Photochemical Electron Transfer in Monolayer Assemblies. 2. Photoelectric Behavior in Chlorophyll *a*/Acceptor Systems

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Abstract: A photoelectric effect has been observed in monolayer assemblies of chlorophyll and acceptor molecules deposited on a semitransparent aluminum electrode. The counterelectrode was mercury. With acceptors containing saturated side chains an open-circuit photovoltage of 150 mV and a short-circuit photocurrent of 34 nA cm^{-2} were detected across a load resistor. The quantum yield of electrons per photon was $\sim 2 \times 10^{-4}$, and the maximum power conversion efficiency was $\sim 4 \times 10^{-5}$. The current-voltage behavior was rectifying with a dark conductivity of $\sim 1.5 \times 10^{-13}\ \Omega^{-1}\ cm^{-1}$. If acceptors with unsaturated side chains were used such as ubiquinone or plastoquinone (10 mol % in stearic acid), the conductivity improved by a factor of 10. The open-circuit photovoltage now was 270 mV and the short-circuit photocurrent detected was 140 nA cm^{-2}. The quantum yield was $\sim 2 \times 10^{-3}$ and the maximum power conversion efficiency was $\sim 4 \times 10^{-4}$. The reduction of the quinone group left the photoresponse unchanged. Similarly, the use of the polyisopropene squalene instead of plastoquinone left the photoresponse unchanged. The suggestion is made that the polyisopropene chain may be acting as "nature's molecular wire" making possible the tunnelling of electrons through lipid membranes.

Introduction

In photosynthesis the *functional unit* is composed of several hundred chlorophyll (Chl) molecules in a protein matrix, a special pair of Chl molecules which are the site of primary photochemistry and a series of primary and secondary donors and acceptors all held in place within the thylakoid membrane.[1] Studies on Chl monolayer assemblies are an attempt to devise a *functional unit* which will mimic the photosynthetic unit.

The primary acceptor in bacterial photosynthesis is very likely a ubiquinone molecule with an iron atom (probably Fe^{2+}) nearby.[2,3] In photosystem II of algal and green plant photosynthesis, the primary acceptor is fairly certain to be a plastoquinone molecule.[4,5] The primary donor and acceptor are separated by a barrier of about 40 Å in thickness.[2,6,7] At present, it is not clear how the electron is able to transfer over this large distance with a quantum yield near unity.[8] Bolton[6] has speculated that an overlapping π system extending from donor to acceptor might be involved in this process. To date, no firm evidence is available concerning the electron-transfer mechanism.

We have used the monolayer technique as a convenient method of manipulating lipid barriers of thickness less than 100 Å. In the previous paper[9] we showed that monomeric Chl in monolayer assemblies can function as a transducer of light energy despite concentration quenching. In this paper, we present the results of photoelectric experiments with Chl monolayer assemblies which shed some light on the mechanism of electron-transfer reactions in the presence of lipid barriers.

The concept of a light-driven electron pump was enunciated by Kuhn[10] and Seefeld et al.[11] They proposed that a dye be sandwiched between a high narrow barrier on one side and a low, broad barrier on the other. The dye then could eject electrons over one barrier and should be supplied with electrons via tunnelling through the other barrier. The use of π systems as low barriers has been reported by Schoeler et al.[12] Polymeropoulos et al.[13] have reported observing the photoconductive effect due to a combination of a dye with a synthetic π system. Seefeld et al.,[11] Sugi et al.,[14,15] and Möbius[16] have reported adjustments to the donor and acceptor levels. The experimental methods involved have been detailed by Kuhn et al.[17] and Mann et al.[18]

In monolayer assemblies of Chl, photoconductivity was reported first by Nelson,[19] and later by Meilanov et al.[20] and by Villar et al.[21] The photovoltaic effect in a system of Chl monolayers with sublimed chloranil was reported by Reucroft and Simpson.[22] Recently, Watanabe et al.[23] and Miyasaka et al.[24] have reported high quantum yields of electron transfer in Chl monolayers on SnO_2 conducting glass. Our work is an extension of the photovoltaic studies. We have found a marked influence on the conversion efficiency as a function of the acceptor layer.

Experimental Section

Monolayer assemblies were deposited on a semitransparent (50% transmittance) aluminum film evaporated at 10^{-4} Torr from a tungsten boat. Other electrode materials such as Pt, Au, Cu, Sn, SnO_2, and In_2O_3 were used but were found to be unacceptable. The monolayers were deposited as described previously.[9] The model system took the form shown in Figure 1. One acceptor layer was laid directly onto the aluminum electrode, followed by four layers of chlorophyll (Chl) and finally one buffer layer, usually stearic acid. This last layer protected the Chl from quenching by the second electrode, mercury. In recent experiments, we have been able to remove this layer if an electrolytic solution was the second electrode. The glass slide bearing the aluminum electrode and the monolayer assembly was clamped to a platinum wire mounted on a Teflon block. The platinum thus contacted the aluminum. The mercury electrode had been machined into the Teflon block. The mercury level could be raised gently until it made contact with the monolayer assembly. The entire assembly was placed inside a stainless steel box for shielding. The electrodes were connected via shielded cable to a bank of resistors and a Hewlett-Packard Model 3420B differential voltmeter whose input impedance was substantially better than $10^{10}\ \Omega$. Illumination was by a 40-W Model LKR Unitron lamp filtered by 1 cm of water and by a red filter (Corning CS2-59) through a 2.5-cm hole cut into the steel box. The light intensity was measured with a Kettering Model 65A radiometer. The photovoltage-photocurrent curve was constructed by decreasing the load resistance, R_L, from a maximum of $10^{10}\ \Omega$ to a minimum of $10^5\ \Omega$. The internal resistance of the sample cell was $\sim 10^7\ \Omega$. For the double flash experiment, a wedge mirror was used. The first flash was from a Photochemical Research Associates Model 610A flash lamp with a pulse width at half maximum of 50 μs, filtered by a Corning (CS2-62) filter. The second flash was from a Photochemical Research Associates Model 610C flash lamp with a pulse width at half maximum of 1.5 μs and was unfiltered. The connecting cables were short (5 cm) and detection was by an Analog Devices

