The Dependence of Electron Transfer Efficiency on the Conformational Order in Organic Monolayers

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The electron transfer through an organized organic monolayer of alkyl chains adsorbed on a silicon wafer has been studied. The silicon was used as an electrode in a three-electrode electrochemical cell, and the current versus voltage response was measured. The results show that when the chains in the monolayer are in the "all trans" configuration, the charge transfer efficiency is higher than when the chains have a "gauche" configuration. A mechanism rationalizing all the observations is suggested.

Electron transfer (ET) processes involving organic molecules are relevant to many biological systems, like vision and photosynthesis (*1*). Therefore, these processes have been studied in much detail, both theoretically (*2–5*) and experimentally (*6–10*). Much attention has been paid to the effect of the intervening material between the donor and the acceptor on the ET rate (*2–11*). One of the central issues in this field is the mechanism of long-range ET, that is, how the electronic coupling of donor and acceptor sites is mediated by the electronic properties of the "bridge." For covalently bonded systems, the coupling is thought to occur "through bond," as opposed to "through space," ET. The donor and acceptor are sometimes situated so far from one another that they are expected to be only weakly coupled. Nevertheless, the ET reaction in donor-bridge-acceptor systems can occur extremely rapidly and with high efficiency and specificity (*12*) over large distances, even through the sigma-bonded networks.

Organized organic monolayers (OOM) are an ideal medium to investigate the effects of both length and structural parameters of the bridge on ET, because their organization ensures a well-defined length and conformation. The study of ET through organic monolayers was pioneered by Kuhn and co-workers (*6*, *13*). Their approach was to "dissolve" inside an OOM a dye that, when excited by light with the appropriate wavelength, served as an electron donor and to combine it in a supramolecular structure with an electron acceptor also mixed inside the OOM. These studies established the dependence of the ET efficiency through such phases on the distance between the electron donor and acceptor. In other studies, measurements of the current (at a given voltage) between two aluminum layers, separated by fatty acid monolayers and multilayers, showed an exponential decrease of the current with an increase in the length of the alkyl chain (*6*). Miller (*10*) has explored the heterogeneous ET through organized monolayers of thiols on gold electrodes, in particular the role of tunneling and the dependence of the ET on the overpotential. Similar experiments have been performed by Chidsey (*7*) using a structure in which the redox couple is tethered to the layer. An unexpectedly high conductance through bridges of aliphatic chains comprising more than 10 carbon atoms was measured with scanning tunneling microscopy (*14*).

The present study focuses on the effect of the conformation of the bridge on the ET process, when the bridge is in the form of an organized monolayer of alkyl chains [formed from octadecyltrichlorosilane (OTS)], which is spontaneously adsorbed on silicon (*15*). The properties of this monolayer have been investigated by various techniques, and it was established that, when formed, the chains are in an "all trans" configuration. On heating of the surface above 453 K, the chains undergo irreversible conformational changes (*16*) in which some of the trans bonds are transformed to a "gauche" conformation (*17*).

To investigate the ET properties through this organized monolayer, OTS was adsorbed by self-assembly on (100) *n*-Si wafers (ρ = 0.02 to 0.1 ohm·cm, that is, $n = 0.4 \times 10^{17}$ to 2×10^{17} cm^{-3}). Before adsorption, the silicon wafers were cleaned, etched in 5% hydrofluoric acid solution for 40 s, and rinsed in deionized water for an additional 2 min. They were then treated in an ultraviolet ozone cleaning system for 5 min to grow a 5 to 10 Å thick oxide layer (*18*), which was necessary for OTS adsorption. They were used as electrodes in a three-electrode electrochemical cell, and the current versus voltage (I-V) response was measured in an aqueous solution of 0.5 M K_2SO_4 with the redox couple $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ (0.01 M each). The counter and reference electrodes were platinum gauze and wire, respectively. The I-V curves were measured, both in the dark and when the electrode was illuminated by white light (intensity of some 80 mW/cm^2) and before and after heating of the silicon-OTS surface to 495 to 500 K in a vacuum chamber (at a pressure of 10^{-6} torr) for 15 min. For reference, the I-V curves of a bare silicon wafer, which underwent the same procedure, were also measured. The current measured in these experiments results from the flow of electrons between the redox species in the electrolyte $\{[Fe(CN)_6]^{3-}$ or $[Fe(CN)_6]^{4-}\}$ and the silicon wafer. The difference between the current measured in the dark and the current measured when the cell is illuminated is the photocurrent.

