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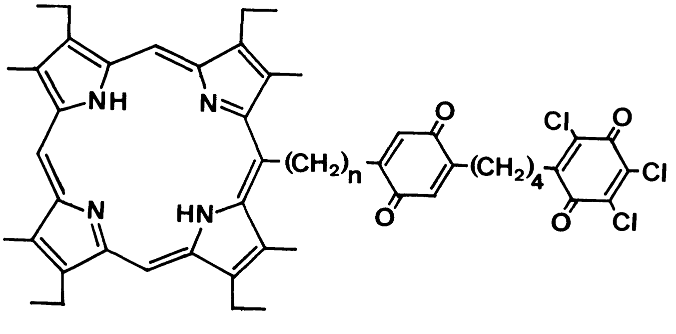
Incorporation of a Synthetic Model Compound into Bilayer Lipid Membranes and Its Transmembrane Photoconduction

Yoshiteru SAKATA,* Hitoshi TATEMITSU,
Elisabeth BIENVENUE,+ and Patrick SETA+*
The Institute of Scientific and Industrial Research, Osaka University,
Mihoga-oka, Ibaraki, Osaka 567
+Laboratoire de Physico-Chimie des Systemes Polyphases,
Associé au CNRS (UA. 330) Route de Mende, BP 5051,
34033 Montpellier Cedex, France

The compound P4Q4Q', where a porphyrin chromophore is covalently linked in series to two different quinones, was incorporated into planar bilayer lipid membranes. Upon irradiation a transmembrane photocurrent due to the intramolecular, multistep electron transfer was observed.

The central event of the early stage of photosynthesis is the stable charge separation which is achieved by the sequential electron transfer through the several kinds of chromophores embedded in the protein matrix.[1)] Previously, we demonstrated the importance of multistep electron transfer for the stable charge separation for the first time by the model compound P4Q4Q'.[2)] The lifetime of the charge separated state $P^{+}4Q4Q'^{-}$, however, is quite short (300 ps) as compared with those of the natural system[3)] and other rigid model systems mimicking the multistep electron transfer (several μs).[4)] This is considered to be due to the flexible structure of P4Q4Q', which enables efficient back electron transfer in coiling back conformations. If, upon incorporation into a bilayer membrane, the lipid environment favors an extended conformation, the charge separated state will have a longer lifetime and the molecule will act as a catalyst for the conversion of solar energy into



PnQ4Q' n=2,4

potential energy. Such attempt was reported for the first time for another synthetic compound by one of the authors.[5)]

Here we report on the incorporation of P4Q4Q' and P2Q4Q'[6)] into planar bilayer lipid membranes (BLM) and their photoelectrochemical properties, especially photocurrents due to the transmembrane electron transfer. The apparatus[7)] employed for the experiment is shown in Fig. 1. It is composed of two electrochemical cells separated by a Teflon divider, Ag/AgCl electrodes, a device for the detection of electrical current, and lasers for irradiation. At the center of the divider there is a 1 mm^2 hole and a phospholipid solution[8)] containing a pigment was applied to this hole. We used four kinds of lipids, i.e., phosphatidylcholine, phosphatidylserine, phosphatidylethanolamine, and diphythanoyllecithine and four kinds of co-solvents, i.e., decane, tetradecane, hexadecane, and squalene. The cells were filled with a supporting electrolyte (0.1M sodium chloride) and a buffer (5×10^{-3}M potassium phosphate). After the formation of a membrane on the hole, potassium ferricyanide was added to the cell (1) as an oxidizing agent and ascorbic acid to the cell (2) as a reducing agent. The thinning of the membrane was checked by monitoring the membrane capacitance.

