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## Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713708471>

### Energy Conversion Via Pigmented Bilayer Lipid Membranes

H. Ti Tien<sup>a</sup>

<sup>a</sup> Biophysics Department, Michigan State University, East Lansing, Michigan

**To cite this Article** Tien, H. Ti(1980) 'Energy Conversion Via Pigmented Bilayer Lipid Membranes', *Separation Science and Technology*, 15: 4, 1035 — 1058

**To link to this Article:** DOI: 10.1080/01496398008076286

URL: <http://dx.doi.org/10.1080/01496398008076286>

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ENERGY CONVERSION VIA PIGMENTED  
BILAYER LIPID MEMBRANES

H. Ti Tien  
Biophysics Department  
Michigan State University  
East Lansing, Michigan 48824

ABSTRACT

One approach to the problem of understanding photosynthesis quantum conversion is to investigate the manner in which the thylakoid membrane of the chloroplast achieves many of its physio-chemical processes. Ideally, a great deal of information may be obtained from electrical measurements in the dark and in the light. This procedure entails the placing of electrodes across the membrane, much as has been done for the nerve membrane of axons. However, such an approach is not yet feasible for most photoactive membranes owing to their tiny size. An alternative approach is to investigate experimental pigmented bilayer lipid membranes (BLM), which are very suited for studying light transduction and light-initiated redox reactions.

This paper will discuss certain photoeffects observed in pigmented BLM in terms similar to those that occur at semiconductor/metal interfaces (Schottky barriers). The pigmented BLM separating two aqueous solutions behaves as a bipolar electrode, into and from which electrons and holes can be transferred. Also owing to its ultra-thickness (<100 Å), a very large field strength can be developed across the BLM under a small electrical bias. General principles for electron transfer processes across the BLM are discussed. The conversion of light into electrical and/or chemical energy by pigmented BLM is demonstrated, and proposed schemes for the understanding of green plant photosynthesis via the thylakoid membrane are described.

BIOLOGICAL MEMBRANES AND THE LIFE CYCLE

The bioenergetics of life as we know it can be described in various ways. One way is shown in Fig. 1, in which the phenomenon of life is interpreted in terms of biological membranes (1).

Functionally, biological membranes may be divided into five basic types as also indicated in Fig. 1. The major constituents of biological membranes are lipids, proteins, and carbohydrates. Pigments constitute a significant minor portion in certain light-activemembranes such as the thylakoid membrane of photosynthesis and the visual receptor membrane of vision. The lipids of biological membrane, which comprise from 20% to 80% of the dry weight, are most unique and are organized as a bimolecular leaflet. This is more commonly called a lipid bilayer. Several lines of evidence support the notion that the lipid bilayer is the key structural element of all biological membranes, onto which proteins, carbohydrates and other minor constituents are located. These are responsible for a host of functions. In the case of the thylakoid membrane the primary function is the conversion of the electromagnetic radiation of sunlight, as we shall describe in more detail in this paper.

Most membrane lipids are amphipathic and their unique position in chemical evolution has been recognized (2-5). Several investigators proposed ways in which bilayer lipid membranes and vesicles could form in nature (1, 2, 6). It has been suggested that, by a process of selective absorption of photoactive pigments such as chlorophylls, these vesicles could be transformed into primitive quantum converters (1). Conversion of light by artificial pigmented bilayer lipid membranes into electrical and/or chemical energy lends credence to these speculations. Further, artificial membrane systems are useful in checking proposed photochemical mechanisms in biological membranes. Therefore, the major part of this paper is devoted to a discussion of energy conversion by pigmented bilayer lipid membranes. Before going into the specifics of photoenergy conversion by pigmented membranes,

