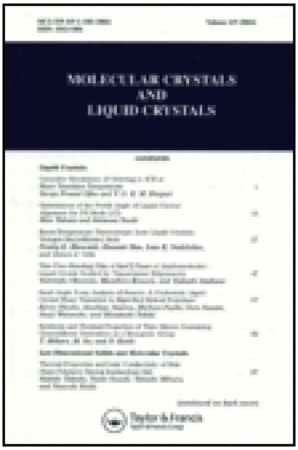
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The effect of photoinduced conformational transitions between closed and open form of an alkyl-substituted spiropyrane derivative upon the conductance of bilayer lipid membranes (BLM) was investigated. BLM were self-assembled and investigated by the tip-dip patch clamp method from natural soybean lecithin (SoyL) or from synthetic diphytanoyl lecithin (DPhL) mixed with 10% wt hexadecylbenzospiropyrane (SP). Photoisomerization (closed-open) of spiropyrane was effected by repetitive UV light pulses. The reverse isomerization (open-closed) was achieved by continuous illumination with white light. Current vs. voltage measurements were performed in dark, after termination of UV or visible light irradiation.

Experimental results with SoyL displayed a reversible increase of the dark BLM conductivity upon UV illumination. However, results with DPhL showed the opposite, although weaker, overal tendency: a visible light-induced increase and a UV-induced decrease. This demonstrated the crucial role of lipid matrix steric asymmetry in the observed photoconductance effects and eventually suggested a different structure of the conducting pores.

Keywords: BLM; photoconductance; patch clamp; soybean and diphytanoyl lecithin; hexadecylbenzospiropyrane

INTRODUCTION

The goal of this study was to investigate the effect of photoinduced conformational transitions between closed and open forms (viz., spiropyrane - merocyanine) of an alkyl-substituted spiropyrane derivative upon the single pore conductance of bilayer lipid membranes. Such biphilic SP derivatives serve as lipid analogues and can be easily incorporated in the bilayer lipid structure, while the conformation of their polar heads can change under UV or visible light illumination[3,4].

MATERIALS AND METHODS

BLMs were self-assembled by the tip-dip method[1] using patch pipettes and mixed lipid monolayers from natural Soybean lecithin (Sigma), or from synthetic Diphytanoyl lecithin (DPhL) (Avanti Polar Lipids), mixed with 10% wt hexadecylbenzospiropyrane (SP) (synthesized in Department of Organic Chemistry, University of Sofia). Monolayers were spread from n-hexane solutions of L and SP, mixed before spreading. Both lipid membranes were in liquid crystal state at ambient temperature (20°C). This is a specific requirement of the tip-dip method operating at room temperature: formation of bilayer patches from crystallized monolayers is not possible. This precludes the usage of lipids with higher gel-liquid crystal transition temperature like DPPC (41°C). On the other hand DPhL is commonly used in as a fully saturated synthetic lipid with high fluidity at room temperature and good sealing properties on glass micropipettes[1]. Same good ability for giga-seal formation was found for SoyL. SoyL was previously applied for photoconductance studies with larger area BLM[6] ; therefore, a comparison between these two types of model membrane systems can be made. However, the possible UV-photochemical degradation of unsaturated lipid species in SoyL mixure calls for another comparison with a fully saturated, albeit highly fluid lipid bilayer matrix. In that sence DPhL is a natural choice.

Conductance effects were recorded by a patch clamp amplifier using a computer-controlled voltage sweep DAC and a current-voltage surfaces' software[2]. The principle of current-voltage surfaces' method consists in the simultaneous recording of transmembrane current in response to slow triangular ramps of transmembrane voltage for a time interval of typically 10 ramp periods, binnig I,V-values in a 360x360 matrix in the I-V plane and finally representing the number of events in each bin by 3 to 4 gray scale density levels. In this way I-V curves belonging to closed or open conductance states were identified on the same compound I-V plot.

From the I-V plots open and closed state conductances were calculated as the slopes of the correponding curves. In case of nonlinearity the slopes of the tangents to the curves in the point of origin were taken. The differences between open and closed conductances were then calculated and represented in histograms, separately for the VIS- and UV-illuminated states of a membrane.

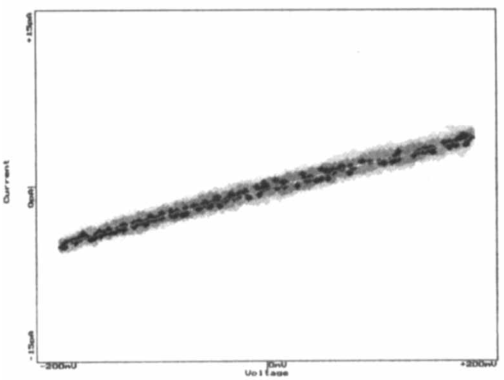
Photoisomerization (closed-open) of spiropyrane was effected by repetitive UV light pulses with the duration of 5 ms from a photoflash[3,4]. The UV dose was varied by varying the number of flashes (typically 20). The reverse isomerization (open-closed) was achieved by continuous illumination with white light for some minutes. Current vs. voltage measurements were performed in dark, after termination of UV or visible light irradiation.

For a given membrane, repetitive cycles of VIS- and UV-illumination were performed, typically about 10. Therefore, the actual statistics of the conductance events exeeded by one order of magnitude the number of investigated membranes of any specific composition and UV dose.

