Light-driven Electron Transport through an Asymmetric Photosynthetic Liquid Membrane

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Light-irradiation of a photosynthetic liquid membrane containing an asymmetric arrangement of chlorophyll a (Chl a), brought about electron transport between two aqueous solutions containing equal amounts of dissolved potassium ferricyanide $[K_3Fe(CN)_6]$ and ferrocyanide $[K_4Fe(CN)_6]$, respectively.

The green plant converts sunlight into chemical energy with extremely high efficiency with the aid of two coupled, different, photosystems which are incorporated one on either side of a bilipid membrane. A number of efforts[1] have been made in the past few years to develop models of naturally occurring photosynthetic membranes which might be used to convert sunlight into electricity and storable fuels. We now report the preparation of an asymmetric liquid membrane (supported on a millipore filter) which contains an electron carrier, 2-ethylanthraquinone (EAQ), and which has a photosensitizer, chlorophyll a (Chl a) located only at one side of the membrane. Such a system is a much simplified artificial photosynthetic membrane, and it permits a light-driven electron transport between two aqueous phases of equal chemical potentials.

Two different types of photosynthetic liquid membranes were prepared supported on a cellulose nitrate millipore filter with a small pore size of 0.025 μm:† (a) Chl a‡ (0.15 μmol) was painted on one side of the filter [soaked beforehand by EAQ (40 μmol) dissolved in 0.12 ml of Ph_2O : $Cl_2CHCHCl_2$ = 9:1 (w/w)] and (b) Chl a (0.15 μmol) was painted on both

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† The circular millipore filters (diameter; 47 mm, thickness; 125—150 μm) purchased from Millipore Ltd., were used in this experiment.

‡ The Chl a used was isolated from spinach and substantially free of chlorophyll b and other pigments.
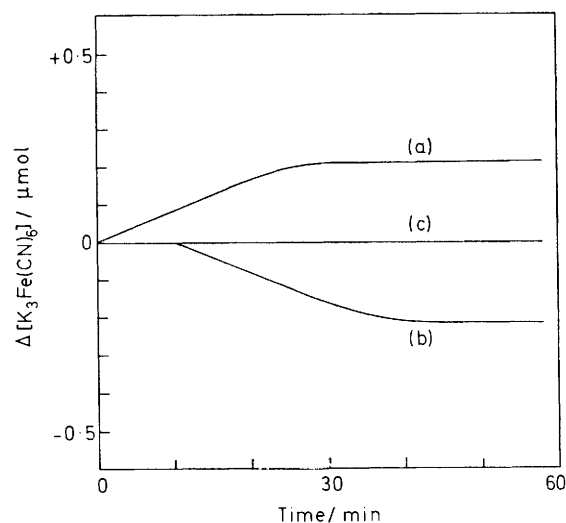
Figure 1. Time-dependence of the changed amounts of $K_3Fe(CN)_6$ (see text) (a) in (I) and (b) in (II) for the asymmetric membrane [whose side painted with Chl a is kept in contact with (I)] and (c) in (I) and (II) for the symmetric membrane (for comparison).

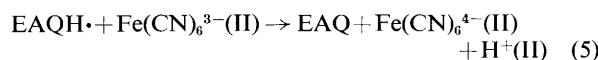**Table 1.** Light-driven electron transport through an asymmetric or symmetric photosynthetic liquid membrane.
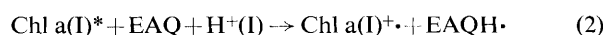
Membrane components	Membrane arrangement[a]	Light	Initial transport rate/ μmol h^{-1}	Transport period/h
EAQ		+	0	
Chl a	A, S	+	0	
EAQ+Chl a	A, S	—	0	
EAQ+Chl a	S	+	0	
EAQ+Chl a	A	+	0.5	0.4
EAQ+Chl a+pheo	A	+	0.9	0.6
EAQ+Chl a+LV²⁺	A	+	0.8	0.6
EAQ+Chl a+CV²⁺	A	+	0.8	0.6
EAQ+Chl a+pheo	S	+	0	

[a] A = asymmetric, S = symmetric arrangement of Chl a in the membranes, respectively.

sides of the soaked filter.§ On the basis of our previous observation that small molecules freely diffuse through the pores, while molecules with a long alkyl chain are confined to the side painted with them,[2] we suggest that in the former membrane there is an asymmetric arrangement of Chl a and there is a symmetric arrangement in the latter, although, of course, EAQ is equally distributed on both sides. We have found a remarkable difference in the light-driven electron transport across these two membranes.