## BIOCOMPOUNDS AND THE LIFE CYCLE

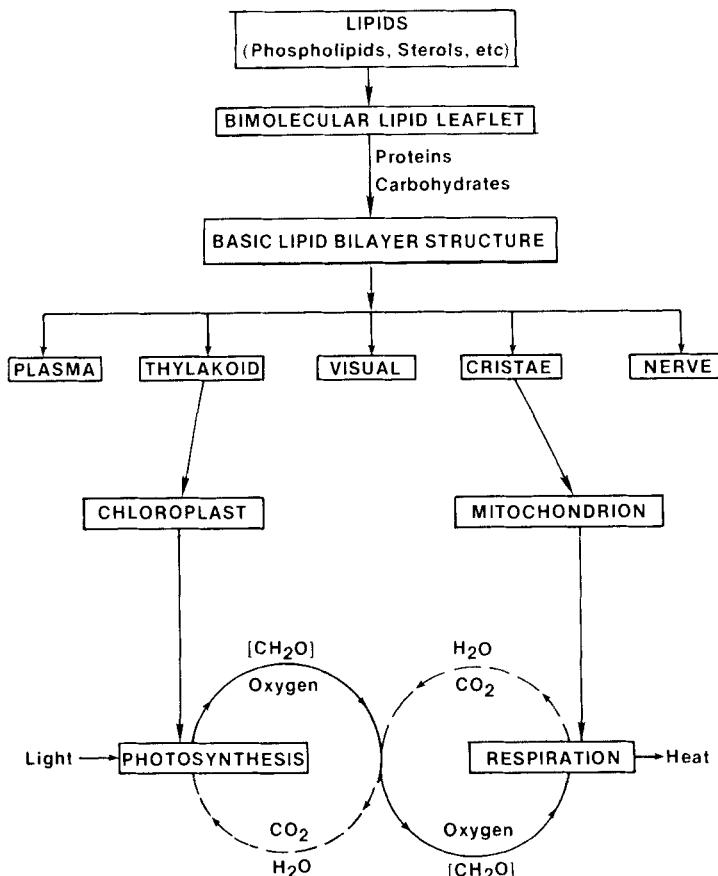


Figure 1. The life cycle in terms of the thylakoid membrane of the chloroplast and the cristae membrane of the mitochondrion. The life cycle consists of two coupled reactions of photosynthesis and respiration, in which the products generated by the former is consumed by the latter, respectively. To sustain these coupled reactions a high potential source (solar energy) and a low potential sink (heat) are necessary. The energy transduced by the system rather than the energy itself is stressed.

an overview of the life cycle is given to complete this introduction.

The life cycle, as we know it, is driven directly by solar energy. This is represented by an infinity sign shown at the bottom of Fig. 1. The two basic processes of life are photosynthesis and respiration, which are carried out by the thylakoid membrane in the chloroplast and the cristae membrane in the mitochondrion, respectively (1). The two coupled cycles depict a steady-state energy transducing system of life. The essential feature of this system is that it represents a steady-state brought about by the flow of energy from a high potential source (sunlight) to a low potential sink (heat). It should be noted that it is not the energy itself that makes life possible, but the flow of energy through the energy transducing membranes of the system (7). Thus, our first task is to understand how energy, in the form of electromagnetic radiation, is transduced into the electrical and/or chemical energy that fuels the life cycle as we know it.

#### PHOTOSYNTHESIS IN VIVO

The overall process of plant and algal photosynthesis occurs in two stages requiring a total of eight photons for each  $\text{CO}_2$  molecule reduced and  $\text{O}_2$  liberated from two molecules of water. To accomplish this task two photosystems (PS-I and PS-II) appear to have evolved in nature (8). PS-I and PS-II are though to be spatially separated in the thylakoid membrane of the chloroplast. Photons absorbed by chlorophylls and accessory pigments drive electrons "uphill" from a redox potential of the  $\text{H}_2\text{O}/\text{O}_2$  couple of about 0.8 volt to that of "X" at about -0.6 volt, resulting ultimately in the reduction of  $\text{NADP}^+$  to NADPH. Fig. 2 (upper) illustrates speculatively the so-called "Z" scheme of photosynthesis, in which the direction of electron transport is also indicated. Freeze-etching electron microscopy has provided much evidence that PS-I and PS-II are located on opposite sides of the thylakoid mem-

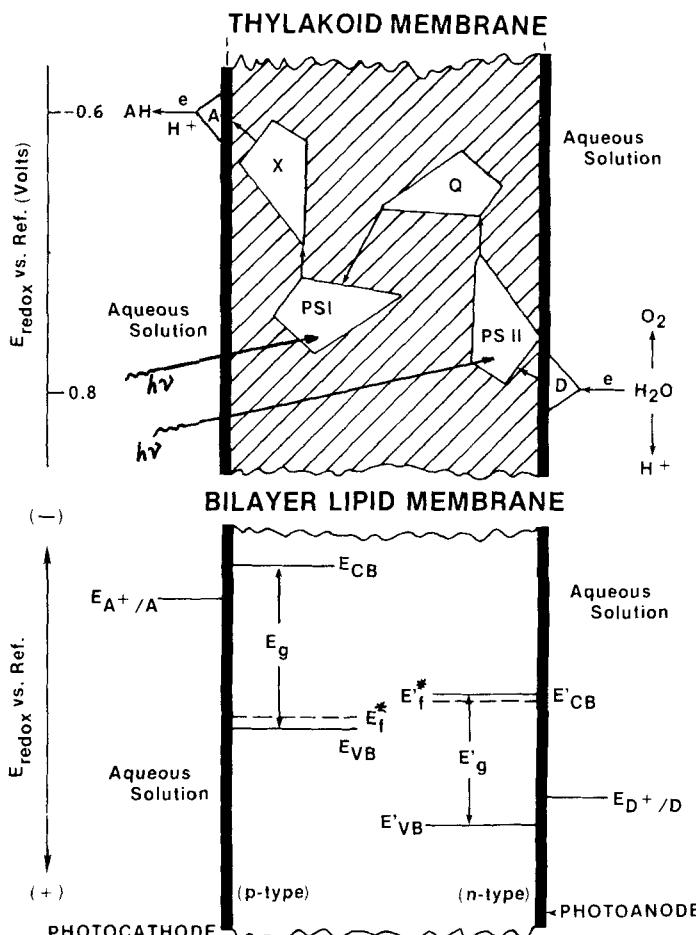


Figure 2. Upper: Diagrammatic representation of electron transfer and coupled reactions in the thylakoid membrane of the green plant. PSI and PSII are the two photosystems located on opposite sites of membrane/solution interfaces. Also shown is a simplified electron transfer pathway, where an electron is donated by water to D (probably a manganese-containing protein). The entire process probably starts upon absorption of photons by PSI and PSII ending with the reduction of NADP<sup>+</sup> to NADPH (AH). Q and X are the still unidentified electron acceptors associated with PSII and PSI, respectively. Note the scheme permits the absorption of two photons per electron transported across the membrane. Lower: Semiconductor hypothesis of energy transduction by pigmented bilayer lipid membrane. The two photosystems of the thylakoid membrane are translated into a p-type and an n-type semiconductor. Under illumination, reduction takes place on the left-hand side (photocathode) of the membrane, with oxidation occurring on the right side (photoanode). This is similar to a push-pull device operating in concert. See Figs. 4-6 and text for further details.

