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Heat-Induced Voltage Generation in Hexadecyl Merocyanine Dye-Probed Planar Lipid Membranes

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ABSTRACT

A hexadecyl merocyanine dye was used as a heat driven proton gate, by incorporating it in a planar lipid membrane which is a good model for biological membranes. Being hydrophobic in nature, it prevents charge recombination, and transmembrane voltages of high magnitude (~310 mV) were obtained upon heating. The process was reversible and the whole cycle took about 20 h, suggesting that the system could be used as a heat driven storage cell. Comparison of the X-ray diffraction patterns of the thin films of the dye at 30°C showed a heat-induced conformational change in the crystalline structure of the dye. From differential thermal analysis three reversible phase transitions were observed, at 39·2°C, 53·7°C and 62·1°C, and the associated enthalpy changes were calculated. The results indicate that the heat-induced conformational change of the dye molecule is responsible for the observed thermovoltage generation.

INTRODUCTION

We have previously reported[1,2] photovoltage generation in a merocyanine dye-probed planar lipid membrane due to the transport of protons from one side of the membrane to the other, caused by photoinduced conformational changes[3,4] of the dye molecule.[5,6] Merocyanine dyes can

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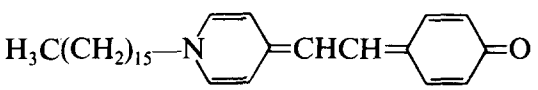
also undergo thermal isomerisation,[3] but this property of the dye molecules has not previously been explored in generating voltage. Using a planar lipid membrane probed with a hexadecyl merocyanine dye, we report here the generation of thermovoltage of high magnitudes. Comparison of the X-ray diffraction patterns of thin films of the dye at 30°C and 65°C under dark conditions showed a heat-induced conformational change in the crystal structure of the dye molecule. The reversibility of the change was confirmed by cooling the heated sample.

Differential thermal analysis of the dye showed three reversible endothermic reactions within the specific temperature range, and the associated enthalpy changes during these processes were calculated. Thus the intrinsic ability of the dye to generate voltage when incorporated in the membrane due to heat/light-induced conformational change, may be utilised to design a storage cell.

METHODS AND MATERIALS

The hexadecyl dye (**I**) was synthesised as previously reported.[7]



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AR grade HCl, KI and *n*-octane (E. Merck) were used. Iodine (E. Merck) was purified by resublimation. Cholesterol (Eastman Organic Chemicals) was oxidised and recrystallised from *n*-octane.

The thermoelectric cell consisted of two L-shaped glass tubes. A micropore glass filter (porosity ~10 μm) was mounted on one tube and this tube was inserted into the other by means of a standard joint (as described in detail in Ref. 1). A chloroform solution of the dye was evaporated to dryness and a saturated solution of oxidised cholesterol in *n*-decane was added to it. This solution (concentration ~3 mM) was brushed onto the glass filter to ensure stable membrane formation.[8] One side of the membrane (side A) was bathed with HCl (concentration ~0·1 M) and the other (side B) with a saturated solution of iodine in 1 mM potassium iodide solution. These two solutions were chosen because the HCl solution acts as a proton source and the I_2/I^- solution acts as a charge acceptor. The open circuit thermovoltage was measured by a Keithley electrometer (Model No. 614) between a pair of platinum electrodes placed symmetrically across the membrane. The cell was immersed in a bath maintained at constant temperature.

X-Ray diffraction patterns were obtained using a Philips PW 1730 diffraction unit fitted with a nickel filter and using CuK_α radiation. A thin film of the dye on a glass plate was used to take the diffractogram.

Thermal analysis was performed using a Shimadzu thermal analyser (Model DT 50), where 30 mg of dry sample was placed in a platinum crucible and heated at a rate of 3°C min^{-1}.

RESULTS AND DISCUSSION

When the dye-probed membrane was heated, a thermovoltage was generated which increased with temperature according to the relation

$$V_T = V_0(1 - \exp(\alpha_1(T_0 - T)))$$

where V_T is thermovoltage at temperature T, V_0 is maximum or saturated value of thermovoltage as obtained at ~65°C, α_1 is empirical constant of the growth curve and T_0 is initial temperature of thermovoltage generation (~32°C).

The cell started to generate thermovoltage very rapidly while being heated and reached a saturation value at ~65°C. The magnitude of the voltage remained at its maximum value for about 1·5 h while the cell cooled down to room temperature (~30°C), and then the thermovoltage started to decrease with time according to the relation

$$V_t = V_0 \exp(-\alpha_2 t)$$

where α_2 is empirical time constant for the decay curve and V_t is thermovoltage at time t.

