

A Self-assembled Pigmented BLM on a Platinum Support: The Light-induced Electrical Effects

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Abstract. The light-induced voltage and current changes under continuous illumination have been investigated in pigmented self-assembled lipid bilayer membranes deposited on a platinum electrode. Such self-organized pigmented bilayer-platinum system containing Zn-Phthalocyanine (ZnPc) as a photosensitizer and glycerol-dioleate (GDO) as a bilayer forming solution has been found to shift its electrode potential to more positive value on light irradiation as well as to increase the cathodic current across the membrane. The results indicate a direct electron transfer from the platinum electrode to hydrogen ion in the electrolyte solution. Furthermore, it has also been demonstrated a dramatic increase of the photocurrent over the time course of BLM formation visualizing a role of the bulk quenching processes which are significantly diminished in thin bilayer membrane.

Key words: Lipid bilayer — Pigmented BLM — Phthalocyanine — Electrical properties — Electron transfer

Introduction

Interest of bimolecular lipid films (BLMs) separating two aqueous phases has grown rapidly since these structures were first reported (Mueller et al. 1962). The formation of experimental bilayer lipid membranes has enabled researchers to perform detailed investigations of the electrical and transport properties of this structure serving as one of the most useful models for the various types of biological membranes. Results of this investigation have greatly contributed not only to advancing the understanding of important membrane processes (Barber 1979; Blank 1986) but also to develop a novel photophysical surface chemistry, membrane biophysics and biochemistry based on membrane-mediated processes (Antolini et al. 1982; Dryhurst and Niki 1988).

Recently, based on the knowledge of these findings the research of bilayer

films has been focused on their practical applications. Advances in microelectronics coupled with a sustained interest in ultrathin organic films, have prompted a number of investigators to exploit the BLM system as a basis for molecular devices as well as for the development of ultimate electrochemical sensors and electrochemical biosensors (Ivanov 1988; Turner et al. 1987; Tien et al. 1988; Tien 1988). However, for long-term basic studies as well as for practical applications a common concern has been the mechanical stability of the BLM. The conventional BLM systems separating two aqueous solutions which can be formed by a variety of techniques (Mueller et al. 1962; Tien 1974; Antolini et al. 1982) rarely last longer than a few hours (Ivanov 1988; Yoshikawa et al. 1987). For this reason there has been searched for a method to produce long-lasting BLMs. Recently, a simple and novel method for the formation of self-assembled BLMs on solid substrates has been reported (Tien and Salamon 1989). As we have shown, this type of BLMs possess the requisite mechanical stability and at the same time desired dynamic properties which distinguish them from other kinds of ultrathin organic films including self-assembled monolayer films (Tien and Salamon 1989; Martynski and Tien 1991; Honeybourne 1987; Bain et al. 1989; Fabianowski et al. 1989).

In this communication results on the light effects of the ZnPc pigmented lipid bilayer deposited on the surface of a platinum wire are reported. It has also been shown, for the first time, how the process of a molecular photojunction between two interfaces is affected by the bulk quenching processes.

Materials and Methods

The pigmented self-assembled BLMs were formed by deposition of lipid layer onto a freshly cut metallic surface of Teflon coated platinum wire. Platinum wire was cut in a lipid forming solution prior to its immersion into a bathing solution of 0.1 mol/l KCl. The surface area of a single wire was 10^{-3} cm², and two such wires were used as the working electrode in the experiments. A second calomel electrode with salt bridge was used for electric contact. As a BLM forming solution 1% glycerol dioleate (GDO, K&K Lab., Inc.) in squalene (Eastman Kodak Co.) saturated with Zn-phthalocyanine was used. The electric parameters (potential of working electrode, current across the membrane and capacitance) of BLMs were measured at room temperature with a high impedance electrometer (Keithly, Model 610 BR), a 417 Keithly picoammeter and low level capacitance meter (IC Electronics, Model I-6). The light intensity was 200 mWcm⁻² from a tungsten projector lamp.

