B is positioned slightly above and not in direct contact with the monolayer-solution interface. These effects highlight the importance of monolayer structure and, particularly, conformation in controlling electronic coupling factors and electron-transfer rates for nonrigid systems.

Discussion

It is of interest to compare the rate constants derived from Figure 4 for the two monolayer types illustrated in Figure 1 with the values for comparable monolayer-coated electrodes that lack conjugated groups in the bridge between the redox molecule and the electrode. Prior work on the electrochemistry of related ferrocene-based monolayer systems provides a means for estimating electron-transfer rate constants for monolayers in which ferrocene groups are directly linked to gold electrodes by thiol-terminated alkane chains.[59] From data on monolayers with nonane, decane, undecane, and dodecane chains linking ferrocene to gold, we estimate by extrapolation that a monolayer with a tetradecane chain linking ferrocene to gold (corresponding to replacement of the 1,4-substituted benzene ring in monolayer A with a butyl chain and treating the ether oxygen as another methylene unit) should exhibit a value of approximately 90 s^{-1} for the standard electron-transfer rate constant for ferrocene. This value is much smaller than the value of 3000 s^{-1} obtained from the fit in Figure 4a for a monolayer of type A. The discrepancy between these two values strongly suggests that the 1,4-substituted phenyl ring greatly enhances the long-range electronic coupling relative to an alkyl chain of comparable length. This result is consistent with prior work that demonstrates particularly strong coupling and rapid redox kinetics for monolayers that contain fully conjugated bridges.[35,38] It stands in contrast to work from Cheng and co-workers, who showed that introduction of electronic conjugation into a bridge by replacement of a carbon−carbon single bond with a double or triple bond yielded a net decrease in the electron-transfer rate at a monolayer-coated electrode.[66] The present findings indicate that what matters most is not the presence of electronic conjugation, but the extent of coupling between conjugated fragments in the bridge and the donors and acceptors attached to the bridge.

A similar line of thinking may by used to interpret the redox kinetics for monolayer B. The extrapolation described above may be used to estimate that a monolayer with a tridecane chain linking ferrocene to gold (which corresponds to replacement of the 1,3-substituted benzene ring with a propyl chain) should exhibit a standard electron-transfer rate constant of approximately 360 s^{-1}, which is in fairly good agreement with the value of 300 s^{-1} obtained for monolayer B from the fit in Figure 4b. The good agreement between these two values suggests that the contribution of the phenyl ring to the overall bridge-mediated electronic coupling in this case is not greatly different from that of an alkane chain of comparable length. The dramatic difference in the contribution of the aromatic ring to the electronic coupling in monolayers A and B highlights the importance of considering not just the degree of conjugation of the bridge components, but also the topology/connectivity of the linkages within the

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(66) Cheng, J.; Saghiszabo, G.; Tossell, J. A.; Miller, C. J. *J. Am. Chem. Soc.* **1996**, *118*, 680−684.

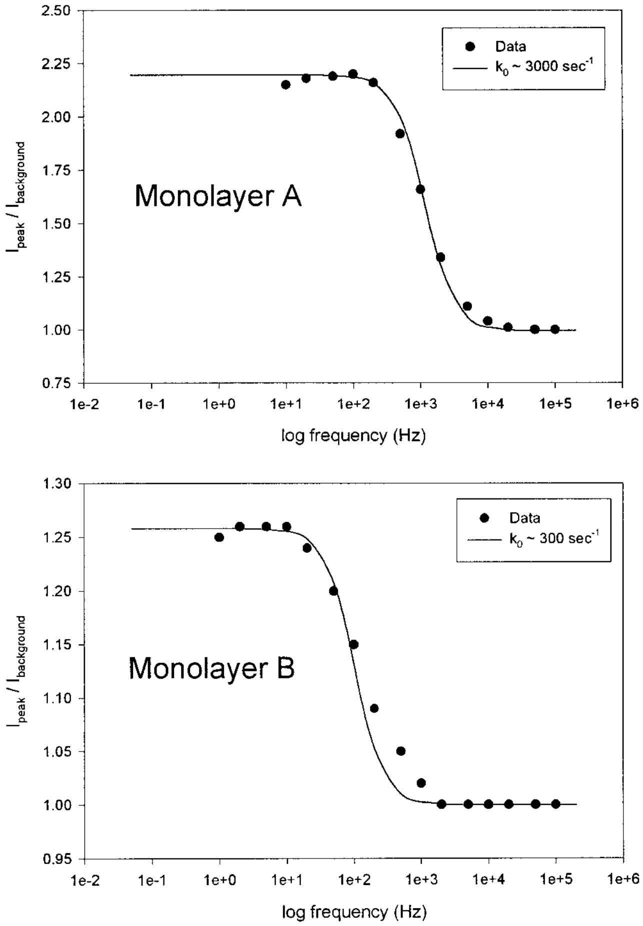

Figure 4. $I_{peak}/I_{background}$ versus log(frequency) plots for mixed monolayers of 1,4-Fc$-C_6H_4-O-C_9H_{18}-$SH (type A) and 1,3-Fc$-C_6H_4-O-C_9H_{18}-$SH (type B) with dodecanethiol as the coadsorbate.