The direction of the current is defined here as in (*19*). When the *n*-Si is negatively biased, the resulting forward current in the dark is due primarily to electron injection from the semiconductor into the electrolyte and is presented here as current flow in the negative direction. Conversely, when the *n*-Si is positively biased with respect to the counterelectrode, that is, reverse bias is applied to the semiconductor, then ideally no current should flow in the dark. However, when the semiconductor is under strong reverse bias, electrons can be injected into the semiconductor by tunneling through the insulating spacer layer. Note that the spacer consists of both an oxide layer and OTS film. Under illumination, electron hole pairs are created in the silicon and are separated by the electric field near the surface. Under reverse bias, holes can flow to the surface and be injected into the electrolyte, thus leading to the photocurrent.

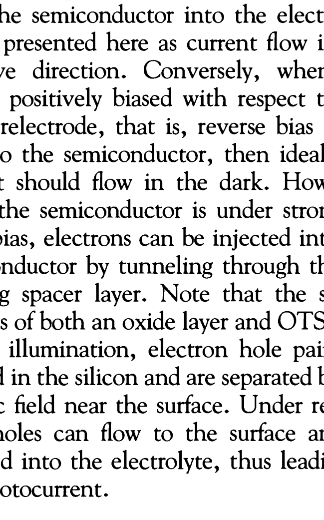

Fig. 1. Current versus the applied voltage on a bare silicon electrode for the dark process (solid line) and when the surface is illuminated (dashed line). (**A**) For bare silicon before heating and (**B**) after it was heated to 495 K in vacuo.

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The band gap of silicon is 1.12 eV. The highest occupied molecular orbitals (HOMO) of the alkane chain lie about 5 eV below the valence band edge of the silicon, and the lowest unoccupied molecular orbitals (LUMO) of the alkane lie near the vacuum level, more than 5 eV above the valence band edge.

Figure 1 presents the I-V curve of the bare silicon wafer in the dark (solid line) and under illumination (dashed line). The I-V curve in Fig. 1A was measured before heating of the wafer, whereas the curve in Fig. 1B was measured after the silicon wafer was heated to 495 K. The values of the reverse currents, measured at a bias potential of +0.2 V, are summarized in Table 1. Upon heating of the silicon wafer, a sixfold decrease in the reverse dark current is observed, as expected when a thicker oxide layer is formed. We may deduce that the thin oxide layer does not efficiently block the flow of holes from the silicon electrode.

Figure 2 presents the same type of measurements as described above, but for silicon coated with OTS. The current was measured before (Fig. 2A) and after (Fig. 2B) the silicon with the monolayer was heated. The photocurrent at 0.2 V decreases by a factor of 60 on heating of the electrode that is covered with OTS, in sharp contrast to the 30% decrease observed in the bare silicon (see Table 1). This 30% drop in the current could arise from a growth of the original oxide layer on the silicon during the heating process. This oxidation, however, cannot account for the large decrease observed on the heating of the Si covered with OTS. Furthermore, repetitive I-V cycles of the bare silicon revealed fast oxidation for each cycle performed, whereas OTS-coated silicon showed slower oxidation.

The reverse current under illumination, in the case of the OTS-coated silicon, seems to be much more affected by the heating than is the dark current, which suggests different charge transfer mechanisms in the dark and under illumination. The correlation between the decrease in the photocurrent and the conformational change of the monolayer after heating indicates that the all-trans monolayers transfer charge more efficiently than the chains that went through the trans-gauche isomerization. Before this conclusion is drawn, some important experimental caveats must be addressed.

When ET is studied through monolayers, the role of pinholes in the monolayer must be considered. It is essential to verify whether the observed current is caused by direct contact between the electrolyte and the silicon at the pinholes or by transfer through the monolayer. To verify that the ET occurs through the monolayer, we consider the difference between the forward currents in Figs. 1A and 2A. Whereas in the case of bare silicon both forward and reverse currents are measured, no appreciable forward current is observed (within the applied potential range) when the silicon is coated with OTS. This observation holds for both the dark and photoinduced currents. We interpret the sharp decrease in forward current, when a monolayer is adsorbed on the silicon, as a result of the monolayer blocking the direct access of the electrolyte to the silicon.