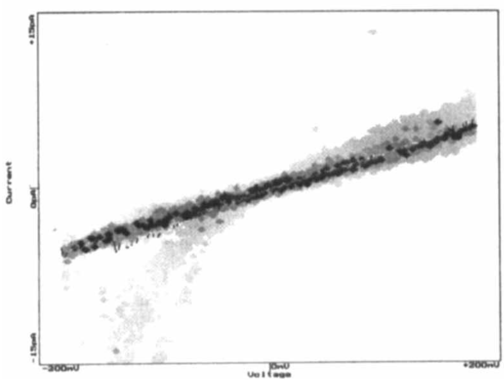
RESULTS AND DISCUSSION

Experimental results with natural Soybean lecithin demonstrated a reversible increase of the dark BLM conductivity upon UV illumination (Fig.1,A-B): With increasing the UV dose (i.e., the number of flashes) discrete conducting states of increasing conductivity (e.g., 15 pS, 35 pS, 80 pS, 115 pS, 145 pS or 225 pS) were excited. In many cases I-V curves of conducting states were non-linear, like those on (Fig. 1B). This may be due to the appearance of a positive electric charge in the open merocyanine form. In such a case the low-voltage conductivity was calculated from the slope of the tangent to the I-V curve at zero voltage.

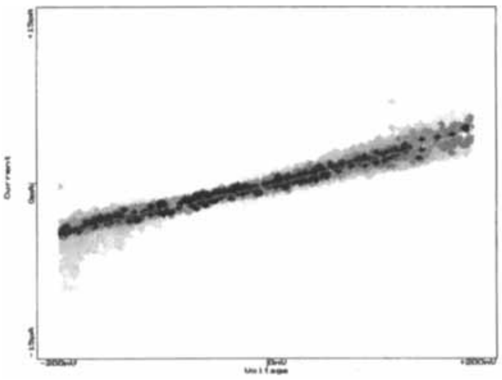
These conducting states closed completely and reversibly after 5 min illumination with white light (Fig 1C). Results from 5 membranes with an average number of 10 cycles UV-VIS per membrane are represented in the histograms (Fig. 2). These results are in accordance with the prediction of liquid crystal approach to toroidal pore formation in lipid bilayers[5], in view of the increased wedge-like asymmetry of the open



A. White light, 5 min
no pores



B. UV light, 25 flashe
pore openings



C. White light, 5 min pore closure

FIGURE 1 Current-voltage surfaces of a SoyL/SP membrane after alternating illumination with visible (A and C) and UV light (B). Densities of the plots represent the height of the surface, as projected over the I-V plane. Currents in response to triangular voltage ramps of ±200 mV amplitude, 20 s period and total duration of 200s are recorded.

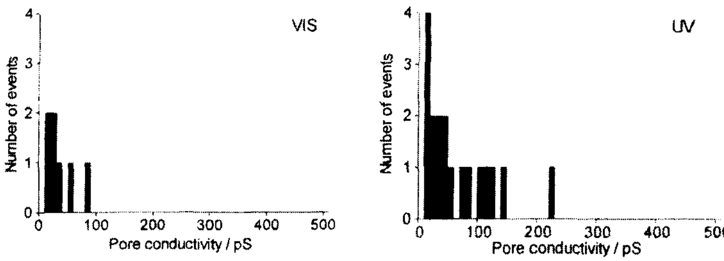


FIGURE 2 Histograms of pore conductivities in SoyL/SP membranes after visible light (VIS) and UV illumination. A total of 5 membranes was investigated, with 10 cycle VIS-UV per each membrane.

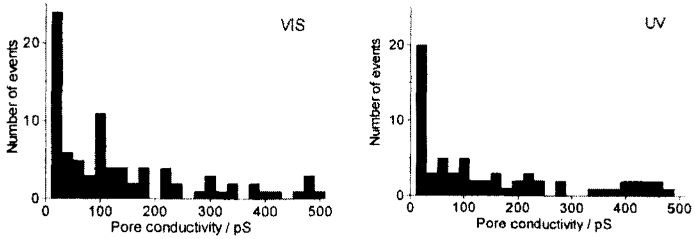


FIGURE 3 Histograms of pore conductivities in DPhL/SP membranes after visible light (VIS) and UV illumination. A total of 13 membranes was investigated, with 10 cycle VIS-UV per each mem.

spiropyrane form. Wedge-like surfactant molecules (with head group cross section larger than the chain one) decrease the edge energy of semitoroidal pores (because they pack more favourably in the curved monolayer edge), and hence, the probability of pore formation. They also correspond to the findings concerning UV-induced total current increase through larger area BLM of the same lipid[6]. In a BLM single pore opening events could not be resolved like in our case; instead, an integrated current through many open pores can be measured.

Control experiments with only SoyL membranes did not show any photoconductance effects at the level of UV doses currently used. Still, in order to avoid the effect of possible UV-oxidation of the double C=C bonds in unsaturated lipid chains of natural lecithin, further experiments with fully saturated, synthetic Diphytanoyl lecithin membranes were performed.

However, results with DPhL showed the opposite overal tendency: a visible light-induced increase and a UV-induced decrease of conductivity (Fig. 3). This tendency is not well expressed, though: some 22 % of the total number of VIS-UV cycles actually displayed the same behaviour like SoyL. This demonstrates the crucial role of lipid matrix steric asymmetry in the observed photoconductance effects and eventually suggests a different structure of the pores (not a semi-toroidal one). One can note from Fig. 3 that DPhL membranes inherently contain more defects than SoyL ones and conductance states of up to 500 pS and even higher (not shown) are readily encountered. Therefore, we conclude that despite its excellent photochemical stability DPhL is not a suitable matrix for spiropyrane - related BLM photoconductance.

CONCLUSION

The importance of these findings is two-fold: first, our system mimics possible photoeffects in native photoactive membranes; second, this system comprising of a patch-clamped, spiropyrane-containing BLM provides a prototype of a self-assembled photo-electric device for the liquid crystal nanoelectronics.

Acknowledgments
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