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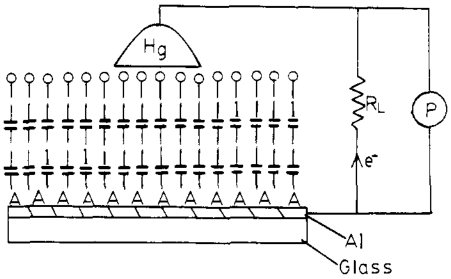


Figure 1. The photovoltaic cell and circuit. Contact with the cell was made by a film of aluminum on glass, and by a drop of mercury. The symbol A represents an accepting species, T represents Chl, and ⫯ represents stearic acid. P is the potentiometer used to measure the voltage drop across the load resistor R_L. The light passes through the aluminum electrode which has an optical transmittance of ~50%.

Model 311 K electrometer with accumulation of the signal in a Fabritek Model 1072' computer (Nicolet Corp.). Quantum yield determinations were made with a He-Ne laser with 1 mW of power at 632.8 nm.

Pressure-area curves were determined on a Cenco Langmuir balance. The tensiometric wire was calibrated by suspending weights from an attached side arm of known length. Chl was deposited as described in the previous paper.[9] Mixtures of stearic acid and plastoquinone, ubiquinone, or unsaturated fatty acids were deposited at surface pressures near 20 dyn cm^{-1}. Additional details are available in ref 25.

Chl was prepared by the method of Iriyama[26,27] and was purified by chromatography on an alumina column. β-Carotene was prepared according to the method of Kuhn and Lederer.[28] Plastoquinone was extracted from algae[29] according to the method of Kohl et al.[30] Ubiquinone-9 was obtained from Sigma. *N,N*-Dioctadecylbipyridinium chloride was prepared according to the method of Sonderman[31] and Möbius and Kuhn.[32] All fatty acids were obtained from Serdary Research Labs. The acceptor *N,N*-distearoyl-1,4-diaminoanthraquinone was synthesized by a normal acylation procedure.[33]

The Chl fluorescence measurements were made with a Perkin-Elmer MPF4 spectrometer. The Chl blue band was irradiated at 430 nm and the red emission at 670-680 nm was detected. The measurements were taken from the front surface or from the back surface of the slide as described previously by Costa et al.[34] The results are the same but scattering is less problematic if the back surface is monitored.

Theoretical calculations were carried out by Baird[35] using the 4-31G model of Ditchfield et al.[36] The binding energies calculated by this model are in good agreement with relative experimental binding energies, but agree only qualitatively with *absolute* binding energies.[36]

Results

All cells of the form Hg/buffer/Chl/acceptor/Al, as shown in Figure 1, showed rectifying and photovoltaic properties. The simplest system, Chl with stearic acid as the acceptor, or with no acceptor at all, showed the rectifying current-voltage plot of Figure 2. A positive voltage corresponds to an aluminum anode. The forward bias corresponds to electron flow from Chl to the aluminum electrode. The specific conductivity of the cell was estimated to be $1.5 \times 10^{-13}\ \Omega^{-1}\ cm^{-1}$ from the relation $\kappa = L/RA$, where L is the thickness of the cell, R is the resistance, and A is the area. These Chl monolayers tend toward the insulator end of the conductivity continuum. The current rises approximately as the square of the applied voltage. This behavior has been observed previously in electrodeposited Chl[37] and also in tetracene[38] films. It indicates that Chl is not an intrinsic semiconductor; its behavior is governed by a high density of shallow trapping sites. Electrons caught in shallow traps can reemerge thermally to hop from site to site, or they can tunnel from site to site.

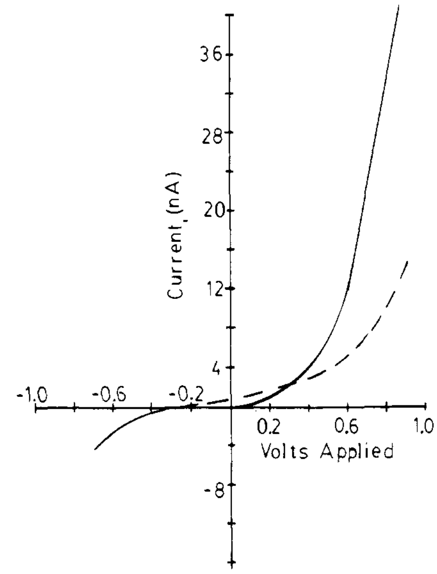


Figure 2. The dark current voltage plot of Chl with only stearic acid as the acceptor, or with no acceptor rises approximately as the square of the voltage (—). When the acceptor AQ with a saturated side chain is incorporated, the curve shifts to the right (- - - -).