The electron-transporting system consisted of two degassed phosphate buffers (I) and (II) (pH 7.0; 50 ml) in which were dissolved, respectively, equal amounts of $K_3Fe(CN)_6$ (100 μmol) and $K_4Fe(CN)_6$ (100 μmol), separated by the liquid membranes as above. Under light-irradiation¶ the asymmetric membrane was found to transport electrons between the aqueous phases. For example, when the membrane side painted with Chl a was kept in contact with (I) and irradiated, electrons were transported from (I) to (II). This is evident from the fact that the amount of $K_3Fe(CN)_6$ gradually increases in (I), while in (II) a corresponding decrease was observed after an induction period of ca. 10 min (see Figure 1). The electron transport proceeded at a rate of 0.5 μmol h^{-1} for an initial period of ca. 30 min, but then stopped because of bleaching of Chl a.[3] The rate was somewhat improved (max. 0.9 μmol h^{-1}) by incorporating a small amount (0.15 μmol) of an additive such as pheophytin (pheo), 1,1'-dilauryl-4,4'-dipyridinium dichloride (LV²⁺), or 1,1'-dicetyl-4,4'-dipyridinium dichloride (CV²⁺) into the above membrane. In addition, the membrane system continued to transport electrons for a longer period of ca. 40 min. Table 1 summarizes the results for each membrane system. Addition of pheo or the
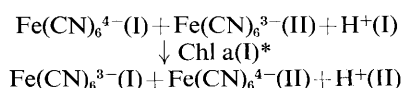
dipyridinium salt brought about an increase in transport rate of 80 and 60%, respectively; all additives gave rise to a ca. 50% increase in transport period.

In striking contrast with the asymmetric membrane, the symmetric membrane exhibited no electron movement even under irradiation. No electron transport was obtained either when the membrane system was supported on a cellulose nitrate millipore filter with a large pore size of 0.45 μm,† even when only one side of the filter was painted with Chl a, showing that the asymmetry in the membrane is dependent on the membrane pore size, as suggested. In each case Chl a was completely bleached within 30 min after the irradiation.

For the asymmetric membrane the light-driven electron transport can be summarized as proceeding through steps (1)—(6) (Med = mediator).

$$\text{Chl a(I)} \xrightarrow{h\nu} \text{Chl a(I)*} \tag{1}$$

$$\text{Chl a(I)*} + \text{EAQ} + \text{H}^+(\text{I}) \rightarrow \text{Chl a(I)}^{+\cdot} + \text{EAQH}\cdot \tag{2}$$

$$\text{or} \begin{cases} \text{Chl a(I)*} + \text{Med} \rightarrow \text{Chl a(I)}^{+\cdot} + \text{Med}^{-\cdot} & (3) \\ \text{Med}^{-\cdot} + \text{EAQ} + \text{H}^+(\text{I}) \rightarrow \text{Med} + \text{EAQH}\cdot & (4) \end{cases}$$

$$\text{EAQH}\cdot + \text{Fe(CN)}_6{}^{3-}(\text{II}) \rightarrow \text{EAQ} + \text{Fe(CN)}_6{}^{4-}(\text{II}) + \text{H}^+(\text{II}) \tag{5}$$

$$\text{Chl a(I)}^{+\cdot} + \text{Fe(CN)}_6{}^{4-}(\text{I}) \rightarrow \text{Chl a(I)} + \text{Fe(CN)}_6{}^{3-}(\text{I}) \tag{6}$$