brane with the water-splitting enzymes on the interior surface (9, 10). As already mentioned, the thylakoid membrane basically consists of a lipid bilayer with proteins either embedded in it or associated with its surface. At the molecular level, chlorophylls can either associate with proteins or disperse in the lipid bilayer with the porphyrin ring oriented at a certain angle at the interface (11). In any event, it is this ultrathin pigmented lipid bilayer separating two aqueous solutions that is responsible for the initial step in the transduction of solar energy. We will now review briefly the mechanisms that have been proposed to explain the primary event of quantum conversion in photosynthesis.

Photosynthesis can be viewed as coupled redox reactions; water is oxidized and carbon dioxide is reduced (Fig. 1). The driving force for the reaction is, of course, solar radiation mediated by chlorophyll. Van Niel (12) first proposed this idea in terms of the oxidant (OH) and reductant (H). In terms of solid-state physics, these entities are positive holes and negative electrons (13). If one assumes that chlorophylls are in an ultrathin liquid-crystalline-like lipid bilayer (11, 14), absorption of light excites an electron to the conduction band and leaves a hole in the valence band. According to E. Katz (13), electrons and holes are free to move around to effect reduction and oxidation, respectively. In other words, chlorophyll aggregate or chlorophyll dispersed in a lipid bilayer acts as a semiconductor. The photogenerated electron can be transferred to an electron acceptor. Similarly, the photogenerated hole can be combined with an electron donor. That chlorophylls and their host, the chloroplast, behave as a semiconductor has long been suggested by many authors including Arnold and Sherwood (11, 13, 15). Recently, owing to the interest in semiconductor electrochemical photocells for solar energy conversion (16), parallels between natural photosynthesis and semiconductor photoelectrolysis have been noted (1, 11, 17, 18).

It seems that in natural photosynthesis the advantage of having a membrane separating two aqueous solutions is two-fold: (i) the membrane, besides providing appropriate environment for the pigments, serves as a barrier to prevent the occurrence of back reactions of the photoproducts, and (ii) with the pigments (or photosystems) located in different parts of the membrane, the absorption of two photons for each electron/hole pair generated is possible, thereby providing a mechanism by which the energy of photons can be upgraded. Fig. 2 shows a highly schematic view of the thylakoid membrane in terms of the two photosystems, redox reactions and electron transfer.

#### ARTIFICIAL PHOTOSYNTHESIS

If the semiconductor model of photosynthesis outlined in the preceding section is of any relevance to the conversion of sunlight into electrical/chemical energy by green plants, experimental tests are obviously in order. There are at least two approaches. First, the most direct kind of experiments would be by placing a pair of microelectrodes across the thylakoid membrane and measuring its electrical properties both in the dark and under illumination. Indeed, the minuteness and complexity of the thylakoid notwithstanding, Bulychev et al. (19) have performed just such an experiment on giant chloroplasts of Peperomia metallica and detected a light-induced potential difference. Although questions may be raised about this interesting finding as to whether or not a transthylakoid membrane potential was measured, the experiments of Bulychev et al. demonstrate provisionally at least, that a photovoltaic effect exist in the chloroplast, as has been observed in a different system by Luttage and Pallagy (20).

The second approach to studies of chloroplast photosynthesis is to investigate "reconstituted" model systems. These include various solutions of chlorophylls (21, 22), pigment-coated electrodes (23, 24), chlorophyll monolayers (25, 25a), micelles

(26, 27), pigmented bilayer lipid membranes of both planar and spherical configuration (11, 28), and related membrane systems (29, 30).

In light of what we know about the photosynthetic thylakoid membrane discussed in the Introduction, it is evident that planar bilayer lipid membranes (BLM) and spherical bilayer lipid membranes (liposomes) are the nearest model systems with which to investigate energy conversion processes and redox reactions. In the following, pigmented liposomes and BLM will be described under separate headings. In particular, I shall discuss some recent results and ideas from our laboratory on the BLM system.

#### A. Photoactive Liposomes

Liposomes are lipid microvesicles suspended in an aqueous medium (31, 32). In this system a bilayer lipid membrane of spherical configuration encloses a volume of aqueous solution. Thus, a liposome resembles a "primitive" cell (1). Since the liposomes are quite stable and can be easily made in quantity, they are ideally suited for studies of permeability, conventional spectroscopy, redox reactions, and energy conversion. The literature up to 1978 on photoactive liposomes has been comprehensively summarized (11, 28), so that only recent work, directly related to the topic under consideration, will be discussed here.