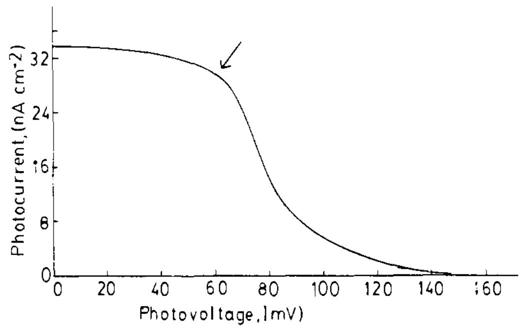


Figure 3. The photocurrent-photovoltage plot for the Chl-only system. The shape of this curve is in sharp contrast to the corresponding curve for the silicon cell, which is almost rectangular. The arrow indicates the maximum power point. The red light intensity was about 1000 W m^{-2}.

Upon illumination at ~1000 W m^{-2}, this cell generated a photovoltage across the load resistor. The photoresponse followed the absorption spectrum of Chl. The Al electrode was negative, so that the light-induced current reinforced the dark current. The maximum open-circuit voltage generated was 150 mV. The maximum short-circuit photocurrent was 34 nA cm^{-2}. The photocurrent-photovoltage plot is shown in Figure 3; it is far from the almost rectangular curve which is so common in semiconductor devices. The hyperbolic behavior indicates that the internal resistance and the shunt resistance are comparable in magnitude. The quantum yield of electrons per photon was $\sim 2 \times 10^{-4}$ and the maximum power conversion efficiency was $\sim 4 \times 10^{-5}$ based on the red photons absorbed. This yield is comparable to that reported by Tang and Albrecht,[39] $\sim 10^{-5}$ and $\sim 10^{-4}$ for microcrystalline Chl cells.

As the number of Chl layers was varied, it was found that four layers develop twice the photoeffect of two layers but six, eight, and ten layers of Chl behave just as four layers. The excitons created beyond the fourth layer must hop so many times that on average they are annihilated before they reach the front surface. Thus, only those layers close to the aluminum electrode contribute to the photocurrent.

At low light intensities, the photocurrent varied with the square of the light intensity; hence the photoelectron transfer mechanism must be biphotonic (see Figure 4). A biphotonic photoeffect in Chl monolayers has been observed previously but was not explained.[22] We postulate that this reaction occurs via the first and second triplet states; the second triplet can be reached by a triplet-triplet absorption. When β-carotene, a

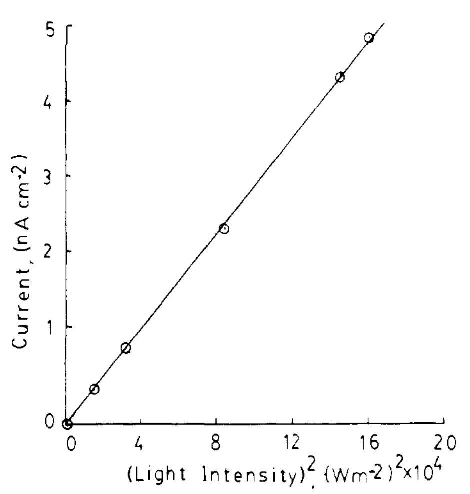


Figure 4. A plot of the photocurrent vs. the square of the light intensity. At low intensity, there is a linear relation.

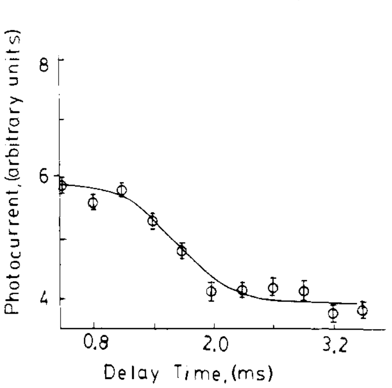


Figure 5. A plot of the flash-induced photocurrent as a function of the delay time between two successive flashes of light. The midpoint of the curve occurs at 1.6 ms. The first flash was filtered by a Corning CS2-62 red filter, while the second flash was not filtered.

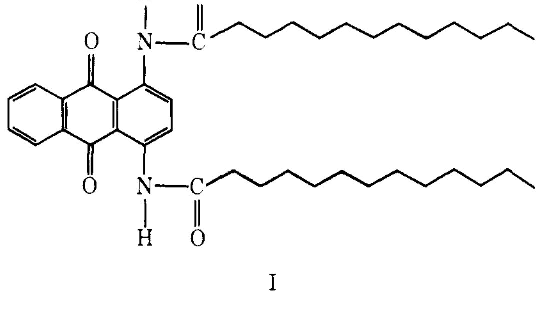
triplet quencher, was mixed into the film at concentrations of 5-10 mol %, the photoeffect was quenched. β-Carotene thus was quenching the excited state. An investigation of the Chl fluorescence at 670-680 nm revealed it to be undiminished as the β-carotene concentration in the monolayer was raised from zero to 12 mol %. Thus, β-carotene was quenching the Chl triplet rather than the singlet, and hence the Chl triplet state must be the metastable intermediate in the electron ejection process.

