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PHOTOELECTRIC EFFECTS IN BILAYER LIPID MEMBRANES CONTAINING COVALENTLY LINKED PORPHYRIN COMPLEXES

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Summary

Complexes of retinal, carotene and quinone covalently linked to porphyrin were incorporated into bilayer lipid membranes (BLMs). The photovoltages and photocurrents in the BLMs were measured on continuous and flash (8 μs) illumination. The photovoltages obtained for tetraphenylporphyrin–carotene and porphyrin–quinone membranes are much larger than those obtained with simple porphyrin membranes. No pigmented BLMs exhibit any latency in their photopotentials when illuminated with a light flash of microsecond duration. The photovoltage and photocurrent action spectra were measured for these pigmented BLMs. The photovoltage and photocurrent observed for the pigmented membranes are explained in terms of a semiconductor model. The enhancement in these photoeffects is explained in terms of intramolecular charge transfer and energy transfer processes.

1. Introduction

The formation of pigmented bilayer lipid membranes (BLMs) of planar and spherical configuration [1, 2] has allowed a variety of photophysicochemical studies to be carried out to investigate the effects of chemical composition, redox compounds and the wavelength of light. The most important feature of such studies may lie in the understanding they provide of the transformation of solar energy into electricity or the storage of this energy in

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chemical compounds as accomplished by green plant photosynthesis for example [3 - 6]. Some of the advantages of the planar BLM system reside in its relatively large size and its configuration which allows access to both its sides and makes it relatively easy for electrical measurements to be carried out. Studies on such pigmented membranes include investigations of membranes formed from chloroplast extract and from purified chlorophylls and their related compounds such as porphyrins with and without added modifiers such as quinones and carotenes [2, 7 - 14].

The photoeffects observed in such pigmented membranes are the result of charge separation and electron transfer reactions (redox reactions) from the excited pigment and suitable electron donors and acceptors at both interfaces. In photosynthetic reaction centers, charge separation and electron transfer take place between the excited chlorophyll molecules and the primary electron acceptors of the electron transport chain [3, 15]. There is evidence that quinones play the role of the primary electron acceptors in these reaction centers and that carotenes act as light-gathering accessory pigments [3, 15]. For these processes to take place efficiently it seems reasonable to assume that a relatively close proximity and proper orientation should exist between the donor species (*e.g.* excited chlorophyll or porphyrin) and the electron acceptor (*e.g.* a quinone).

To test these hypotheses several groups of workers have synthesized covalently linked porphyrin–quinone and porphyrin–carotene complexes [16 - 20]. These investigators have studied the photophysical and photochemical properties of these compounds in bulk solutions or on surfaces. Quenching of the porphyrin fluorescence in the presence of either quinones or carotenes was observed. A similar effect was observed in chlorophyll liposomes containing β-carotenes [21]. The quenched fluorescence of chlorophyll was ascribed to a static process of electron transfer or chlorophyll–chlorophyll interactions brought about by β-carotene.

The effect of quinone and β-carotenes on some membrane model systems has also been investigated. Barsky *et al.* [22] have reported an increase in photovoltages generated across a planar membrane containing reaction centers from photosynthetic bacteria when 1,4-naphthaquinone is added to the aqueous phase and when ubiquinone 30 is added to the membrane. The presence of certain quinones in BLMs containing chlorophyll a has been found to enhance both dark conductivity and photoconductivity [10]. Similarly, an increase in the photovoltage was found in the presence of β-carotene in the chlorophyll BLM [2].

In all these previous studies dealing with the effect of quinones and carotenes in pigmented BLM, however, compounds of porphyrins and/or carotenes were either dissolved in the membrane-forming solution or added to the aqueous phase, and the increase in the photoeffect was relatively small. We report here the photoelectrochemical properties of BLMs containing retinal, carotene and quinone compounds covalently linked to porphyrin. Preliminary results for quinone complexes have been communicated previously [23].

