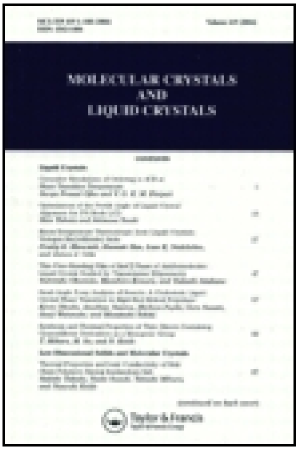

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Photochemical Switching of Ion Transport Through 'Quasi-Channels' Incorporated into Black Lipid Membrane

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PHOTOCHEMICAL SWITCHING OF ION TRANSPORT THROUGH 'QUASI-CHANNELS' INCORPORATED INTO BLACK LIPID MEMBRANE

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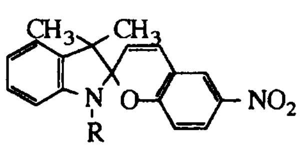
Abstract We fabricated the black lipid membrane (BLM) of soybean lecithin doped with spiropyran derivatives. When a positive DC voltage was applied on the BLM, the membrane current changed under alternate irradiation with ultraviolet light and visible light. The change in the membrane conductivity due to photoisomerization is responsible to the change in the ion permeability across the membrane. The photoresponsive BLM cell exhibited nonsymmetric current-voltage characteristics, which suggest the localization of spiropyran molecules on one side of the membrane.

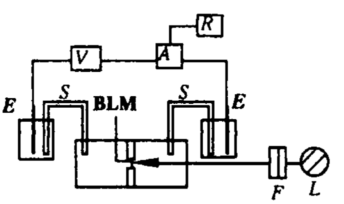
INTRODUCTION

Artificially-reconstituted black lipid membranes (BLM) have attracted attention in the field of membrane sciences because the transport of charged species can be monitored as the membrane current.[1] We have fabricated photoresponsive BLM systems doped with photochromic dyes such as azobenzene[2] and spiropyran.[3] The photochromic reaction is suited to investigate the role of molecular interactions between the dopant and the lipid membrane, because a change in the structure of the chromophoric moiety of dye molecules leads to a reversible change in the membrane properties. Previously, we reported the ion permeability change of the phospholipid membranes doped with an azobenzene derivative, 4-octyl-4'-(5-carboxypentamethyleneoxy) azobenzene (8A5) through a local packing mismatch of membranes, which we call a 'quasi-channel' formed by *trans*-to-*cis* photoisomerization.[2] The ion permeation through a quasi-channel is significant firstly because the size of a quasi-channel is smaller than conventional natural ion channels and secondly because the open-close characteristics could be controlled by the photochemical method. In this study, we have observed for the first time an asymmetric ion transport across the BLM doped with spiropyran derivatives.

Soybean lecithin and 1-alkyl-3,3'-dimethyl-6'-nitrospiro[indoline-2,2'-[2H][1]benzopyran], SP12 (n-dodecyl), SP18 (n-octadecyl), were purchased from Wako Chemicals Co. and Japanese Research Institute for Photosensitizing Dyes Co., respectively. The BLM was fabricated in a similar manner as reported before[3] under irradiation with visible light (wavelength, λ = 550 nm). For example, the membrane forming solution consisted of 100 mg of soybean lecithin plus 6.6 mg of SP12 (7.3 mg of SP18) in 1.30 ml of n-decane: $CHCl_3$ solution (10:3 by volume). The molar concentration ratio of spiropyrans to soybean lecithin was kept 0.10. The BLM cell and equipments used for the measurement of the membrane current were almost the same as before.[3] The cell compartments were filled with a 500 mM aqueous solution of KCl. Ultraviolet (UV) light and visible light selected from a 500-W high-pressure mercury lamp were illuminated on the BLM through a quartz window. Applied DC voltage to the cell, V_{app} (mV), was -100 - +50 mV. Here, we named one compartment of the cell faced to the mercury lamp trans-side, and the other cis-side. V_{app} was either 'positive' or 'negative' according as the cis-side being at the positive or negative voltage. All the measurement was carried out at room temperature in air.



R = $C_{12}H_{25}$: **SP12**
R = $C_{18}H_{37}$: **SP18**



A rough sketch of experimental set-up.
L, lamp; F, filters; V, power supply; S, salt bridges; E, electrode; A, picoammeter; R, recorder.