In an attempt to characterize the triplet-triplet upconversion a double flash experiment was attempted. The delay time between flashes was gradually increased. Figure 5 shows that as the delay time between the two flashes was increased the light-induced current diminished sharply. The midpoint of the changeover from high to low yield occurs at 1.6 ms. The kinetic profile of a single flash-induced signal shows a biphasic decay; the fast component was $t_{1/2} \sim 0.1$ ms, while the slow component has $t_{1/2} > 4$ ms.

Mau and Puza[40] have reported the triplet lifetime of Chl to be 1.7 ms in a mixed glass (ether-isopentane-ethanol, 5:5:2). Because this solvent is very polar, the species observed was possibly the Chl monomer. Because our EPR data indicate that the monomeric Chl is likely the photoactive species,[9] the data in Figure 5 in all likelihood also refer to the monomer. The changeover from high to low yield supports the idea that the triplet state of monomeric Chl is the metastable intermediate.

This biophotonic mechanism is similar to the upconversion proposal of Fong for photosynthesis.[41] However, the sheer inefficiency of this biphotonic process would indicate little or no support for Fong's theory. The excited Chl finding itself in an insulating square well can do little else but undergo fluorescence or intersystem crossing with subsequent phosphorescence or triplet-triplet upconversion.

The incorporation of the acceptor AQ (I), having a saturated side chain, causes the current-voltage plot to shift right as shown in Figure 2. This shift indicates that this acceptor behaves as an electron trap. Upon illumination again a photocurrent and photovoltage were developed. However, the response differed very little from the Chl-stearic acid system. The Chl-AQ spacing was ~15 Å and the acceptor-electrode spacing was ~25 Å. Other AQ derivatives with alkyl chains as short as 12 carbon units (acceptor-electrode separation ~17 Å) caused no improvement in the photoresponse. Also, use of the acceptor *N,N*′-dioctadecyl-4,4′-bipyridyl dichloride with the head group adjacent to the aluminum electrode did not improve the photoresponse or change appreciably the current-voltage plot from that shown in Figure 2 for the AQ acceptor.



I

A study of the temperature dependence was undertaken to separate the tunnelling effects from thermally activated processes. A positive temperature effect was found with an activation energy of 35 ± 2 kJ mol^{-1} (0.35 eV). At −25 °C, the photocurrent dropped to 10% of its value at room temperature. Considering that in the Chl-chloranil system light-induced electron transfer was observed by EPR at temperatures down to 100 K,[9] it would seem reasonable then that the barrier occurs at the lipid-electrode interface rather than between the donor and acceptor. Such electrode barriers are quite common in organic solar cells[37] and may be due to the oxide film on the aluminum electrode. The barrier is less likely to be located at the mercury-lipid interface since Corker et al.[37] report that mercury makes a reasonably ohmic contact with organic materials such as microcrystalline Chl. In our monolayer cell, the mercury is in contact with stearic acid. Since both Chl and stearic acid are essentially lipids, the mercury-lipid interface is probably similar in the two cases.

Ideally, the barrier should be a low Schottky barrier, where the light-induced current occurs in the *opposite* direction to the dark current. For this reason, a search for an alternative electrode material was undertaken. However, sputtered platinum was found to be too nonpolar, as reported previously,[42] as was sputtered gold. Similarly, the monolayers did not cling firmly to sputtered nickel, evaporated copper, tin oxide, or indium oxide semiconducting electrodes.

The model based on a biphotonic mechanism as developed to this point is shown in Figure 6. Under steady-state illumination Chl absorbs a photon, is raised to its first excited singlet state, and then crosses over to the lowest triplet state. If a second photon arrives at the molecule within the lifetime of the triplet state (1.6 ms), the second triplet is reached and an electron is ejected from that state.

The energy levels in Figure 6 were estimated as follows. The ionization potential of Chl has been estimated to be −4.8 eV by Vilesov and Akopyan.[43] We have estimated it to be −5.2 eV based on the oxidation potential of +0.72 V vs. NHE[44]

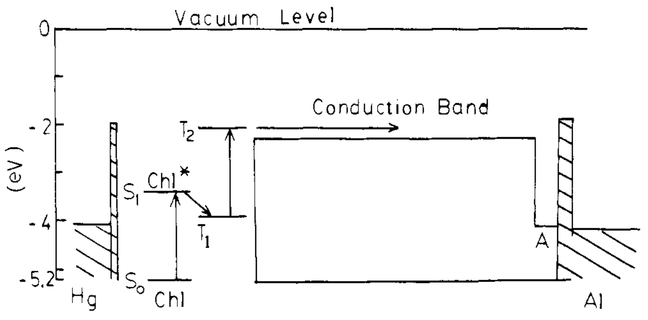


Figure 6. A potential energy diagram showing the mechanism of the observed photocurrent. The conduction band is 2.2 eV below vacuum.[18]