Table 1. Electron-transfer Rates for the 1,4-Fc$-C_6H_4-O-C_9H_{18}-$SH (Type A) and 1,3-Fc$-C_6H_4-O-C_9H_{18}-$SH (Type B) Monolayers with Various Coadsorbates

	k_o (sec^{-1})	
coadsorbate	type A	type B
$C_{14}H_{29}-$SH	3.0 E + 03	n/a
$C_{13}H_{27}-$SH	2.9 E + 03	5.0 E + 02
$C_{12}H_{25}-$SH	3.1 E + 03	3.0 E + 02
$C_{11}H_{23}-$SH	2.8 E + 03	3.0 E + 02
$C_{10}H_{21}-$SH	2.5 E + 04	1.3 E + 04
$C_9H_{19}-$SH	3.5 E + 04	9.1 E + 03
HO$-C_{10}H_{20}-$SH	3.3 E + 03	3.1 E + 02
HO$-C_9H_{18}-$SH	2.6 E + 04	1.6 E + 03

bridge. Electronically conjugated groups will not provide any special enhancement of long-range electronic coupling in bridges unless they are incorporated into the bridge in such a way that the molecular orbitals of the conjugated group can couple with the electronic orbitals of the redox molecule, the bridge, and the metal electrode to provide an overall enhancement of the coupling across the bridge.

The topological effects observed in the present work are consistent with prior work on electronic coupling and electron-transfer mediated by bridges that include phenyl rings with varying isomeric substitution patterns. For example, Richardson and Taube reported in 1983 on charge-transfer spectroscopy data for cyanopyridine- and dicyanobenzene-bridged mixed-valent ruthenium dimers which indicate that electronic coupling is much stronger (6−10 times) across 1,4-substituted bridges than across 1,3-substituted bridges.[29] Similar behavior was noted in more recent work by Patoux and co-workers on mixed-valent bis(cyclometalated) ruthenium dimers[51] and on mixed-valent diferrocenylbenzenes[50] and by Liu and co-workers in work on mixed-valent complexes containing ferrocenylpyridine and rutheniumamines.[52] These observations were rationalized intuitively by Richardson and Taube as reflecting "general experience with the transmission of electronic effects through conjugated bond systems".[29] A more quantitative approach was followed by Patoux and co-workers, who considered the manner in which metal, ligand, and bridging-group molecular orbitals combine to dictate the electronic coupling between two ferrocenyl groups attached across a bridging benzene ring.[50] They explained the poor coupling in 1,3-diferrocenylbenzene in terms of a quantum interference phenomenon involving a cancellation of contributions of two separate electron-transfer pathways, each involving a different bridge orbital. The coupling depends on both the energy and the sign of the relevant orbitals, and a cancellation occurs when the two principal orbitals involved have similar energies (i.e., they are quasi-degenerate) but different signs on the relevant carbon atoms. In the case of 1,4-diferrocenylbenzene, the two principal bridge orbitals involved in the coupling have similar energies and signs on the relevant carbons, such that their contributions are additive and do not cancel. It seems likely that a similar effect is operative in the present work.

Nearly all of the prior work on topological effects in bridge-mediated electron transfer has been directed at understanding electronic coupling in bridged donor−acceptor molecules. To our knowledge, the present work is the first to demonstrate a strong topological effect in bridge-mediated electron transfer between a redox molecule and a metal electrode. It is not obvious that one would expect to see such an effect in a system involving a metal electrode. Topological effects in bridge-mediated electron transfer depend critically upon the symmetry relationships among the relevant orbitals; for example, in the bis(ferrocenyl)benzene system studied by Patoux and co-workers, the coupling is thought to depend on the symmetry of the $d_{x^2-y^2}$ orbitals on the iron atoms, the p orbitals on the bridgehead cyclopentadienyl carbons, and the molecular orbitals of the bridging benzene bridge.[50,67] The continuum of electronically delocalized orbitals in the metal electrode may not have the proper symmetry requirements to achieve topological control of the electronic coupling. In fact, the present work demonstrates that the topological effects in electronic coupling across substituted phenyl rings can still be achieved even when only one position on the ring is attached to a redox molecule and the other position is attached to an alkoxy chain that is linked at its other end to a gold electrode. Further work will be required to establish the generality of this result; however, if it proves general, it would suggest that one can achieve topological control of bridge-mediated electron transfer even when only one participant in the reaction has the necessary symmetry requirements for selective coupling with the relevant bridge orbitals.

The results presented in Table 1 suggest strongly that electron-transfer rates in the present monolayers depend critically on the conformation of the bridging group that links the redox molecule to the electrode. This idea is also consistent with prior work on related systems. For example, Finklea and co-workers have studied alkanethiol-based monolayers in which the chain lengths of the electroactive (ruthenium complex) and nonelec-

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(67) Boukheddaden, K.; Linares, J.; Bousseksou, A.; Nasser, J.; Rabah, H.; Varret, F. *Chem. Phys.* **1993**, *170*, 47−55.

troactive components are very different and have suggested that in such cases, the monolayers adopt “looped” conformations in which the electronic coupling pathway becomes dominated by contributions from the nonelectroacive components in the monolayer.[65] These effects are important because they re-affirm that one must consider both bridge primary structure and conformation to fully understand the relationship between structure and electronic coupling.

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Supporting Information Available: The information includes synthetic procedures and ^{1}H NMR data. This material is available free of charge at http://pubs.acs.org.

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