Result and Discussion

Some photoelectrochemical properties of the (ZnPc-GDO) bilayer deposited on

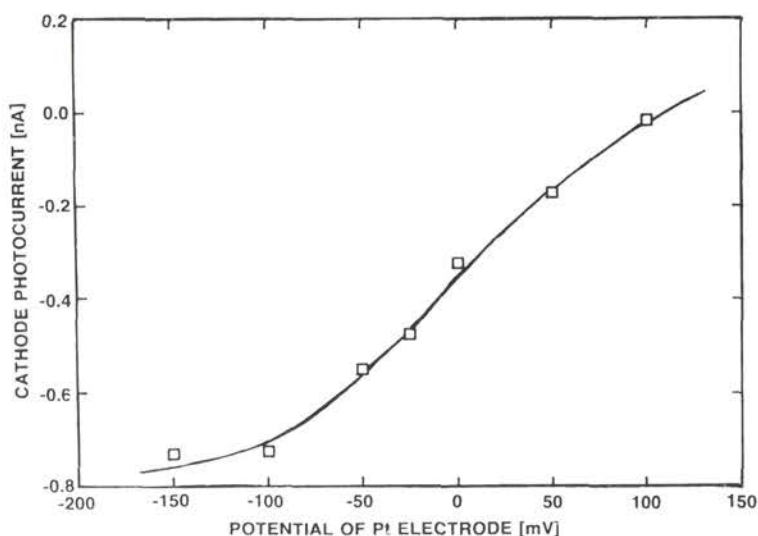


Fig. 1. Dependence of photocurrent generated by white light (200 mW cm^{-2}) across the bilayer membrane on the working electrode potential.

a platinum surface have been demonstrated in the first report (Tien and Salamon 1989). We have already shown that the dark electrical parameters of such kind of BLM in the bathing solution of 0.1 mol/l KCl are very similar to those observed with a GDO bilayer. This observation indicates that the presence of ZnPc molecules does not affect significantly the BLM structure. However, the light irradiation causes both a reversible positive shift of the already positive dark platinum electrode potential and the increase of a dark cathodic current. As it has been shown (Tien and Salamon 1989) the spectral sensitivity of a photocurrent corresponds well to the absorption spectrum of the ZnPc in the BLM forming solution, and the magnitude of the photoresponse is linear to the light intensity used (at low light intensities). Thus, the previous findings provide clear evidence that the photoactive compound is incorporated into a supported BLM and that the photocurrent is a result of the ZnPc photoexcitation. The relationship between photocurrent and the potential of working electrode (i.e., platinum electrode) is presented in Fig. 1. There is a linear increase of photocurrent with a cathodic polarization of the platinum electrode between +100 mV to -100 mV at the light intensity used. The result shows that photoelectrochemical reduction in which an electron is enforced to flow from the metal surface to electrolyte on light irradiation of the (ZnPc-GDO) bilayer takes place. Since the electrolyte contains KCl, the potassium ion and proton are the only redu-

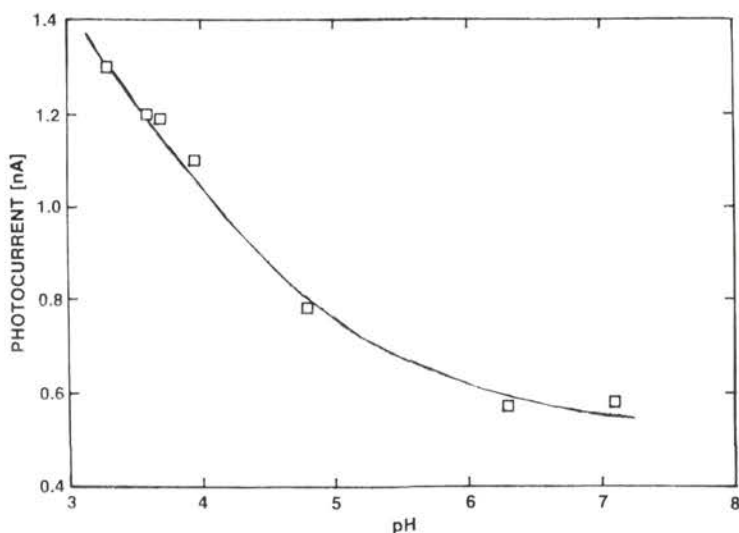


Fig. 2. Dependence of the photocurrent generated by white light (200 mW cm^{-2}) at constant potential of working electrode (-50 mV) on pH of the electrolyte solution.

cible species, i.e., electron acceptors. According to redox potential data (Dobos 1975) proton is much easier to be reduced as compared with potassium ion. Such possibility of a direct electron transfer from a photoexcited chlorophyll-liquid crystal electrode to water has been demonstrated (Aizawa et al. 1977). In our case this idea seems to be proven by results presented in Fig. 2. Fig. 2 shows that photocurrent at a constant potential (-50 mV) depends on pH of the bathing solution. As can be seen the photocurrent is enhanced by decreasing pH which strongly suggests that the photoinduced cathodic reaction results from reduction of water to hydrogen by an electron donated from the excited ZnPc molecules. This process generates cation radicals ZnPc^+ which are reduced by the electrons from the platinum electrode.