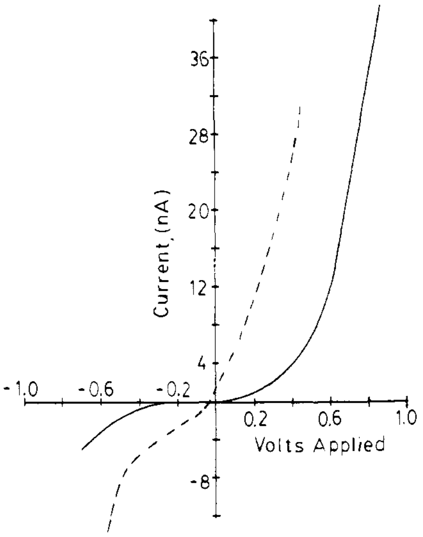
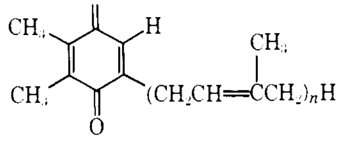


Figure 7. The dark current-voltage plot of Chl only (—), and of the Chl-PQ cell (- - - - -).

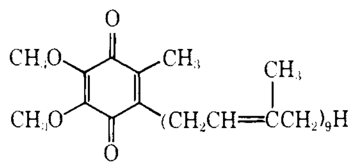
while the NHE is 4.5 V below vacuum.[45] The lipid conduction band is probably 2.2 eV below vacuum (Mann et al.).[18] Thus, the conduction band is ~3 eV above the ground state of Chl. Can two photons raise an electron up to this level? We can estimate the energy level T_1 to be 1.3 eV above the ground state on the basis of the phosphorescence maximum which occurs at 950 nm.[40] This estimate agrees with the figure of 1.32 eV reported by Connolly et al.[44] The absorption spectrum of the triplet has its maximum at 462 nm (2.68 eV), although it is a broad absorption extending as far as 750 nm.[46] Thus, ample energy is available for excitation to the lipid conduction band. Even a photon absorbed at 680 nm in the tail of the triplet absorption spectrum provides 1.8 eV, yielding a total of 3.1 eV.

Acceptors with Unsaturated Side Chains. Neither plastoquinone (PQ) nor ubiquinone (UQ) forms stable monolayers[34] because of the unsaturation of the polyisoprene side chain. However, when diluted 10:1 with stearic acid the fatty acid provides a stable matrix to hold the polyisoprene chain linear. Such a layer was deposited with the quinone head toward the aluminum electrode. Using this layer in the donor-acceptor cell the dark current-voltage curve shifted left as shown in Figure 7. The conductivity of the cell is greatly improved as the slope indicates. Upon illumination (~1000 W m^{-2}) the power output was improved by a factor of ~10. The upper curve in Figure 8 shows the photocurrent-photovoltage plot. An open-circuit photovoltage of 270 mV can be obtained, and the maximum short-circuit photocurrent is 140 nA cm^{-2}. The energy conversion efficiency now is ~4 × 10^{-4} based on red photons absorbed, and is approximately constant across the voltage range. The curve is still not the near-rectangle which is common for silicon cells. The quantum yield is 2 × 10^{-3}.



plastoquinone

n = 6–10



ubiquinone

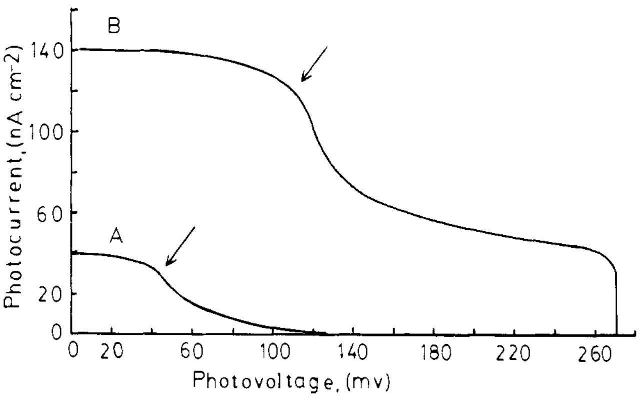


Figure 8. The photocurrent-photovoltage plot for the Chl-PQ cell (B) as compared to the Chl with no acceptor (A). The arrows indicate the maximum power points. The light intensity was ~1000 W m^{-2} of red light.

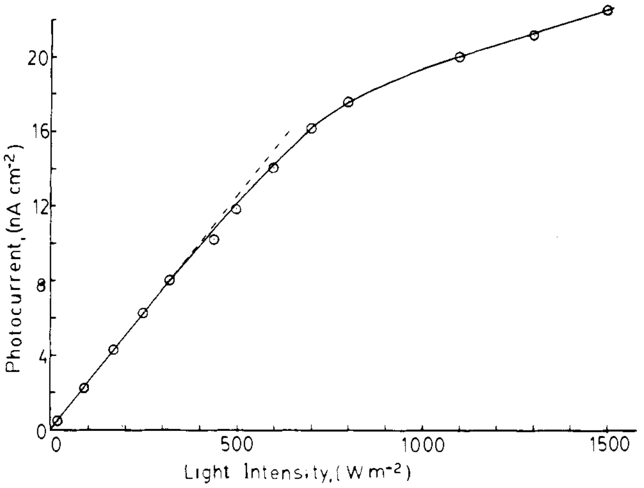


Figure 9. The effects of light intensity on the photocurrent in the Chl-PQ cell. At low intensities, there is a linear relation.

