Photoinduced Potential of Langmuir–Blodgett Membranes Composed of Spirobenzopyran

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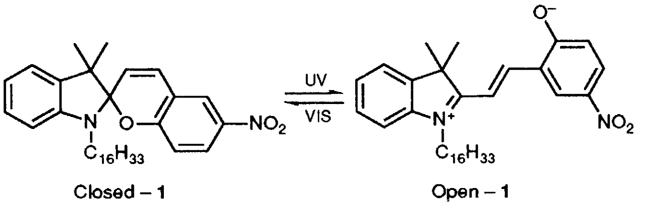
Photoinduced potential changes are observed for Langmuir–Blodgett membranes composed of a photochromic spiropyran, 1′-hexadecyl-3′,3′-dimethyl-6-nitrospiro(2*H*-1-benzopyran-2,2′-indoline) **1**.

The optical properties of Langmuir–Blodgett (LB) membranes composed of photochromic spiropyrans have been studied extensively for the development of molecule-based optical devices such as high density optical memory.[1–3] The photoswitching of the optical properties of spiropyran LB membranes is based on the colour changes originating from the photochemical interconversion of spiropyrans between the closed- and open-form. On the other hand, little has been reported on the photoswitching of electrochemical properties of spiropyran LB membranes, in spite of the fact that UV irradiation induces electric charges on the spiropyran molecule in its open form. In this connection, polymer membranes



Scheme 1

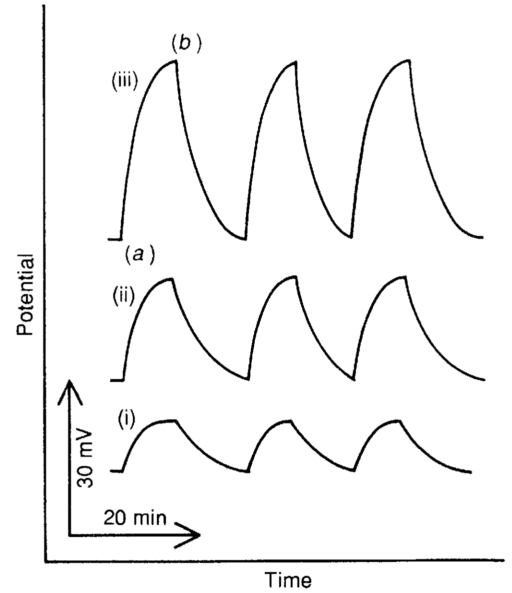


Fig. 1 Photoinduced potential changes of LB membranes composed of **1** : stearic acid = 3 : 2 mol. The LB membranes of 2- (i), 10- (ii) and 22- (iii) layers were irradiated in pH 5.0 buffer. UV-light was switched on at (*a*) and off at (*b*).

have been modified with spiropyran derivatives to study the electrochemical properties.[4–6]

We report here the photoswitching of the electric potential of spirobenzopyran **1** LB membranes which are deposited on a glassy carbon electrode. To the best of our knowledge, this is the first observation of the photoinduced potential for LB membrane.

Compound **1** was prepared previously.[6] The mixed monolayers of **1** and stearic acid were used in this study because the monolayer **1** by itself was not stable.[7] The measurement of surface pressure–area isotherms and the deposition of LB membranes was carried out with a Langmuir trough with an electric microbalance (Kyowa Kaimen Kagaku Co.).

The mixed monolayers were prepared on pure water at 18 °C and deposited on a glassy carbon plate (2 × 3 cm) at a constant surface pressure of 25 mN m^{-1}. For the measurement of absorption spectra, the LB membranes were deposited on a hydrophobic glass plate. All monolayers tested gave Y-type deposition with a deposition ratio of unity.

The electric potential of the deposited LB membranes was measured with a high impedance electrometer using a Ag/AgCl reference electrode (0.1 mol dm^{-3} tetramethylammonium chloride liquid junction) in phosphate buffer (5 mmol dm^{-3}). A 500 W xenon lamp was used as a light source, with glass filters for isolating UV ($320 < \lambda < 380$ nm) and visible ($\lambda > 500$ nm) light. All measurements were carried out at *ca.* 23 °C.

The spirobenzopyran **1** exhibited normal photochromism in the LB membrane: a closed form (colourless) under visible light or in dark and an open form (purple) under UV irradiation. The isomerization of **1** in the LB membrane was reversible and the absorption maximum of the open-**1** was found to be around 560 nm.

The electric potential changes induced by irradiation are illustrated in Fig. 1 for 2-, 10- and 22-layer LB membranes.

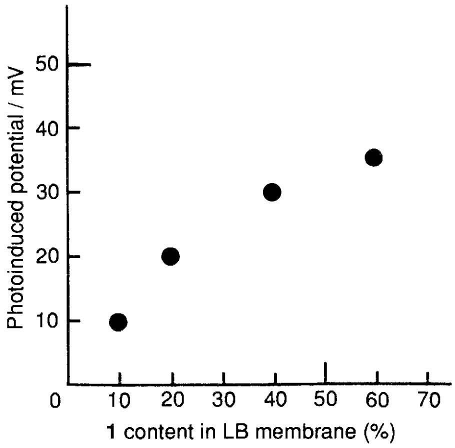


Fig. 2 Effect of **1** content in the LB membrane upon the photoresponse. 22-Layer LB membranes were irradiated in pH 5.0 buffer.

After steady state potentials had been reached under dark, positive shifts of the potential were induced by UV irradiation. The initial potentials were recovered within 10 min by turning off the UV light or by visible-light irradiation. The photoresponse was fully reversible during our experimental period. The potential shifts should be ascribable to the charge density changes in the LB membranes, which, in turn, originate from the photogenerated open-**1**.

The positive shifts of the electric potential of the LB membranes suggest that the LB membranes are positively charged as a result of the formation of open-**1**. This view can be rationalized by assuming the protonated open-**1** as an origin of positive charge in the LB membranes. This was supported by the pH dependent photoresponse of the membranes: the magnitude of the photoinduced potential of 22-layer LB membrane was +35, +20 and +15 mV in pH 5.0, 5.7 and 7.0 buffers, respectively.

The thickness of the LB layer (or the number of depositions) had a significant influence upon the photoresponse of the membrane (Fig. 1). The magnitude of photoresponse increased with increasing the thickness of the LB layer. It was independently checked that the photoresponse of bare glassy carbon was negligibly small under identical experimental conditions. We also examined the effect of **1**: stearic acid ratio in the LB layer upon the photoresponse. For this purpose the content of **1** was varied from 10 to 60% in each mixed monolayer. Fig. 2 shows the magnitude of photoinduced potential of 22-layer LB membranes with different ratios of **1** : stearic acid. The magnitude was enhanced for the LB membrane with higher content of **1**. These data clearly show that the photoinduced electric potential originates from the photoisomerization of **1** in the LB membranes.

Thus, we have demonstrated that the electric potential of LB membranes composed of photochromic spiropyran can be switched by light signals. The present system may be useful for the development of LB membrane-based electronic devices.

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