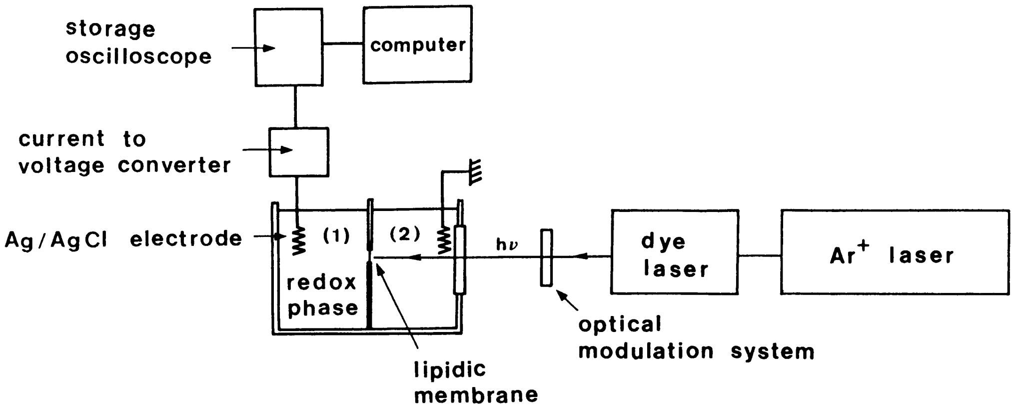


Fig. 1. Schematic diagram of the apparatus for photocurrent measurements.

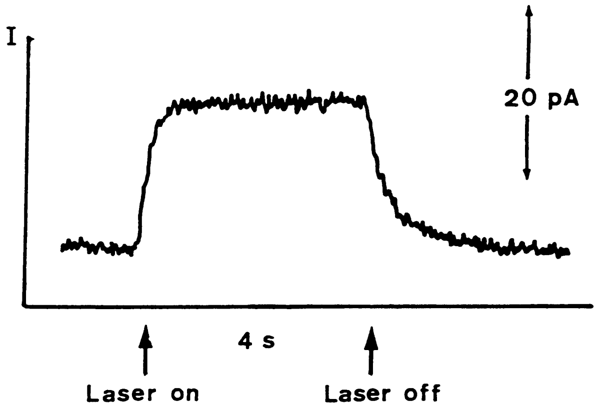


Fig. 2. Photocurrent upon light excitation.

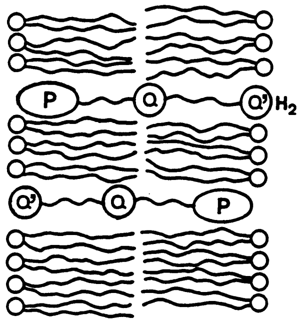


Fig. 3. Expected location of P4Q4Q' in BLM. The quinone Q' is in the reduced form at side (2), due to the presence of ascorbic acid.

In the dark no current flow was observed for membranes containing PnQ4Q'. Upon irradiation of the membrane in the presence of aqueous redox phases, only the membrane composed of phosphatidylcholine-P4Q4Q'-tetradecane showed a photo current across the membrane (Fig. 2). No photocurrent was detected for P4Q4Q' in other conditions by changing the combination of lipid and co-solvent and for P2Q4Q' in all the conditions described above. The failure of the photocurrent in the membrane containing P2Q4Q' is probably due either to faster back electron transfer9) from P^+2Q^-4Q' or to less fitness of P2Q4Q' to the membranes. Since the thickness of the hydrocarbon part of the bilayer lipid membrane composed from lipid-tetradecane is considered to be around 37 Å10) and the edge-to-edge distance of P4Q4Q' in its extended conformation is 28 Å,11) one P4Q4Q' molecule is expected to cross the membrane as shown in Fig. 3. Therefore, in the vicinity of interface (2) the porphyrin cation radical is reduced and in phase (1) the quinone anion radical is oxidized as schematically shown in Fig. 4. The stationary photocurrent in Fig. 2 indicates the existence of a transmembrane electron displacement. The present result demonstrates that like the triad of the type (donor)-(porphyrin)-(quinone),5) (porphyrin)-(quinone-1)-(quinone-2) shows a biomimetic character at the membrane level. The multistep electron transfer appears to be the key of an efficient charge separation and can be improved in a membrane environment. The way of more sophisticated models such as (donor)-(porphyrin)-(quinone-1)-(quinone-2) is now open.