Because of the dramatic improvement in the observed photoresponse, a series of questions was raised.

(a) Has the photophysics of this reaction changed?

(b) How is the quinone group involved?

(c) What is the role of the double bonds?

(d) Is the polyisoprene chain special in promoting electron transfer?

(e) Has the role of the barrier changed?

To investigate the photophysics, the effect of light intensity was studied, and it was found that the photocurrent increased linearly with light intensity as opposed to the previous square-law dependence. Figure 9 shows the resulting graph.

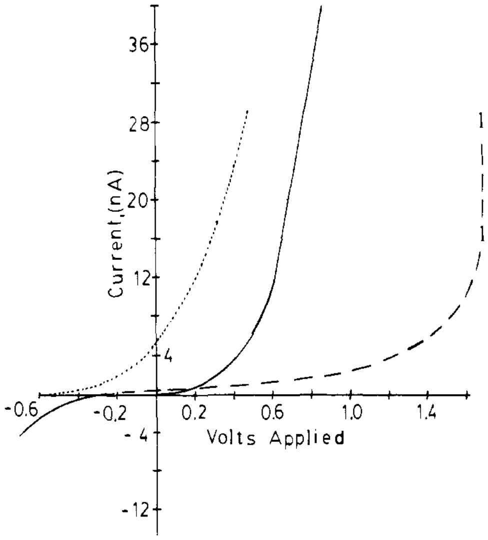
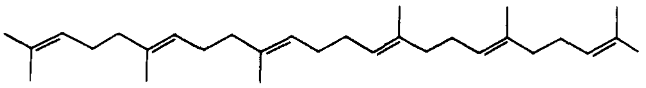


Figure 10. The dark current-voltage plot for the Chl-only cell (—) and for the Chl-reduced UQ cell (- - -). The dotted line represents the light curve for the Chl-reduced UQ acid cell under an illumination of about 1000 W m^{-2}.

The electron ejection process now probably occurs from the first excited triplet. Parallel samples of the high- and low-yielding cells incorporating β-carotene in concentrations of up to 10 mol % were prepared. The result was a parallel quenching of the photoeffect. As indicated earlier, the fluorescence intensity of Chl monolayers remained unchanged by the presence of β-carotene in this concentration range. Therefore, the parallel quenching in the low- and high-yielding cells indicates again triplet involvement in the monophotonic process. Indeed, incorporation of an acceptor layer containing 10 mol % β-carotene resulted in partial quenching of the photoeffect while simultaneously reducing the internal resistance. Thus, the photophysics is similar in both cases in that the effect proceeds via the triplet in both cells but differs in that only the lowest triplet is involved in the high-yielding cell.

To investigate the involvement of the quinone head group, question (b), a cell was constructed incorporating a reduced ubiquinone-9 acceptor. Figure 10 shows a typical dark current-voltage plot and a light current-voltage plot. The dark plot has shifted right, but in the light the behavior of the cell is virtually unchanged. The quinone head group was therefore not required for the improved photoresponse. Further, the use of the polyisoprene squalene resulted in both a high power efficiency and a dark current-voltage behavior very similar to that of the PQ case shown in Figure 7.



squalene

Further experiments incorporating one, two, three, etc., double bonds are being conducted in an effort to determine why squalene should cause a different dark current-voltage plot than reduced ubiquinone-9.

On the basis of these photoelectric experiments, we feel that possibly the polyisoprene chain is a special moiety of nature used to promote electron transfer. Recent work by Hauska[47] using liposomes provides strong confirmation of this hypothesis. His work demonstrates that it is the polyisoprene chain in ubiquinone which greatly facilitates electron flow across membranes. Molecular models show that the head-to-tail distance from one double bond to the next in the polyisoprene chain is only ~2.5 Å.

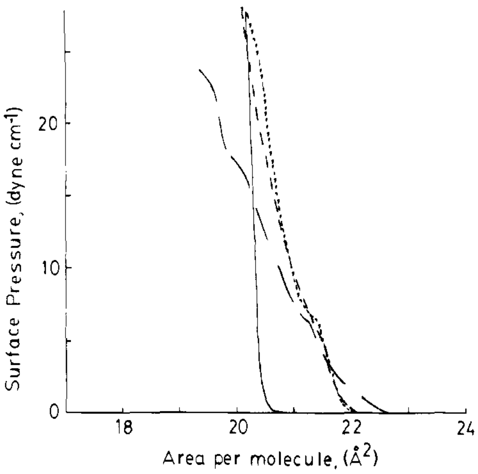


Figure 11. The pressure-area curves of stearic acid and of three unsaturated compounds as 10 mol % mixtures in stearic acid: stearic acid (—); elaidic acid ($C_{18:1}$) (- - - - -); linoleic acid ($C_{18:2}$) (— —); squalene (- - -).