To mimic light-induced reactions in the thylakoids of chloroplasts, we have formed chlorophyll-containing liposomes separating two aqueous solutions in the presence of redox agents, as has been done with the BLM. The experiments were designed to test the photoassisted decomposition of water. A Clark-type electrode was used for detecting oxygen. No oxygen evolution was observed after numerous attempts (33). However, other investigators using a similar system have reported photosensitized oxygen evolution (34). Toyoshima et al. prepared their pigmented liposomes containing 0.1M potassium ferricyanide (a Hill reagent) in the inside and observed oxygen evolution as monitored by a Clark electrode, which is very sensitive to temperature

changes. Since the temperature of the reaction chamber employed by these workers was not controlled, the results obtained therefore were suspect. The other difficulty associated with the system is the lability of chlorophyll molecules, which are easily irreversibly bleached (35). In spite of these complications, Kurihara et al. (36) have recently reported photo-induced charge separation in chlorophyll-liposomes in which ferricyanide is reduced.

In view of the above experiments showing that simple chlorophyll-containing liposomes probably did not generate oxygen in the light, we tried a different approach by incorporating oxygen evolving complexes (OEC) into liposomes (37). The OEC used, which are assumed to be pigment-protein complexes, were obtained from spinach chloroplasts. Our experience with pigmented BLM has shown that an intact membrane system of high electrical resistance is a pre-requisite for the generation and separation of charges by light. Therefore it would also be of interest to demonstrate that a sealed (intact) thylakoid is necessary for oxygen evolution. For these purposes, two kinds of experiments were carried out: (i) the OEC were incorporated directly into the lipid bilayer in the process of liposome formation, and (ii) the OEC were added to performed liposomes (37). Indeed, we have found that broken thylakoids that contain OEC, when fused with phosphatidyl choline liposomes, evolved oxygen profusely. Also, incorporation of OEC into liposomes apparently stabilized the OEC and prolonged the system to generate oxygen.

The other recent work of interest related to chlorophyll-liposomes is the experiment of Fragata (38), who reported the fluorescence of chlorophyll (Chl) containing liposomes with and without all-*trans*- $\beta$ -carotene. The quenched fluorescence of chlorophyll, observed in the  $\beta$ -carotene-liposomes, is interpreted as the consequence of Chl-Chl interactions brought about by  $\beta$ -carotene. The result may be explained by the mechanism of concentration quenching (39), in which energy migration between Chl

molecules proceeds by a Forster hopping mechanism and, when in close proximity Chl-Chl interactions occur thereby leading to quenching. If so, the Chl molecules in the thylakoid membrane are probably not simply dissolved in the lipid bilayer but bound in Chl-protein complexes (9) in order to reduce undesired Chl-Chl interactions.

The lability of Chl to photooxidation has been known for many years, the order of which is organic solvents <liposomes< thylakoids (11), being least stable in organic solvents. Therefore, a number of investigators (40) have formed photoactive liposomes that contain a stable dye such as tris (2,2'-bipyridine) ruthenium (II) instead, and have reported light-induced electron transfer across a bilayer lipid membrane. The membrane, made of egg lecithin, vitamin K, hexadecylviologen and decachloro- $\text{m}$ -carborane in addition to the ruthenium dye, was interposed between a solution of ethylenediamine- $\text{N},\text{N},\text{N}',\text{N}'$ -tetraacetic acid (EDTA) and a solution of methyl viologen and zinc acetate. Upon illumination, EDTA was irreversibly oxidized and methyl viologen reduced, which was monitored spectrophotometrically. Ford et al. (40) further reported a net gain of about 20 Kcal. per mole EDTA consumed for the system and explained the result as a photo-sensitized coupled redox reaction. Thus, the ruthenium dye in their membrane must act as an "electron pump" driven by light. If so, it would be of interest to examine the system electrically and to assess more precisely the role played by each of the numerous constituents in the membrane. Photoelectric BLMs described in the following section are eminently suited for such purposes.

#### B. Photoelectric Bilayer Lipid Membranes

Bilayer lipid membranes (BLMs) of planar configuration are ultrathin structures of molecular dimensions and are usually formed by spreading a droplet of lipid solution over a small hole in the wall of a Teflon cup immersed in aqueous solution (41, 42). Many investigators have been able to modify their passive

characteristics by adding substances which endow BLMs with dynamic properties. The modified BLMs exhibit some features resembling certain aspects of biological membranes. For example, BLMs containing pigments are photosensitive and have been used as models for the thylakoid membrane of the chloroplast and the visual receptor membrane of the eye (11, 28, 43). These pigmented BLMs are photoelectric in that they are capable of transducing light into electricity. Here I shall discuss only the results of our hitherto unpublished experiments on photoelectric BLMs.

1. Experimental Details and Results. The chlorophyll-bilayer lipid membrane (Chl-BLM) forming solution was prepared using the standard procedure and the BLM was formed in the usual manner (42). Resistance, voltage and currents were measured using a high impedance electrometer (Keithley Model 610). A light intensity of  $200\text{mW/cm}^2$  could be projected onto the BLM from a tungsten halogen lamp. A heat filter and a 8-cm water bath were inserted between the light source and the BLM, and the experimental area was shielded from spurious light. Aqueous solutions containing various compounds were used in different experiments as given in Fig. 3. In brief, the electron acceptor,  $\text{FeCl}_3$ , was added to one side while the electron donor, chlorophyllin, was added to the opposite side. The chlorophyllin, a water-soluble chlorophyll, enhanced the blue response (peak at 395 nm) of the Chl-BLM. No photoresponses were observed however from oxidized cholesterol-lecithin BLM in the presence of chlorophyllin alone, but these non-pigmented BLM were quite photoactive if electron acceptors such as  $\text{FeCl}_3$  or  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$  and donors such as  $\text{FeCl}_2$  were present. All the experiments reported here had a hydrogen ion concentration gradient of 4.3 pH units across the BLM. This was necessary since  $\text{FeCl}_3$  and chlorophyllin are only soluble at acid and alkaline pH, respectively. The photoresponses of Chl-BLM under various conditions are shown in Fig. 3. Fig. 3A illustrates a small photoemf obtained from a Chl-BLM under a pH gradient in the absence