Net reaction:

$$\text{Fe(CN)}_6{}^{4-}(\text{I}) + \text{Fe(CN)}_6{}^{3-}(\text{II}) + \text{H}^+(\text{I})$$
$$\downarrow \text{Chl a(I)*}$$
$$\text{Fe(CN)}_6{}^{3-}(\text{I}) + \text{Fe(CN)}_6{}^{4-}(\text{II}) + \text{H}^+(\text{II})$$
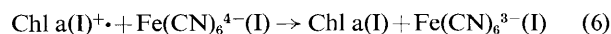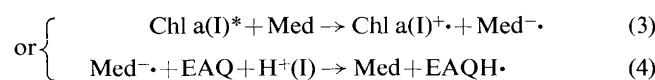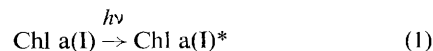
Transport of one proton through the membrane occurs simultaneously in the same direction as the electron transport (two electrons and two protons can be transported simultaneously in an alternative scheme involving an EAQ–EAQH₂ shuttle). Presumably, the rate-acceleration effect of pheo, LV²⁺, and CV²⁺ on the electron-transporting system is attributable to their participation as electron mediator in the electron transfer step from Chl a(I)* to EAQ (steps 3 and 4); the estimated redox potentials of the additives (ca. −0.6 V for pheo[4] and ca. −0.4 V for LV²⁺ and CV²⁺)[5] are between the potentials for Chl a* (< −0.8 V)[4] and EAQ (ca. +0.1 V).[5] It should be noted that among the electron mediators used the most efficient (pheo) is considered to be a primary electron acceptor of the charge separation induced by light in photosystem II of plant photosynthesis.[6] For the symmetric membrane it is possible that the reverse electron transport from $Fe(CN)_6{}^{4-}$(II) to $Fe(CN)_6{}^{3-}$(I) proceeds as above with the aid of Chl a(II)*. This would result in no apparent electron movement if the opposing reactions occur simultaneously.

The present electron-transporting system with its asymmetric

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§ The Chl a was dissolved in ca. 0.1 ml of hexane. After the solution was painted on the membrane, the hexane solvent was evaporated as thoroughly as possible.

¶ Visible light of >490 nm, where EAQ has no absorption, was irradiated from both sides of the membrane by using a 500 W halogen lamp and a glass cut filter. During irradiation the aqueous solutions were kept at a constant 30 °C and gently vibrated to facilitate mixing by argon bubbling. The extent of electron transport was obtained from the concentration change of $K_3Fe(CN)_6$ in (I) and (II), which were determined spectrophotometrically by monitoring the absorbance at 421 nm.

photosynthetic liquid membrane involves the storage of free energy; thus it constitutes a new type of light-driven concentration cell, from which electricity could be produced.

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References

1 M. Calvin, *Photochem. Photobiol.*, 1976, **23**, 425; D. S. Berns, *ibid.*, 1976, **24**, 117; K. P. Seefeld, D. Möbius, and H. Kuhn, *Helv. Chim. Acta*, 1977, **60**, 2608; S. Valenty, *Macromolecules*, 1978, **11**, 1221; M. Calvin, *Acc. Chem. Res.*, 1978, **11**, 369; J. M. Mountz and H. T. Tien, *Photochem. Photobiol.*, 1978, **28**, 395.

2 T. Sugimoto, J. Miyazaki, T. Kokubo, S. Tanimoto, M. Okano, and M. Matsumoto, *Tetrahedron Lett.*, 1981, 1119; *J. Chem. Soc., Chem. Commun.*, 1981, 210.

3 W. Stillwell and H. T. Tien, *Biochim. Biophys. Acta*, 1977, **461**, 239.

4 I. Fujita, M. S. Davis, and F. Fajer, *J. Am. Chem. Soc.*, 1978, **100**, 6280.

5 W. H. Clark, 'Oxidation-Reduction Potentials of Organic Systems,' Williams and Wilkins, Baltimore, 1960.

6 V. V. Klimov, A. V. Klevanik, V. A. Shuvalov, and A. A. Krasnovskii, *FEBS Lett.*, 1977, **82**, 183; K. Sauer, P. Mathis, S. Acker, and J. A. Van Best, *Biochim. Biophys. Acta*, 1978, **503**, 120.