To establish further the role of the monolayer, a "bad" monolayer was examined. This monolayer was less well packed than the one used for the experiment presented in Fig. 2. The quality of the monolayer was determined from measurements of its contact angles with water and bicyclohexyl (BCH). Whereas the well-packed monolayer showed a contact angle of 110° ± 1° for water and 48° ± 1° for BCH, the angles for the bad monolayer were 105° ± 1° and 45° ± 1°, respectively. The reduction in the photocurrent after heating of the bad monolayer is only by a factor of 10, whereas for the good monolayer the reduction was by a factor of almost 60. Clearly the results obtained with the bad monolayer represent an intermediate case between the bare silicon and the silicon covered with a well-packed OTS.

Upon adsorption of the OTS layer, the onset voltages for the reverse and forward currents on illumination shift to negative potentials by about 250 and more than 500 mV, respectively. Whereas the shift for the reverse current is about the same as the decrease in the work function (about 200 meV) measured by a Kelvin probe, the shift in the forward current is considerably larger. The change in the onset voltage when the monolayer is adsorbed and the fact that the change is not the same for the forward and reverse currents are an indication that a barrier exists between the silicon and the electrolyte when OTS is deposited on the surface and that the barrier is not the same for forward and reverse ET. The existence of such a barrier is inconsistent with the possibility of direct contact between the electrolyte and the silicon. Therefore, the "monolayer structural effect" is not a result of pinholes. The effect is caused by charge transfer through the chains and not by irregularities in the monolayers that would allow access of the electrolyte to the silicon surface.

We now turn to the question of the mechanism of ET through the organized monolayer and the reason for its dependence on the conformation of the chains. One possible explanation for the charge transfer process under illumination is hole transfer through the occupied molecular orbitals of the chains. This argument follows the ideas suggested by McConnell (*20*), Hoffmann (*21*), and others (*2, 11, 12*) in which the charge transfer is mediated by electronic coupling through the bonding and antibonding orbitals of the "inert" spacer layer. Previous theoretical studies have demonstrated the "all trans effect" (*3, 12, 22*), and it is well known that the all trans configuration leads to stronger electronic coupling through the chain. The importance of non-nearest neighbor interactions has been used to explain this large coupling. The experimental confirmation of an all trans effect in rigid alkane ring spacer (*12*) can be understood as an ex-

Table 1. Reverse current values. The current was recorded when a potential of +0.2 V was applied on the silicon.

Sample	Current (μA)	
	Dark	Under illumination
Bare Si*	30 ± 5	450 ± 5
Bare Si after heating	5.0 ± 0.5	300 ± 5
Si covered with OTS	4.5 ± 0.5	18.5 ± 0.5
Si covered with OTS after heating	0.20 ± 0.05	0.45 ± 0.05
Si covered with "bad" monolayer of OTS†	7.0 ± 0.2	22.0 ± 0.2
Si covered with "bad" monolayer of OTS, after heating	1.3 ± 0.1	2.8 ± 0.1

*Bare silicon indicates a control silicon piece treated in hydrofluoric acid and deionized water and then in an ultraviolet ozone cleaning system for 5 min. †"Bad" monolayer was assembled on the Si electrode after heating of the silicon to 495 K in vacuo.

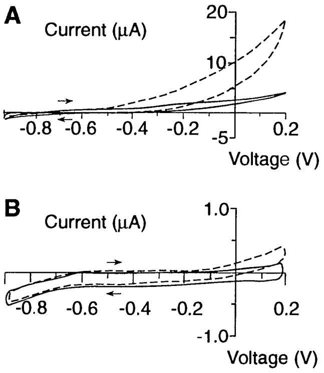

Fig. 2. Current versus potential applied to a silicon wafer coated with an organized organic monolayer. (**A**) Current measured on freshly made monolayer and (**B**) current measured after the silicon electrode with the monolayer was heated to 495 K. The current was measured for the dark process (solid line) and when the surface is illuminated (dashed line).

treme case of a conformational effect on ET. This conformational effect is expressed as the effect of the protein's secondary structure on the rate of long-range electron transfer (*23*).