2. Materials and methods

Anhydrous sodium acetate (AnalaR grade), $FeCl_3$ (AnalaR grade; Mallinckrodt Inc.), ascorbic acid, phosphatidylserine, phosphatidylcholine and phosphatidylethanolamine (Sigma Chemical Co.) were used without further purification. However, cholesterol (Fisher Scientific Co.) was purified by repeated crystallization. The porphyrins with ester side chains were prepared by the condensation of dipynomethene. The amines were obtained from alcohols and mesylates [24]. The quinone compounds were prepared following the published methods [16, 17]. However, in our case silver oxide was used to oxidize the dihydroxy groups. Porphyrin–retinyl was obtained by the condensation of porphyrin amine and retinal. All these compounds were prepared under minimum illumination to protect them from photodecomposition and were stored at a low temperature. The purities of the final compounds were checked by thin layer chromatography and mass and optical spectroscopy. The tetraphenylporphyrin (TPP)–carotene complex was a generous gift from Professor Gust, Arizona State University. The synthesis and characterization of this complex has already been published [19]. *n*-octane (Fisher Scientific Co.) and doubly distilled water were used as solvents.

A solution of phosphatidylcholine, phosphatidylethanolamine, cholesterol and phosphatidylserine in the ratio 3.1:1.7:1.1:1.0 by weight was prepared in *n*-octane to a final concentration of approximately 7%. A saturated solution of each porphyrin compound in the above solution was used as the membrane-forming solution.

The membranes were formed by ejecting a small amount of membrane-forming solution over the orifice (1 mm in diameter) of a 10 ml Teflon cup separating two aqueous solutions (0.1 M sodium acetate buffer, pH 5.0) using a Hamilton microsyringe. The Teflon cup was placed in a Plexiglas chamber. The two faces of the Plexiglas chamber, one for illuminating and the other for viewing the membrane, contained optically flat glass windows. Calomel electrodes with salt bridges were used in the usual manner for electrical contact [2]. The aqueous solutions were continuously agitated by magnetic stirring bars in each of the chambers. The thinning of the membrane to the secondary black state was observed with a binocular microscope. $FeCl_3$ and ascorbic acid were added to the inner and outer chambers respectively to a final concentration of 10 mM after the membranes had thinned and reached the black state.

The photopotentials and photocurrents were measured using a Keithley 610 electrometer and a Keithley 417 picoammeter connected to a Keithley 370 or Bausch and Lomb recorder. In some cases the signal was amplified through a high impedance amplifier and recorded on a Tektronix R5031 dual-beam storage oscilloscope. The closed-circuit measurements were performed by applying a potential through an external resistance which was nearly equal to the membrane resistance in the dark. The membranes were illuminated with white light from a 250 W tungsten–halogen lamp or a

1000 W xenon lamp. Microsecond flash (8 μs) illumination experiments were performed using a General Radio Strobotac 1538A xenon flash lamp assembly. All the other experimental arrangements were the same as described elsewhere [2].

The experimental set-up for recording the action spectra consisted of a 1000 W xenon lamp assembly (Schoeffel), a Bausch and Lomb 250 mm grating monochromator, a pair of calomel electrodes, a Keithley 610 electrometer and a Bausch and Lomb or Plotamatic 715M recorder. The spectra were measured by rotating the diffraction grating with a slow speed motor or manually point by point in increments of 10 nm. The action spectra were corrected for constant illumination intensity with a calibration curve obtained for the experimental arrangement using a Scientific Instrument Kettering radiant power meter. The absorption spectra for BLM-forming solutions (saturated solution of pigment) were recorded on a Varian Cary 219 spectrophotometer by sandwiching the solution between two glass plates. All the experiments were performed at 23 ± 1 °C.

3. Results

The membranes reached the black state 5 - 15 min after their formation. The membrane resistance R_m in the dark was measured by applying an external voltage through a high resistance ($R_s \approx 10^8\ \Omega$) in series. The values of R_m for BLMs containing various porphyrin compounds are given in Table 1. These values were measured after 3 - 4 h of membrane formation when they were almost constant.