That the polyisoprene chain could stack well in a lipid matrix may be illustrated by the pressure-area curves of a series of unsaturated compounds as 10 mol % mixtures in stearic acid. Figure 11 shows that, while stearic acid forms a nearly incompressible layer with an area per molecule of about 20.4 Å^2, the presence of elaidic acid ($C_{18:1}$, a chain of 18 carbon units with one double bond) with one trans double bond reduces the slope and increases the area per molecule to about 21.5 Å^2. The presence of two cis double bonds in linoelaidic acid continues both of these trends. The slope of the π-A curve is related to the two-dimensional compressibility which would be written as

$$-\frac{1}{A_0}\left(\frac{\partial A}{\partial \pi}\right)_T, \text{ where } A_0 \text{ is a reference area}$$

the two-dimensional analogue of the ideal gas compressibility. Figure 11 also shows the pressure-area curve of a 10 mol % mixture of squalene, a polyisoprene chain, with all trans double bonds in stearic acid. The area per molecule is larger than in the case of stearic acid, but this curve resembles the elaidic acid curve, where only one trans double bond was present in the chain. These two graphs represent direct confirmation that a polyisoprene chain should stack reasonably well within a stearic acid monolayer matrix. However, a rigorous proof of specific orientation of the squalene chain in the stearic acid layer would involve the study of the polarized ultraviolet absorption spectrum of this monolayer assembly.

Still to be addressed is question (e), on the role of the barrier. A temperature study was again undertaken to find the height of the barrier. The activation energy now was found to be 136 kJ mol^{-1} (1.41 ± 0.1 eV). This barrier is some four times larger than it was when acceptors with saturated chains were used. Indeed, this finding is consistent with the postulate that the barrier exists at the lipid-electrode interface. The presence of the isoprene chain allows electron ejection from the lowest Chl triplet state and as a result the barrier to the external circuit has increased.

Since a polyisoprene chain promotes tunnelling, a series cell of the form

Hg | buffer | Chl | squalene | Chl | squalene | Al

was prepared in the hope that this cell might provide a larger voltage and thereby aid in surmounting the barrier. However, this cell behaved just as if it were a single cell. Thus, while the barrier causes severe inefficiency, it is also the Schottky barrier which is required for the rectifying behavior.

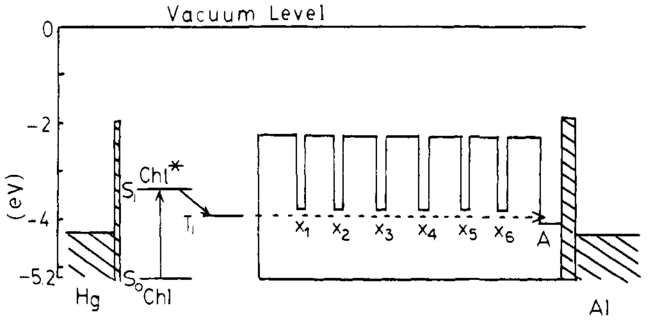


Figure 12. A modified potential-energy diagram showing the intermediate wells and the resulting tunnelling mechanism.

Discussion

Does molecular orbital theory support the idea that a double bond forms a gap or intermediate well in a lipid layer and that these gaps promote tunnelling? Baird[35] has carried out calculations to find how much lower in energy the first empty orbital of ethylene is as compared to that of ethane. It was estimated to be 1.58 eV lower. This figure may be taken as a rough measure of electron-accepting ability of the double bond as compared to a single bond. The model of the monolayer system may now be amended to include these intermediate wells, and it is shown in Figure 12. These wells are ~1.42 eV above the ground state of Chl; the T_1 state is 1.3 eV above the ground state. Morsey et al.[48] have shown that the tunnelling probability increases sharply as the number of intermediate wells increases. Experimentally, the conductivity improved by about a factor of 10.

From the dark current-voltage plots, it is not clear why the presence of squalene should shift the curve left while reduced UQ_9 shifts the curve right. One obvious difference between these two compounds is the length of the chain. Polymeropoulos et al.[13] have demonstrated that the orientation of a π system in a monolayer assembly is critical in terms of promoting tunnelling. The fact that UQ_9 has a chain length of 36 carbon units, which is much longer than stearic acid, would force many double bonds into skewed configurations within the matrix. These might behave as sites for trapping electrons rather than promoting tunnelling. All of these sites would have to be filled before electrons could reach the electrode. This question concerning the number and orientation of double bonds is under further investigation.

The fact that the light-induced current reinforces the dark current rather than opposing the dark current is most peculiar. We feel that this effect may be related to the extraordinary height of the Schottky barrier. Quite possibly, as an electric field is applied, hole injection from a positively biased aluminum electrode might proceed much more easily than electron flow over the high barrier from a negative aluminum electrode in the opposite direction. Further work will attempt to reduce this barrier with the idea of making this cell a normal Schottky device.

The two-electron ejection mechanisms, biphotonic and monophotonic, found in the Chl monolayer assembly may be considered as two competing deexcitation processes. Whether the reaction proceeds biphotonically or monophotonically probably depends critically on the tunnelling time through the lipid barrier.