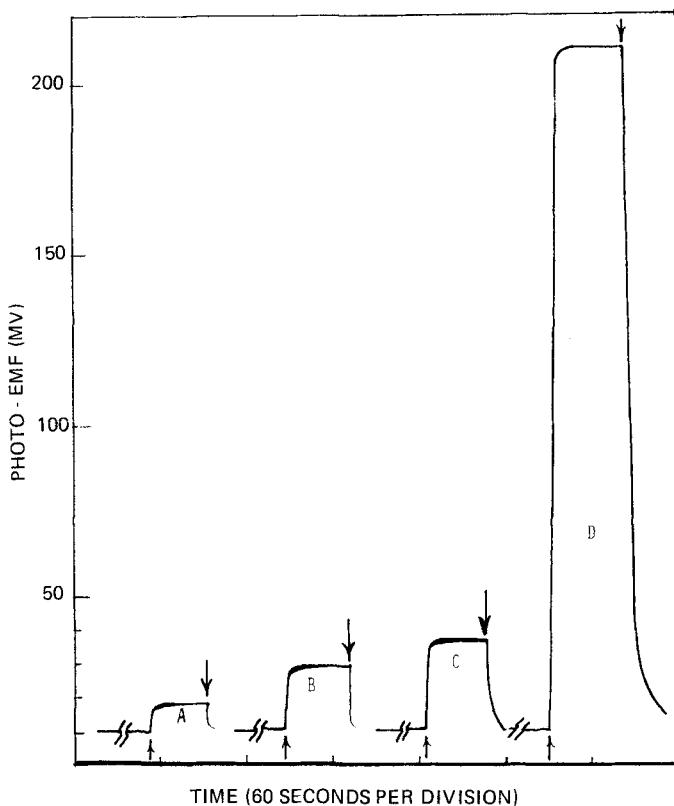


Figure 3. Photoresponses of pigmented BLMs under various conditions. The membrane forming solution consisted of chloroplast extract in *n*-octane and *n*-butanol mixture. For all membranes, the bathing solution adjacent to light contained 0.1M K acetate at pH 4.3 whereas the other solution was 0.1M KCl at pH 8.6 in addition to the other compounds present as specified in the following:

- (a) Bathing solution/PBLM/bathing solution
- (b) Bathing solution/PBLM/5% chlorophyllin
- (c) 10 mM  $\text{FeCl}_3$ /PBLM/bathing solution
- (d) 10 mM  $\text{FeCl}_3$ /PBLM/5% chlorophyllin

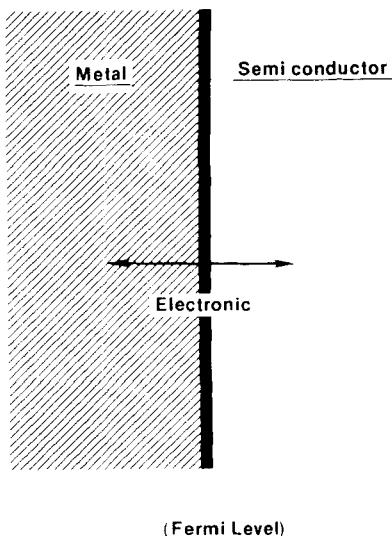
Upward arrows - light on, downward arrows - light off.

of electron donor and acceptor. Twice the photovoltage was detected when chlorophyllin, which acts as an electron donor, was added to the high pH sides as shown in Fig. 3B. In the absence of a chlorophyllin but with the presence of  $\text{FeCl}_3$  in the low pH side, a higher photo-emf was obtained, which is illustrated in Fig. 3C. However, the most dramatic photoresponse was observed when the two light absorbers (chlorophyll and chlorophyllin) and the electron acceptor ( $\text{FeCl}_3$ ) were all present, a nearly ten-fold enhancement of the photo-emf was elicited from the membrane. This is shown in Fig. 3D. It is obvious that the existence of a pH gradient alone, as well as if one of the redox compounds (acceptors and donors) is present is ineffective in generating large photo-emfs. It should be noted that lipid-soluble chlorophyll can be replaced by porphyrins such as Mg-meso-tetraphenyl porphyrin and water-soluble chlorophyllin can be substituted by dyes such as eosin B and thionine (11,30).

2. Theoretical Considerations. The BLM formed from chloroplast extracts is pictured as similar to that of a liquid crystal in two dimensions (14) and behaves as an organic semiconductor (1). If these assumptions are granted, the observed photoelectric effects of pigmented BLM are most easily explained in terms of the band theory of semiconductors (44), with particular reference to the junctions between metals and semiconductors (SC). These junctions are known as Schottky barriers. Such a Schottky barrier is illustrated in Fig. 4 (left). It will be discussed presently that the interface between a pigmented BLM and an aqueous solution is analogous in many ways to a Schottky barrier.