Open-circuit photo-e.m.f.s for various BLMs in the presence of $FeCl_3$ and ascorbic acid in the aqueous solutions are given in Table 1. For most of the compounds a small and slow photo-e.m.f. was observed initially; however, with time the photopotential showed an increase in magnitude and a decrease in the response time and finally after 3 - 4 h it became almost constant. This behavior was observed in BLMs containing porphyrin, porphyrin-C_{12} and TPP–carotene. However, the response for the BLMs containing porphyrin–quinone and porphyrin–retinyl was fast initially and became much faster with time with a simultaneous increase in the magnitude. The rise and decay of the open-circuit photo-e.m.f. with continuous illumination is shown in Fig. 1(a) for BLMs containing porphyrin, porphyrin–quinone and porphyrin–retinyl. All the values of the open-circuit photo-e.m.f.s given in Table 1 for BLMs containing various compounds were recorded after 3 - 4 h of membrane formation when the photo-e.m.f. was almost constant. The values of the photo-e.m.f. given in Table 1 clearly indicate that it is enhanced in all BLMs containing monosubstituted compounds except the BLM containing porphyrin-C_{12}. The BLMs containing TPP–carotene and porphyrin–quinone showed more than threefold enhancement compared with the BLM containing porphyrin. In BLMs containing disubstituted complexes the photo-e.m.f. was almost equal to or lower than that of the BLM containing porphyrin.

TABLE 1

Photovoltage, photocurrent and membrane resistance for bilayer lipid membranes containing porphyrin complexes

Compound	*Photovoltage* (mV)		*Photocurrent with continuous illumination* (nA)	R_m ($\times 10^8\ \Omega$)
	Continuous illumination	*Flash illumination*		
Porphyrin	83	0.4	0.10	4
Porphyrin–retinal	154	20	1.3	3
Porphyrin–diretinal	70	3.0	0.6	8
Porphyrin–quinone	302	42	22	8
Porphyrin–diquinone	92	1.0	1.2	3
Porphyrin–dodecyl	83	0.25	0.15	8
TPP–carotene	300	4.0	1.2	11

The intensity of white light in continuous illumination was 250 mW cm^{-2}. The values of the photo-e.m.f.s with flash illumination were measured 100 μs after the flash. The structural details of the compounds are given in Appendix A.

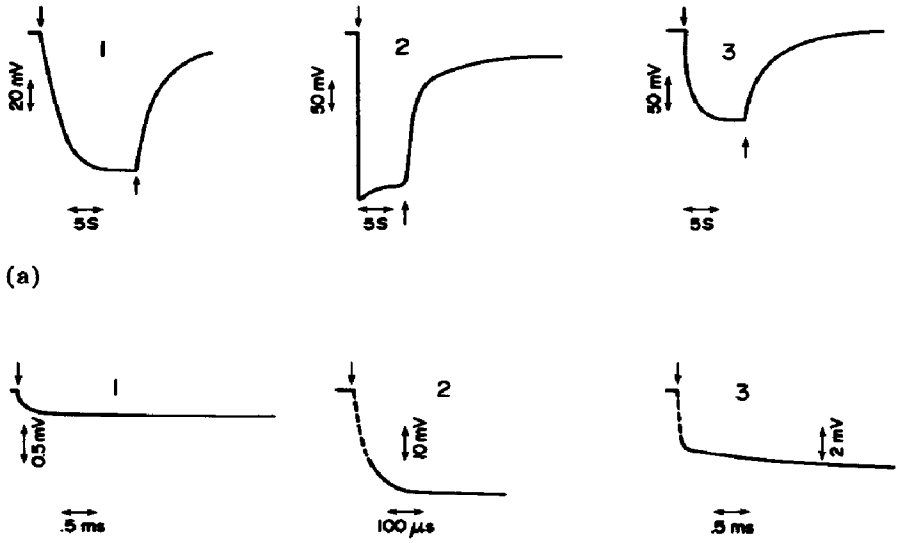

Fig. 1. (a) Development of the photovoltage under continuous illumination with white light for BLMs containing porphyrin (curve 1), porphyrin–quinone (curve 2) and porphyrin–retinyl (curve 3) (↓, light on; ↑, light off); (b) development of the photovoltage under flash illumination (8 μs duration) for BLMs containing porphyrin (curve 1), porphyrin–quinone (curve 2) and porphyrin–retinyl (curve 3) (↓, onset of flash illumination). The pigmented BLMs were formed in 0.1 M sodium acetate buffer (pH ≈ 5.00) with the outer solution containing 10 mM ascorbic acid and the inner solution containing 1 mM $FeCl_3$. The intensity of the white light was 250 mW cm^{-2}.