The optical spectroscopy of the Chl monolayer with various acceptors is an interesting study in itself. Harris[49] reports that a series of natural quinones such as ubiquinone, vitamin K_1, and tocopherylquinone in monolayer assemblies all quench Chl fluorescence. Undoubtedly plastoquinone would do the same. We have found that squalene in a stearic acid layer (10 mol %) quenches the major portion of the Chl fluorescence. However, we have not investigated the question of whether any of these compounds quenches the Chl triplet state. A polyisoprene such as squalene should have energy states not unlike those of ethylene. Ethylene has an ionization potential of 10.5 eV[50] and a triplet state 4.6 eV above the S_0 state. This level is below the Chl S_0 state. Thus, the isoprene triplet state could be nearly 2 eV below the Chl triplet state. It would seem unlikely that the polyisoprene could quench the Chl triplet by energy transfer; quenching by electron transfer would appear to be much more likely.

In view of the fact that UQ and PQ are commonly found in the electron transport chain of photosynthesis and in the photosynthetic reaction center, we suggest that the polyisoprene chain may function as "nature's molecular wire". Electrons are hereby enabled to flow in the normally nonconducting biological tissues. This is not to suggest that the quinone head group is superfluous to photosynthesis. It is used to store electronic charges temporarily to prevent recombination.[51] After all, reaction centers have no Schottky barriers to provide rectifying behavior.

Conclusions

In this paper, we have shown that Chl monolayers sandwiched between an aluminum electrode and a mercury electrode have a high resistivity, but can eject electrons outward to the aluminum electrode. The mechanism probably proceeds via the first two excited triplet states of Chl, the conduction band of the lipid layer, followed by thermal activation over a barrier at the aluminum electrode. Incorporation of electron acceptors with saturated side chains was found to be ineffective in improving the photoresponse. However, incorporation of 10% UQ or PQ reduced the internal resistance and raised the power conversion efficiency tenfold.

Reduction of the quinone head group or substitution of the quinone by the polyisoprene squalene or certain unsaturated fatty acid derivatives left the photoresponse unchanged. The photoeffect now varied linearly with light intensity but still probably proceeded by the Chl triplet state. The electrons probably tunnelled through the lipid matrix where the double bonds formed local wells which improved tunnelling efficiency. The electrode barrier now was found to be much higher (1.41 eV) than in the biophotonic mode. We believe that the polyisoprene unit may have been chosen by nature to serve as its molecular wire across or through membranes.

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Triplet State Photophysical Properties and Intersystem Crossing Quantum Efficiencies of Homologues of Retinals in Various Solvents

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Abstract: Employing the techniques of pulse radiolysis and nitrogen laser flash photolysis, several photophysical properties of the lowest triplet states of a series of polyenals related to retinals as homologues have been studied in various polar and nonpolar solvents. The series includes two polyenals not heretofore studied, an all-trans 17-carbon homologue (shorter than retinal by one double bond) and an all-trans 24-carbon homologue (longer than retinal by two double bonds). The former polyenal has high quantum efficiencies of occupation of the lowest triplet (ϕ_{T_1}) in both polar and nonpolar solvents and the latter polyenal has very low ϕ_{T_1} values in any solvent. The results are discussed in relation to the state order as a function of chain length along the series in general and as a function of the nature of the solvent in the case of certain specific members.

Introduction

Because of their importance as chromophores in rhodopsin, bacteriorhodopsin, and related pigments, the retinyl polyenes have been extensively studied regarding their intersystem crossing efficiencies and triplet state photophysical properties.[1-13] The quantum efficiencies of the lowest triplet occupation (ϕ_{T_1}) are relatively high (0.4-0.7) for retinals[2-7] at room temperature in nonpolar solvents and an excitation wavelength dependence of ϕ_{T_1} is observed[6,8,9] for these systems. On the other hand, the retinols, retinyl Schiff bases, and protonated retinyl Schiff bases are found to have relatively very low ϕ_{T_1} values.[4,10-12] This, and the fact that the intersystem crossing efficiencies of retinals are considerably decreased in polar/hydrogen-bonding solvents[4,9] as well as in the presence of a hydrogen-bonding agent (phenol),[13] has been attributed to state orders where the relative disposition of a low-lying $^1(n,\pi^*)$ state plays a significant role.[1,4,9,13]

The state ordering of retinals has long been of great interest and controversy. Three closely located states (^1B_u, $^1(n,\pi^*)$, and ^1A_g) are generally recognized to be the low-lying singlet excited states involved in the photodynamics of retinals.[14-16] Recently we have reported in detail on the absorption and emission spectral properties of a large number of polyenals and polyenones related to retinals as homologues and analogues.[17] A complementary study[18] has been performed on the triplet state properties of some of these carbonyl-containing polyenes in hexane by the methods of pulse radiolysis and laser flash spectroscopy. The present work is meant to provide a broader understanding of the photophysical dynamics of these polyene systems and includes two members not heretofore studied regarding their triplet state photophysical properties. These two members are the 17-carbon homologue with chain length shorter than that of retinal by one double bond (henceforth called C_{17} aldehyde) and the 24-carbon homologue with chain length longer than that of retinal by two double bonds (henceforth called C_{24} aldehyde). As far as intersystem

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