Since most interfaces are electrified, BLM/ $\text{H}_2\text{O}$  interfaces therefore are expected to possess similar characteristics. The space charge in a Schottky barrier is built up only in the semiconductor (SC) owing to the fact that the metal has a far greater density of charge carriers. Also, in a Schottky barrier, the conduction is electronic and probably takes place by electrons and holes tunnel through the barrier. The potential of

### A Schottky Barrier



### PBLM/H<sub>2</sub>O Interfaces

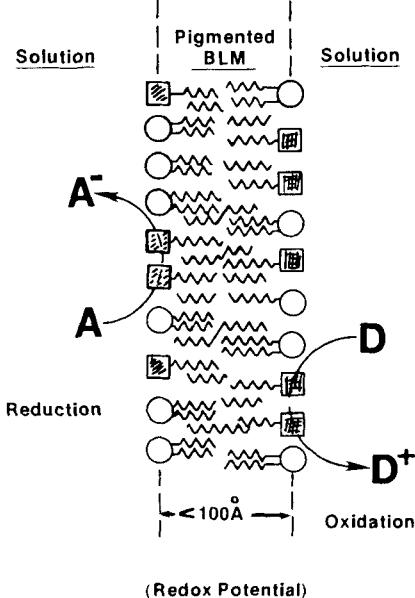


Figure 4. Comparison of the Schottky barrier model with that proposed for pigmented BLM/H<sub>2</sub>O interfaces. Left: A Schottky barrier is a junction between a semiconductor and a metal (or an electrolyte), where space charge is built up only in the semiconductor and no electrochemical reactions take place across the barrier. Right: Pigmented BLM/H<sub>2</sub>O interfaces are depicted. The components in the membrane are lipids (circles with zig zag lines), pigments (squares with zig zag line) and  $\beta$ -carotene (zig zag lines only). A=electron acceptor, A<sup>-</sup> = reduced A, D=electron donor, D<sup>+</sup> = oxidized D.

electrons (holes) is given by the Fermi level in the SC. In the case of pigmented BLM/H<sub>2</sub>O interface, the aqueous solution plays the role of the metal, because it has a much higher density of charge carriers than the BLM. The results is a formation of a space charge region in the BLM at each interface of the membrane. Since an aqueous solutions is not an electronic conductor, redox reactions involving ionic species must take place across

each BLM/H<sub>2</sub>O interface, if an electric current is to flow across the BLM. However, the current within the lipid bilayer may be electronic. For all practical purposes, an unmodified lipid bilayer behaves essentially as an organic SC. Thus, we can also use the Fermi level to describe the electron potential in the BLM. For aqueous solutions bathing the membrane, the chemical potential of electrons (holes) is most naturally described by the redox potentials of the electron acceptors and donors present in the solution. Fig. 4 (right) shows a pigmented BLM separating two aqueous solutions modeled on the photosynthetic membrane of green plants. The most important feature shown in Fig. 4 (right) is that an ultrathin pigmented lipid bilayer (semiconducting) separates two aqueous solutions (highly conducting). Across the interfaces of such an ultrathin structure, a field of more than 100,000 volts per cm can be easily developed.

Before considering what happens at the two interfaces of a pigmented BLM under illumination, let us complete the band theory of semiconductors as applied to the BLM system. We have already mentioned that a BLM is similar to a two-dimensional liquid crystal. Into this array of lipids, two different pigments (or dyes) may be incorporated at opposite sides of the membrane. If these pigments (and/or dyes) were so chosen, one BLM/H<sub>2</sub>O interface could be made to behave as a p-type SC in contact with a redox couple and the other interface acted as an n-type SC in contact with a different redox couple. Such a system is shown in the lower portion of Fig. 2, in which the energy levels of conduction band (E<sub>CB</sub>) and valence band (E<sub>VB</sub>) as well as the Fermi level (E<sub>f</sub>) for the p-type BLM are indicated (the various quantities for the n-type BLM/H<sub>2</sub>O interface are primed). E<sub>g</sub> stands for the energy gap between the two bands. It should be noted E<sub>f</sub><sup>\*</sup> and E<sub>f'</sub><sup>\*</sup> shown are the Fermi levels in the light. Illumination of such BLM/H<sub>2</sub>O interfaces with light of energy greater than E<sub>g</sub> (or E<sub>g'</sub> for the interface at right) can result in the generation of electron-hole pairs in the space charge

regions (depletion layers) where the band bendings have taken place (Fig. 5). At each  $\text{BLM}/\text{H}_2\text{O}$  interface of the space charge region, these pairs are separated by the electric field. At the left region the minority charge carrier (i.e. electron) comes to the  $\text{BLM}/\text{H}_2\text{O}$  interface and is available for a reduction reaction, for example,  $\text{A} + \text{e} \rightarrow \text{A}^-$ . Thus, the left side of the BLM interface acts as a photocathode, whereas the right BLM/ $\text{H}_2\text{O}$  interface, in which minority carriers for n-type BLM are