The membranes containing TPP–carotene, porphyrin–retinal and porphyrin–quinone all exhibit a small photovoltage in the absence of a donor or an acceptor in the bathing solution. The photopotential was found to increase after the addition of $FeCl_3$ to the inner chamber and showed further enhancement after the addition of ascorbic acid to the outer chamber. However, if only ascorbic acid was added to one side with no $FeCl_3$ on the other side, the photopotential observed was smaller than that observed in the presence of $FeCl_3$ only.

All photovoltage and photocurrent measurements were carried out in the presence of 1 mM $FeCl_3$ in the bathing solution in the inner chamber and 10 mM ascorbic acid in the bathing solution in the outer chamber. However, for some membranes, the open-circuit photo-e.m.f.s were also measured for different concentrations of $FeCl_3$ while the ascorbic acid concentration was kept constant (10 mM). The dependence of the photo-e.m.f. on the $FeCl_3$ concentration for a BLM containing porphyrin–quinone is shown in Fig. 2.

Open-circuit photo-e.m.f. measurements were also carried out on BLMs containing some of these compounds at higher pH values (sodium acetate (0.1 M) buffer, pH $\approx$ 7.5) in the presence of $FeCl_3$ and ascorbic acid or of ethylenediamine tetraacetic acid and anthraquinone-2-sulfonate but the magnitude of the photo-e.m.f. was lower at this pH. Our results are similar to those reported by Jimbo *et al.* [25] for TPP-coated electrodes in the presence of some quinones. These workers have suggested that the protonation of the porphyrin film surface plays an important role in the charge transfer process.

Short-circuit photocurrent measurements with continuous light were also made for BLMs containing porphyrin compounds in the presence of

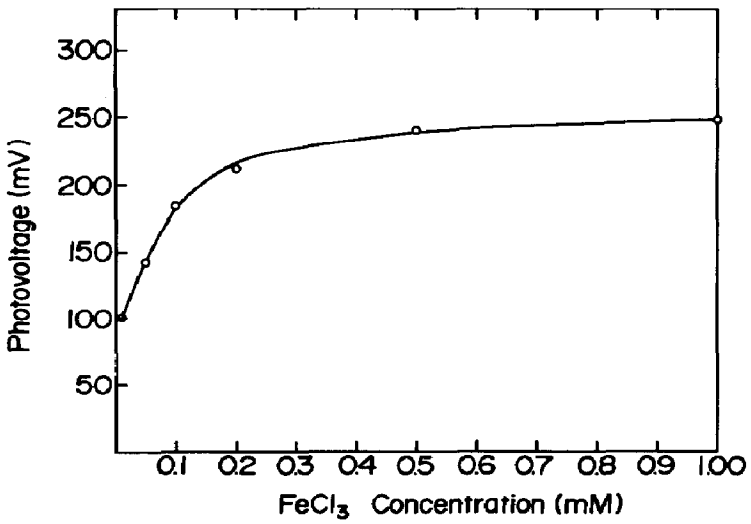

Fig. 2. Dependence of the photovoltage on the $FeCl_3$ concentration in the inner chamber of the bathing solution for a BLM containing the porphyrin–quinone complex. The bathing solution was 0.1 M sodium acetate buffer (pH $\approx$ 5.00) and the outer chamber contained 10 mM ascorbic acid. The intensity of the white light was 250 mW cm^{-2}.

$FeCl_3$ and ascorbic acid and the results are given in Table 1. For BLMs containing porphyrin–quinone compounds the short-circuit current is about 200 times higher than for the BLM containing porphyrin.

The open-circuit photo-e.m.f. and the short-circuit photocurrent for the BLMs were also measured for different intensities of white light. These results are shown in Fig. 3 for the BLM containing porphyrin–quinone. Both photovoltage and photocurrent are almost linear initially (*i.e.* for low light intensities) but the saturation point is reached much earlier for the photovoltage. Our results are similar to those previously observed for the chloroplast extract BLM and for photovoltaic cells [1, 2]. Similar experiments were also performed for light of wavelength 400 and 500 nm using interference filters and the results are similar to those obtained for white light illumination.