In order to visualize the influence of the photocurrent by the bulk quenching processes the photocurrent as a function of lipid layer thickness was measured. The capacitance of a BLM, along with optical reflectance, is a well established parameter for estimating the thickness of lipid bilayers (Tien 1974; Leidheiser and Deck 1988). We therefore used the capacitance measurements to monitor a BLM formation process and to estimate the thickness of the lipid layer. A sample of pigmented lipids deposited on a metal electrode and immer-

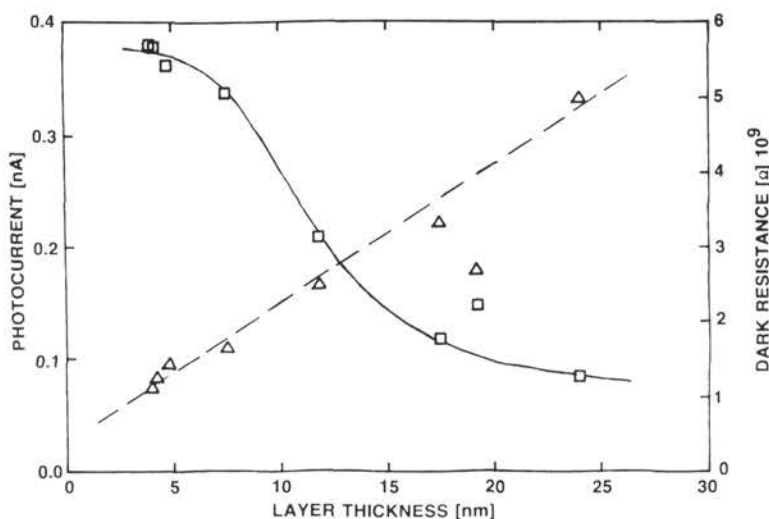


Fig. 3. Photocurrent (□) and dark resistance (△) as the function of lipid layer thickness.

sed in an electrolyte solution constitutes a parallel plate capacitor with an area A and thickness t_m . The capacitance is

$$C_m = \alpha \alpha_0 A / t_m \quad (1)$$

where α and α_0 are dielectric constants of pigmented lipids and vacuum, respectively. Assuming the value of α , we have estimated the thickness of the lipid layer (Tien and Salamon 1989). Fig. 3 shows a correlation between (ZnPc-GDO) layer thickness and both dark resistance and photocurrent generated by white light. The results demonstrate very interesting facts: (i) dark resistance decreases linearly as theoretically has been expected, with decreasing the pigmented lipid layer thickness (in the range of 25 nm—4 nm). This linear relationship provides from one side additional evidence that the process of the BLM formation occurs, and from the other side allows to estimate a constant value of resistance of the BLM forming material (R_0). This estimation gives $R_0 \sim 10^{17} \Omega/\text{m}$ which for hydrocarbon molecules should be expected. (ii) Results in Fig. 3 also show an even more interesting feature that the photosensitivity of the membrane increases with decreasing thickness. At the beginning of experiment when a thick layer of ZnPc-GDO absorbs much more light energy one can hardly see its photoresponse, whereas after the process of the BLM formation is completed and a much thinner layer is formed, which means less light energy is absorbed, the photoreaction of the system is significantly enhanced. Assuming

that an optical density (O.D.) of the pigmented layer follows its thickness (O.D. $\sim t_m$) one can estimate from data in Fig. 3 that in the layer thickness range between 25 nm—4 nm photoefficiency of the system measured by the photocurrent change increases as much as 20 times. This observation shows, for the first time, how the process of molecular photojunction between two interfaces of a lipid layer is affected by the bulk quenching effects occurring within the lipid film, and proves again very strongly the advantages of practical applications of such ultrathin, solid supported BLM systems.

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