### BLM/ $\text{H}_2\text{O}$ Interfaces, Illuminated

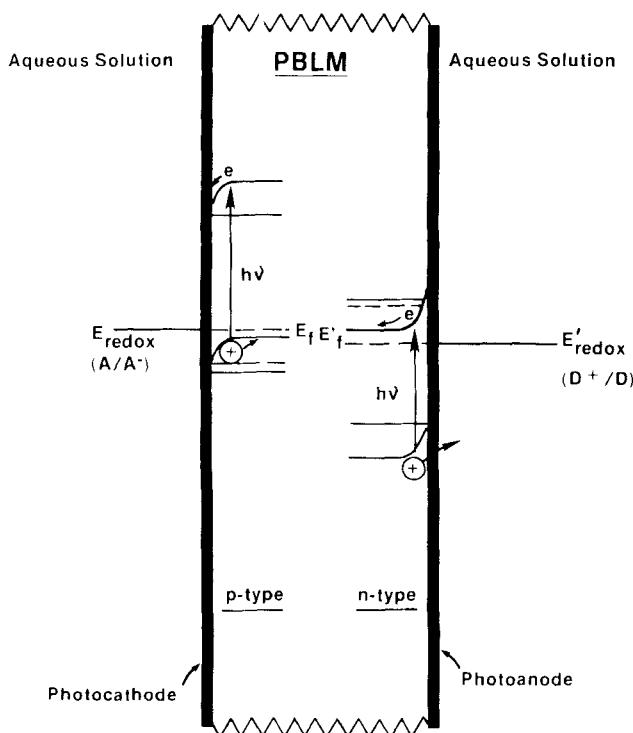


Figure 5. Schematic of a pigmented BLM under illumination with the p-type  $\text{BLM}/\text{H}_2\text{O}$  interface acting as the photoanode and the n-type  $\text{BLM}/\text{H}_2\text{O}$  interface functioning as the photocathode.

holes, is the site for oxidation and therefore functions as a photoanode. Fig. 5 shows an up-to-date version of light-induced redox reactions across a pigmented BLM (45). It should be mentioned that the scheme illustrated, in a sense is analogous to the p-n junction in a photovoltaic cell. One major difference is that, in a solid-state p-n junction device, the majority carriers generated in the bulk of the SC are involved.

Of importance to note in Fig. 5 are the relative positions of the conduction band ( $E_{CB}$ ) and the valence band ( $E_{VB}$ ) with respect to the redox level ( $E_{redox}$ ). When the appropriate band overlaps the redox level of the solution, fast electronic transfer across the interface is expected. The maximum output photovoltage, as can be seen in Fig. 5, is the sum of  $(E_f^* - E_{redox}) + (E_f^{*'} - E'_{redox})$ , which is determined by the properties of pigmented BLM and redox couples present in the bathing solutions. For the quantum efficiency of the system, one would expect that the relative rates of charge transfer across the two interfaces and photoelectron and photohole recombination are the major governing factors.

In previous papers (46) we have considered two types of light-induced processes that are possible in pigmented BLM: exothermic and endothermic. In the former, the overall free energy is negative ( $\Delta G < 0$ ) and in the latter the free energy of the overall reaction is positive ( $\Delta G > 0$ ). For energy-storing processes such as photosynthesis by green plants, we are interested in the endothermic reaction. This means that, for a p-n pigmented BLM, conduction band of the p-type BLM must be more negative than the more negative redox couple and conduction band of the n-type BLM must be more positive than the more positive redox couple. In other words, for an energy storing pigmented BLM, the positions of  $E_{CB}$  and  $E_{VB}$  must be, respectively, above  $E_{redox}$  ( $A/A^-$ ) and below  $E'_{redox}$  ( $D^+/D$ ). However, if these conditions are not met, the system can still be operated as an energy storer, provided an external voltage is applied so that

the applied bias is equal to or greater than  $E_{CB}$  and  $E_{redox}$  ( $A/A^-$ ). Otherwise the energy of light will not be stored; it merely acts as a "catalyst" to lower the energy of activation for the reaction (17, 46).

3. Complete Circuit for a Photoelectric BLM. We can now readily explain the much enhanced photoresponse shown in Fig. 3D. The essence of the system is an asymmetrical pigmented BLM in which lipid-soluble chlorophyll is present at one interface in contact with an electron acceptor ( $Fe^{3+}$ ) and water-soluble chlorophyllin is bound to the other, which at the same time acts as an electron donor. Upon illumination with photons of energy equal to or greater than the band gaps ( $E_c - E_v$  and  $E'_c - E'_v$ ) excitons are generated. These excitons (say, 1.8 eV) may decay by a variety of processes, one of which is exciton-exciton fusion generating higher energetic species than are available in the exciting photon. It seems likely that such a process of upgrading light energy can take place in pigmented lipid membranes. Referring to Fig. 6, excitons thus formed under the influence of the electric field can be separated into electrons and holes. If so, electrons move to the surface (the left BLM/ $H_2O$  interface) where they are captured by electron acceptors to produce a reduction. On the other hand, holes drift towards the interior of the lipid bilayer. In an analogous manner, an oxidation reaction takes place at the right-side membrane/redox solution interface where electron donors are located. In this case, electrons move to the left; holes move to the surface of the pigmented membrane and are injected into the bathing solution. The interesting result is a sum of the two photoevents operating in concert. Moreover, the photo-induced chemical reactions are carried out by one electron-hole pair for each two photons absorbed. In this case the energy of light is converted into chemical energy of the redox compounds separated by the membrane. Thereby the back reactions are prevented as shown in Fig. 5. If one is interested in generating electricity by light, each side of the pigmented BLM