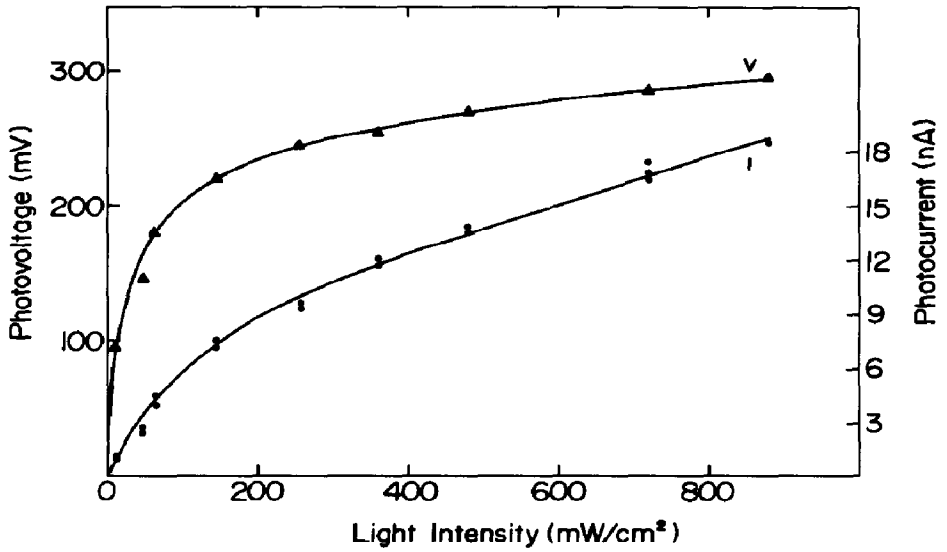

Fig. 3. Dependence of the photoeffects on the intensity of the illuminating light for a BLM containing porphyrin–quinone: ▲, photovoltage; ●, photocurrent. The bathing solution was 0.1 M sodium acetate buffer (pH ≈ 5.00) with 1 mM $FeCl_3$ in the inner chamber and 10 mM ascorbic acid in the outer chamber.

Apart from the continuous illumination, the open-circuit photovoltages were also measured under flash illumination (8 μs) for BLMs containing different porphyrin compounds and the photoresponses were observed. The magnitudes of the photovoltage 100 μs after the flash are listed in Table 1. The development of the photovoltage for BLMs containing porphyrin, porphyrin–quinone and porphyrin–retinyl is shown in Fig. 1(b). No delay was found from the flash to the generation of the photovoltage, which was limited by our 8 μs flash unit. This behavior is similar to that observed earlier for a chloroplast extract BLM [26].

The action spectra for the photoeffects of the porphyrin-containing BLMs were obtained. In general these spectra follow the absorption spectra

of the specific porphyrin complex present in the membrane, *i.e.* the positions of the maxima in the action spectra match the positions of the peaks in the absorption spectra. Moreover, the positions of the maxima in the action spectra and in the absorption spectra for the different porphyrin complexes (including simple porphyrin) are almost identical. These results indicate that the species responsible for the photoeffects is the porphyrin ring. However, the relative intensity of the peaks in the action spectra for each porphyrin-containing membrane is different from the relative intensity in their corresponding absorption spectra. The difference is observed in the relative ratio of the band at 400 nm (Soret band) to the bands in the lower energy region beyond 450 nm (maxima at 500, 534, 574 and 624 nm). To investigate this in more detail the photocurrent action spectrum for the porphyrin–quinone membrane was measured (Fig. 4). A difference in the ratio of the bands in the photocurrent spectrum compared with the absorption spectrum was also observed. These results suggest that the quantum efficiency for the photocurrent may be different for the different absorption bands. A calculation of the relative quantum efficiency at the different bands suggests that the quantum efficiency at the lower energy bands is about twice the quantum efficiency at 400 nm. A higher quantum efficiency for red light compared