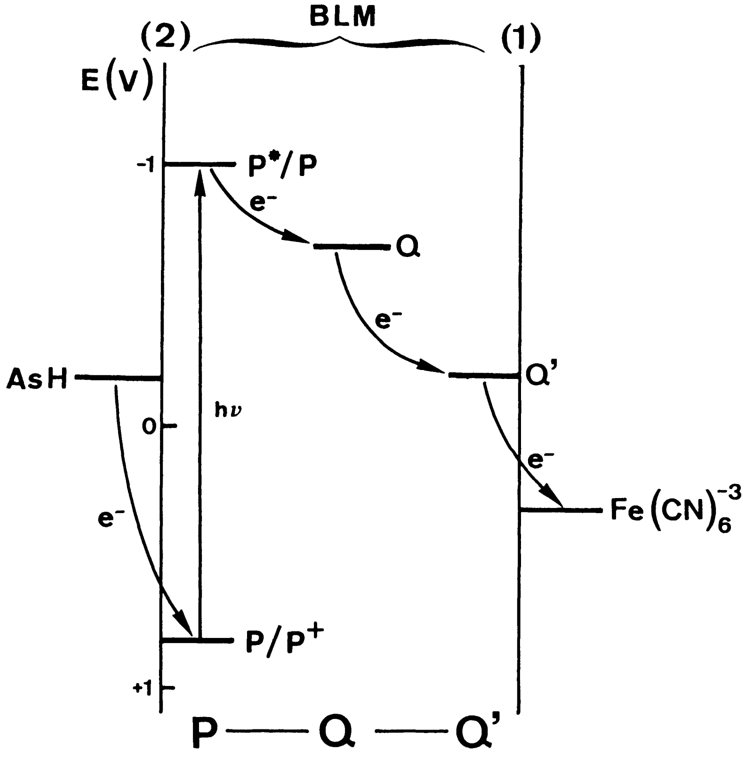


Fig. 4. Electrochemical thermodynamics.12)

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6) The synthesis of P2Q4Q' was carried out by the method similar to P4Q4Q'.$^{2)}$ P2Q4Q': dark red micro crystals from benzene-hexane; dec>140 °C. NMR ($CDCl_3$, 100 MHz) δ -2.87(br.s,2,NH), 1.30(br.s,4,CH_2), 1.73-1.92 (m,12,$CH_2\underline{CH_3}$), 2.37-3.03(m,6,CH_2), 3.56(s,6,CH_3), 3.59(s,6,CH_3), 3.96 - 4.12(m,8,$\underline{CH_2}CH_3$), 5.2-5.6(m,2,CH_2), 6.48(s,1,quinone-H), 6.57(s, 1, quinone-H), 9.83(s,1,meso-H), 10.05 ppm(s,2,meso-H). FD-Mass 875,876,878,879,880(M^+). Anal. Found: C, 68.11; H, 5.92; N, 6.31; Cl, 12.38%. Calcd for $C_{50}H_{51}Cl_3N_4O_4$: C, 68.37; H, 5.85; N, 6.38; Cl, 12.11%.
7) A. Hofmanova, E. Bienvenue, P. Seta, and M. Momenteau, Photochem. Photobiol., 44, 87 (1986).
8) The solution is composed of lipid (2%) and pigment (0.1%) in co-solvent (100 μl) and a few drops of CH_2Cl_2.
9) The lifetime of P^+ is 60 ps for P2Q4Q' and 130 ps for P4Q.
10) R. Fettiplace, D. M. Andrews, and D. A. Haydon, J. Membrane Biol., 5, 277 (1971).
11) The value was estimated on the basis of molecular model considerations.
12) The representation is only indicative, because the redox potential values given in the scheme correspond to unrealistic equimolecular oxidant and reductant concentrations.

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