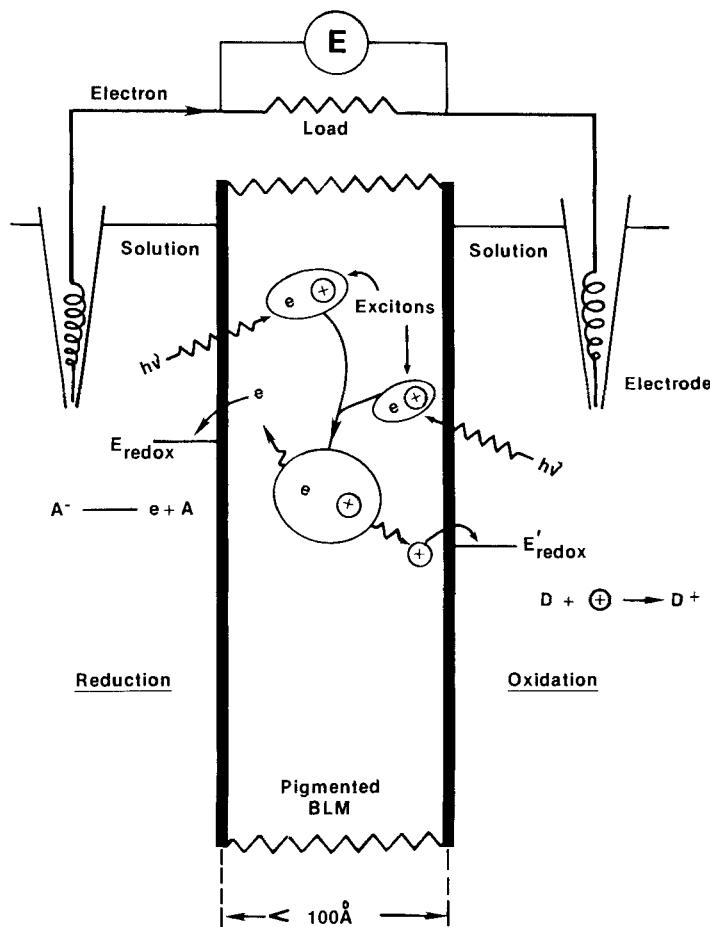


Figure 6. Complete cell diagram for the transduction of light via exciton fusion process, electron (and hole) transfer and redox reactions taking place in a pigmented BLM.

can be coupled to an appropriate half-reaction via an inert electrode (e.g., Pt) and the half-cells connected through an external load as shown in Fig. 6. Thus, the flow of electrons from  $D$  to  $A$  through the external connection performs useful work and restores  $D^+$  to  $D$  to its original state. In this scheme the pigmented BLM

merely acts as a light-driven "pump" moving electrons from one side of the membrane to the other.

Summarizing, the following points may be listed for the light transduction by pigmented photoelectric BLM:

- (a) Absorption of light produces excitons (electron-hole pairs),
- (b) Excitons may interact and/or directly dissociate into electrons and holes in the space regions of the BLM adjacent to the aqueous interfaces,
- (c) Electron injection can occur from the p-type BLM (photocathode) into the bathing solution to produce a reduction,
- (d) Hole injection can take place from the n-type BLM (photocathode) into the bathing solution containing donor to effect an oxidation,
- (e) In order for the redox reactions to proceed in the bathing solutions, redox potentials of involved species must bear a special relationship to the band energies of the semiconducting BLM, and
- (f) For the processes to continue with finite rate, the kinetics of charge transfer must be favorable to preclude undesired reactions.

Figs. 5 and 6 illustrate further these points. The results presented in Fig. 3 are consistent with the suggested mechanisms. To repeat, the uniqueness of the ultrathin liquid-crystalline structure of the BLM in which the two independent interfaces are connected electronically through the lipid bilayer should be stressed. The situation is equivalent to a combination of a p-type and an n-type semiconductor joined together by an ohmic contact (16). An earlier article by Gerischer should be consulted for further details (47). At present, it seems clear that an ultra-thin semiconducting membrane is advantageous in: (i) permitting the development of very large electric field, (ii) facilitating charge separation and collection, and (iii) separating the photo-products. Finally, it should be stated that it may be naive to believe that the primary event in photosynthesis is carried out in the simple manner described. Nevertheless, the experiment using Chl-BLM offers an approach which might provide some insight into the nature of energy transduction in green plants (9, 41, 45).

## PERSPECTIVE

The experimental work described in this paper has demonstrated that electron transport processes across artificial bilayer lipid membranes can be achieved using suitable pigments and redox agents and that such electron transport is driven by light. Apart from the obvious relevance to the photosynthetic thylakoid membrane, such pigmented membrane systems provide an approach to the characterization of pigments and dyes as well as redox compounds. The systems discussed in this paper can be made more durable and practical either for the production of a fuel (e.g., hydrogen) or for the generation of electricity (30). In this area, our effort is just beginning. It is hoped that the fusion of ideas from semiconductor photochemical cells, bilayer lipid membranes and green plant photosynthesis results in a better understanding of all these systems in the endeavor to convert and utilize solar energy.

ACKNOWLEDGMENTS

This work was supported by the National Institutes of Health (GM-14971).

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