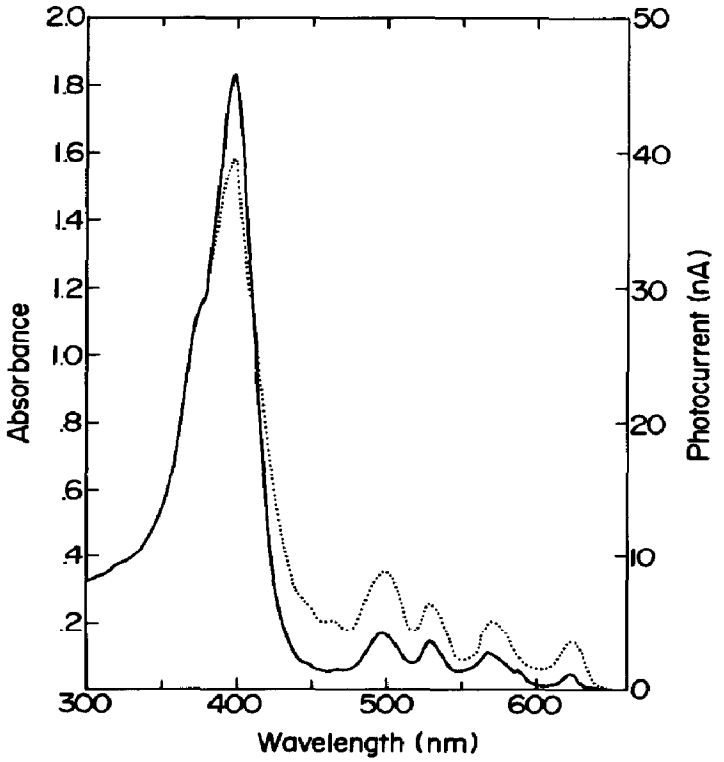

Fig. 4. Absorption spectrum of a saturated solution of the porphyrin–quinone-3 complex in the BLM-forming solution sandwiched between two thin glass plates (———); photocurrent action spectrum of a BLM containing the porphyrin–quinone-3 complex corrected for constant intensity of illumination (·····).

with blue light has been reported for electrodes coated with manganese(III) porphyrin [27]. One possible explanation for this difference may be the decrease in absorbance at the Soret band for higher pigment concentrations. However, in our studies the absorption spectrum used for comparison is that of a saturated solution. The only way to be certain would be to measure the absorption spectrum of the membrane itself. Owing to the thinness of the BLM, this is a very difficult task. This is also the reason why we have not measured the absolute quantum efficiency for any of the porphyrin complexes.

4. Discussion

The photoelectric effects observed for BLMs containing porphyrin complexes can be explained in the same way as for membranes made from chloroplast extracts [2]. The observed photoelectric phenomena are due to redox reactions occurring at both membrane–electrolyte interfaces with electrons acting as the charge carriers across the membrane [1, 2, 7 - 14]. In this respect the pigmented BLM is assumed to be an organic semiconductor [2, 4] which is analogous to a Schottky barrier except that the BLM system has two interfaces. Bearing this assumption in mind, one side of the membrane acts as a photocathode (p-type junction) and the other side acts as a photoanode (n-type junction) as shown in Fig. 5. The aqueous solution plays the role of the metal at the BLM–electrolyte interface. The photovoltages observed are influenced by the redox compounds (electron donors and acceptors) present in the bathing solution and/or externally applied voltages. It should be pointed out that current flow in the BLM is due to photogenerated and dissociated electron–hole pairs (excitons); however, unlike the metal in a Schottky-type cell, the aqueous solution is not an electronic conductor. Therefore redox reactions must take place at both interfaces in order to complete the circuit. A more detailed description of the semiconductor model of charge separation in BLMs has been discussed in detail elsewhere [2, 28].