An alternative perspective on this mechanism arises from a solid-state origin. For the all trans configuration a periodicity exists in the chain, and one can consider the bonding and antibonding orbitals, resulting in a nascent valence band and conduction band, respectively (*24*). In this case, the molecular states through which the coupling occurs are fully delocalized over the chain units. The tunneling of the charge through the layer may be considered as the migration of the electron mediated by the conduction band or as the migration of the hole by way of the valence band. When the chains become disordered, the periodicity (or the symmetry) is broken and the orbitals are less delocalized. Either of these viewpoints appears valid, and it seems likely that they are equivalent.

The large decrease in the reverse current, when OTS covers the electrode, reflects the presence of a wider, and perhaps higher, barrier than is present with just the oxide overlayer on the electrode. In principle, ET between the silicon and the electrolyte can occur either through the HOMO or the LUMO of the intervening phase. When the energy of the electron donating, of the electron accepting, or of both states lies closer to the HOMO than to the LUMO, coupling through the HOMO by way of the hole mechanism should dominate. Because the energy of the valence band edge is closer to the HOMO than to the LUMO, it is likely that this mechanism dominates the hole transfer (reverse current under illumination) and that the LUMO mechanism dominates the electron transfer (forward current).

Alternatively, the shifts in the onset voltage may reflect properties of the oxide layer as much as those of the alkane layer. In particular, defect states in the oxide layer of the electrode may mediate the forward current. Addition of the OTS may block this pathway for the forward current. In this scenario, the charge transfer through the alkane layers could be a mixture of the HOMO and LUMO mechanisms. The results reflect, therefore, the weaker coupling of the LUMO to the defect states of the oxide. Both of these explanations are consistent with the data.

The present experiment demonstrates the important role of symmetry (or periodicity) in the determination of electronic coupling and hence ET efficiency. These results clearly show that the ordered, all trans monolayer has a higher charge transfer efficiency than a disordered monolayer. Furthermore, the data suggest a hole mechanism for the electronic coupling.

Note added in proof: Recently a theoretical analysis of ET (*5*) showed that, for small energy differences between donor and acceptor, a complex distance dependence results. Such a dependence is predicted to be sensitive to the properties of the bridging material. Our results present direct experimental evidence for such sensitivity.

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Crystal Structure, Bonding, and Phase Transition of the Superconducting Na_2CsC_{60} Fulleride

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The crystal structure of superconducting Na_2CsC_{60} was studied by high-resolution powder neutron diffraction between 1.6 and 425 K. Contrary to the literature, the structure at low temperatures is primitive cubic ($Pa\bar{3}$), isostructural with pristine C_{60}. Anticlockwise rotation of the C_{60} units by 98° about [111] allows simultaneous optimization of C_{60}-C_{60} and alkali-fulleride interactions. Optimal Na^+-C_{60}^{3-} coordination is achieved with each sodium ion located above one hexagon face and three hexagon-hexagon fusions of neighboring fulleride ions (coordination number 12). Reduction of the C_{60} molecule lengthens the hexagon-hexagon fusions and shortens the pentagon-hexagon fusions (to ~1.43 angstroms). On heating, Na_2CsC_{60} undergoes a phase transition to a face-centered-cubic $Fm\bar{3}m$ phase, best modeled as containing quasi-spherical C_{60}^{3-} ions. The modified structure and intermolecular potential provide an additional dimension to the behavior of superconducting fullerides and should sensitively affect their electronic and conducting properties.

Superconducting alkali metal fullerides (*1*) with stoichiometry A_3C_{60} (A = K, Rb) adopt a merohedrally disordered face-centered-cubic (fcc) structure (*2*) ($Fm\bar{3}m$). In these solids, each C_{60}^{3-} ion is located at an fcc lattice site and is randomly distributed between two orientations related by 90° rotations about the cubic [001] directions. This type of structural disorder is recognized as being principally responsible for many of the electronic properties of these systems (*3*, *4*), with a close connection existing between the orientational state of A_3C_{60} and its superconducting properties. Superconductivity in the fullerenes has been

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