RESULTS AND DISCUSSION

Spiropyran derivatives undergo reversible photoisomerization from a spiropyran (SP) structure to merocyanine (MC) structure under alternate irradiation with UV light (λ = 365 nm) and visible light (λ = 550 nm).[4] Figure 1 shows a typical photoresponse of the membrane current of the BLM at V_{app} = 0 mV. Under irradiation with visible light, the membrane current was 1.2 pA. Irradiated with UV light, photoisomerization of SP12 molecules brought about an increase in the DC current (4.0 pA). The current returned to the original value when visible light was irradiated again. The current-voltage characteristics of the BLM cell are shown in Figure 2. It appeared that the BLM cell exhibited asymmetric current-voltage characteristics. At V_{app} = -30 - +50 mV, the

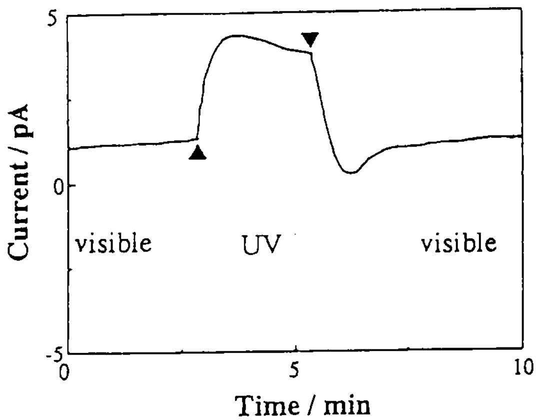


FIGURE 1 Change in the membrane current across the BLM containing SP12 under continuous irradiation with UV and visible light. The arrows indicate the change from UV to visible light or *vice versa*. V_{app} = 0 mV.

membrane current took two steady values responsible to the SP and MC structures. The steady current was proportional to (V_{app} + 30 mV) and electric conductivities of the BLM, G, were G(SP) = 334 pS and G(MC) = 376 pS.

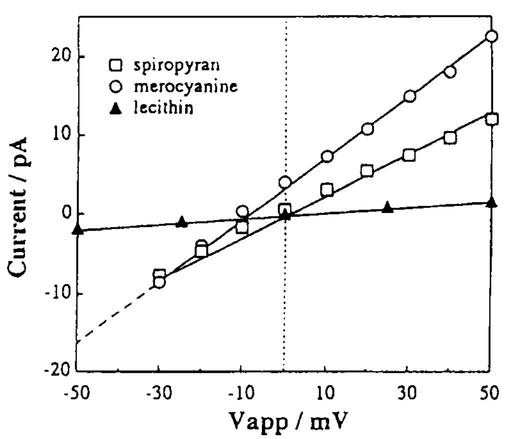


FIGURE 2 Current-voltage characteristics of the BLM doped with SP12. As a reference, that of the soybean lecithin BLM is also given.

On the other hand, when V_{app} was more negative than -30 mV, the shape of the photoresponse signal became considerably different (Figure 3). As shown in the figure, when the cell was irradiated with UV light, the membrane current slowly drifted to the higher negative value. On irradiation with visible light, the current gradually returned to the original value. Indeed the membrane current somewhat changed according as the alternation of incident light, the current signals looked rather unstable. A crude estimation of the electric conductivity for V_{app} = -50 - -30 mV yielded G = 260 - 480 pS. Similar asymmetric current-voltage characteristics were also observed in the BLM doped with SP18. As a reference, the current voltage characteristic of the soybean lecithin BLM is included in Figure 2. In this case, the current-voltage characteristics were almost symmetric with respect to the inversion of V_{app} = 0 mV, when bulk solutions in both compartments were the same. In addition, we previously observed that the current-voltage characteristics of the BLM cell doped with 8A5 was also symmetric with respect to V_{app} = 0 mV. Such observations would suggest the localization of spiropyran molecules on one side of the membrane, on which SP $\rightleftarrows$ MC photoisomerization takes place. On the other hand, azobenzene molecules seem to locate in the midst of the BLM, giving rise to symmetric current-voltage characteristics.

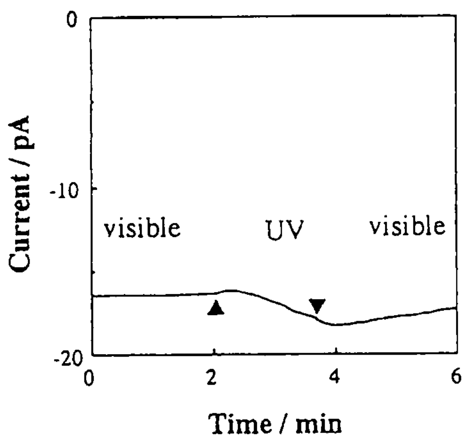


FIGURE 3 Another type of the photoresponse of the BLM doped with SP12 at V_{app} = -50 mV. The arrows indicate the change from UV to visible light or *vice versa.*

We have thus succeeded in the fabrication of asymmetric BLM by using spiropyran derivatives, which seems to be promising for future applications of the BLM systems to bioelectronic devices[1]. In view of slow and reduced photoresponse at large negative V_{app}, quasi-channels formed by spiropyrans seem to be considerably different from those formed by photoisomerization of the azobenzene derivative.

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