The larger photoeffects observed in these experiments for the porphyrin complexes as compared with simple porphyrin can be explained in terms of two processes taking place between the porphyrin and the covalently linked compound: (i) charge transfer and (ii) energy transfer. In the case of the complexes consisting of benzoquinone molecules covalently linked to a porphyrin molecule, the enhancement in the photoresponse is believed to be due to the first process, *i.e.* intramolecular charge transfer between the donor (porphyrin) and the acceptor (quinones). This intramolecular charge transfer depends on the overlap between the highest filled donor orbitals and the lowest filled acceptor orbitals and is determined by the interaction between the π electrons in the donor–acceptor pair. This interaction should depend on the distance and orientation between the donor and acceptor parts of the covalently linked complex. Evidence for this is given by the fact

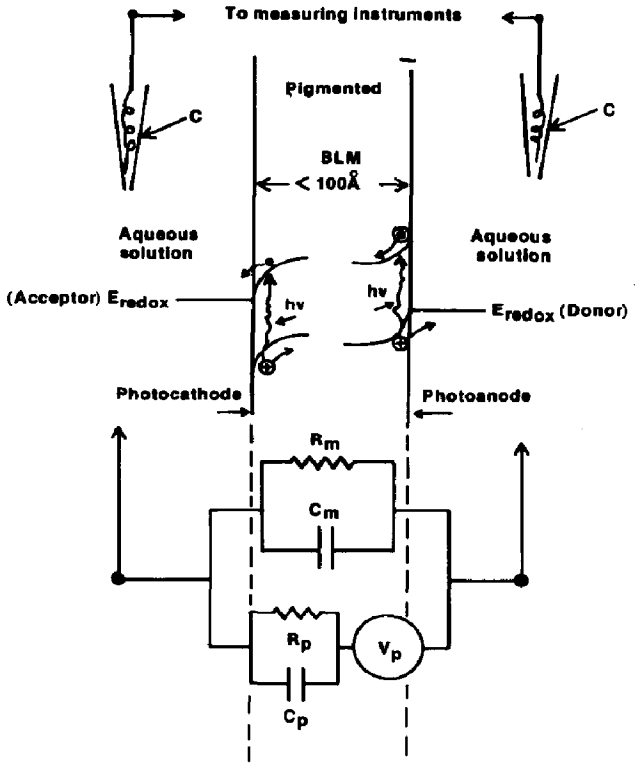

Fig. 5. Schematic diagram and equivalent circuit of a pigmented BLM under illumination with one membrane–electrolyte interface acting as the photocathode and the other as the photoanode: c, calomel electrode; E_{redox}, standard redox potential; R_m, membrane dark resistance; C_m, membrane capacitance; R_p, membrane photoresistance; C_p, membrane photocapacitance; V_p, membrane photopotential (see refs. 8, 12 and 27).

that the magnitude of the photoeffects varies for the quinones linked by different chain lengths to the porphyrin (see ref. 23). The largest enhancement is observed for the quinone linked by the chain with the largest number of atoms. The smaller photoresponse for the shorter chain may be due to improper orientation between the two groups or too short a distance between the two moieties. A smaller photoresponse for a closer proximity could be due to a higher probability of the back reaction regenerating excited porphyrin and the oxidized acceptor competing strongly with the charge separation reaction. A possible explanation for the smaller photoresponse in the double quinone complexes is related to the number of pigment molecules in the membrane. It was observed that the solubility of the double quinone complexes was much lower than that of the single quinone complexes. Our results on the enhancement of the photoeffects in these quinone–porphyrin complexes is further supported by some recent studies on fluorescence quenching in similar types of complexes [16 - 20]. Quenching of the porphyrin fluorescence would indicate that there would be more excited molecules available for competing non-radiative processes including charge transfer to take place. It should be mentioned, however, that the probability

for non-radiative processes may be increased more than that for charge transfer since total quenching of fluorescence has been observed for a complex containing four quinones covalently linked to a porphyrin [19].

In the case of the covalently linked porphyrin–retinyl and TPP–carotene the enhanced photoeffects can be explained in terms of intramolecular energy transfer processes as well as intramolecular charge transfer processes. Here we believe that the stacked conformation in which the π electron of the retinyl or carotene chromophore resides lies just above the mean porphyrin plane. The retinyl or carotene moiety performs an antenna function by transferring the energy of the absorbed light to the singlet excited state of the porphyrin moiety as was observed by Moore *et al.* [19] in their optical and nuclear magnetic resonance bulk phase studies. These workers have also observed a substantial quenching of porphyrin fluorescence by the carotenoid moiety which suggests the possibility of the formation of a charge-separated state and results in the enhanced photoeffect across the BLMs in the present experiments. The quenching of chlorophyll fluorescence by carotenoids was explained similarly by electron transfer from carotenoid to chlorophyll by Beddard *et al.* [29]. Thus pigmented BLMs containing porphyrin–retinyl or TPP–carotene complexes may be very useful from the photosynthetic point of view because they can act both as antennae for gathering light energy and as efficient charge separators. Again it is interesting to note that the photoeffects in covalently linked porphyrin–diretinyl complexes were smaller than in the single retinyl complexes. This can be explained in the same way as in the case of covalently linked porphyrin–diquinones.

Finally in the case of the porphyrin–dodecyl complexes, no enhancement of the photoeffects was observed relative to simple porphyrin. The covalently linked moieties in this case cannot act as light-gathering entities nor can they act as electron donors or acceptors. This is additional evidence in support of our hypothesis of intramolecular charge transfer and energy transfer in the quinone–porphyrin and retinyl–porphyrin complexes. We propose that a porphyrin ring containing both covalently linked quinone and β-carotene would probably generate a very large photovoltage and photocurrent. This type of compound may prove to be very useful in solar energy conversion [3, 4, 6].

Acknowledgments

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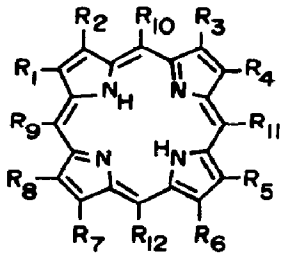
Appendix A



Porphyrin: $R_1 \equiv R_3 \equiv R_5 \equiv R_7 \equiv CH_3$; $R_2 \equiv R_6 \equiv C_5H_{11}$; $R_4 \equiv R_8 \equiv (CH_2)_2COOCH_3$; $R_9 \equiv R_{10} \equiv R_{11} \equiv R_{12} \equiv H$.

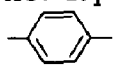
Porphyrin–retinal: $R_1 \equiv R_4 \equiv R_5 \equiv R_7 \equiv CH_3$; $R_2 \equiv R_3 \equiv R_6 \equiv C_5H_{11}$; $R_8 \equiv (CH_2)_2—COOC_{20}H_{29}$; $R_9 \equiv R_{10} \equiv R_{11} \equiv R_{12} \equiv H$.

Porphyrin–diretinal: $R_1 \equiv R_3 \equiv R_5 \equiv R_7 \equiv CH_3$; $R_2 \equiv R_6 \equiv C_5H_{11}$; $R_4 \equiv R_8 \equiv (CH_2)_2—COOC_{20}H_{29}$; $R_9 \equiv R_{10} \equiv R_{11} \equiv R_{12} \equiv H$.

Porphyrin–quinone: $R_1 \equiv R_4 \equiv R_5 \equiv R_7 \equiv CH_3$; $R_2 \equiv R_3 \equiv R_6 \equiv C_5H_{11}$; $R_8 \equiv (CH_2)_3—N(Bu)—CO—C=C—C_6H_3O_2$; $R_9 \equiv R_{10} \equiv R_{11} \equiv R_{12} \equiv H$.

Porphyrin–diquinone: $R_1 \equiv R_3 \equiv R_5 \equiv R_7 \equiv CH_3$; $R_2 \equiv R_6 \equiv C_5H_{11}$; $R_4 \equiv R_8 \equiv (CH_2)_3—N(Bu)—CO—C=C—C_6H_3O_2$; $R_9 \equiv R_{10} \equiv R_{11} \equiv R_{12} \equiv H$.

Porphyrin dodecyl: $R_1 \equiv R_4 \equiv R_5 \equiv R_7 \equiv CH_3$; $R_2 \equiv R_3 \equiv R_6 \equiv C_5H_{11}$; $R_8 \equiv (CH_2)_2—CONHC_{12}H_{25}$; $R_9 \equiv R_{10} \equiv R_{11} \equiv R_{12} \equiv H$.

TPP–carotene: $R_1 \equiv R_2 \equiv R_3 \equiv R_4 \equiv R_5 \equiv R_6 \equiv R_7 \equiv R_8 \equiv H$; $R_9 \equiv R_{10} \equiv R_{12} \equiv$  ;

$R_{11} \equiv$