For the hexadecyl merocyanine dye, the maximum value of thermovoltage (V_0) was 310 mV when $T \sim 65$°C (Fig. 1), and the total decay process (the time to return to the initial value when cooled) took about 20 h, indicating a good storage capacity of the cell (Table 1).

Differential thermal analysis of the dye showed three reversible endothermic phase transitions within the temperature range 30–65°C, at 39·2°C,

TABLE 1
Thermovoltaic Character of Hexadecyl Merocyanine Dye

Peak value of voltage	*Growth temperature*		*Decay time*	*Time for one complete cycle*
	Start	*End*		
310 mV	32°C	65°C	17 h	17·5 h

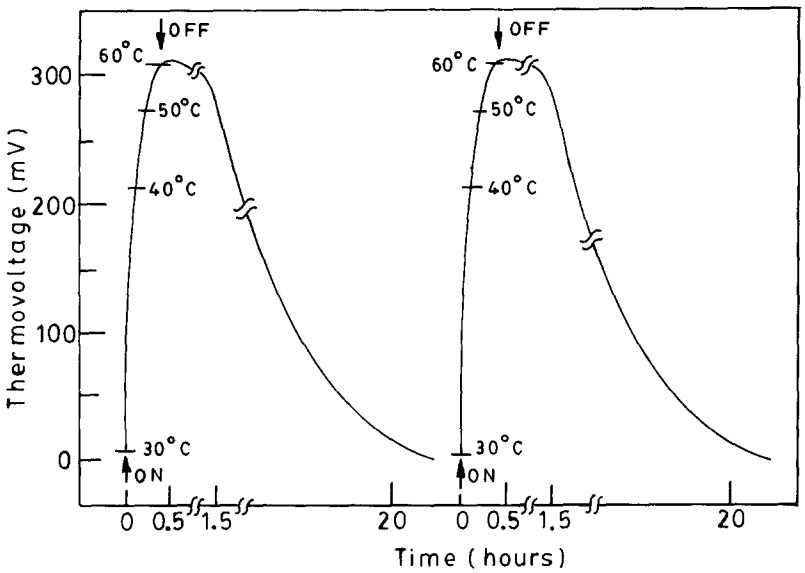

Fig. 1. Growth and decay curves of thermovoltage generation in hexadecyl dye-probed lipid membrane.

53·7°C and 60°C (Fig. 2). The changes in enthalpy associated with these transformations were calculated from thermal analysis (Table 2).

From the X-ray diffraction patterns it was observed that the dye remained in its crystalline form throughout the temperature range of the phase transition. Comparison of the diffractograms of the dye at 30°C and 65°C showed identical peaks at identical 2θ position. However, the peak corresponding to $\theta = 3{\cdot}8°$ became more intense at 65°C compared

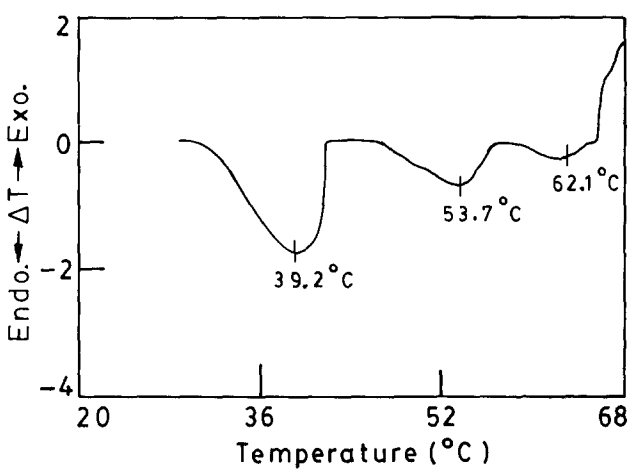

Fig. 2. DTA curve of hexadecyl merocyanine dye.

TABLE 2
Thermal Analysis Data of Hexadecyl Merocyanine Dye

Serial number	*Type of reaction*	*Reaction range (°C)*			*Enthalpy ($J\,g^{-1}$)*
		Start	*Peak*	*End*	
1	Endothermic	31·5	39·2	41·7	7·74
2	Endothermic	46·3	53·7	56·6	3·82
3	Endothermic	58·85	62·1	65·25	2·74

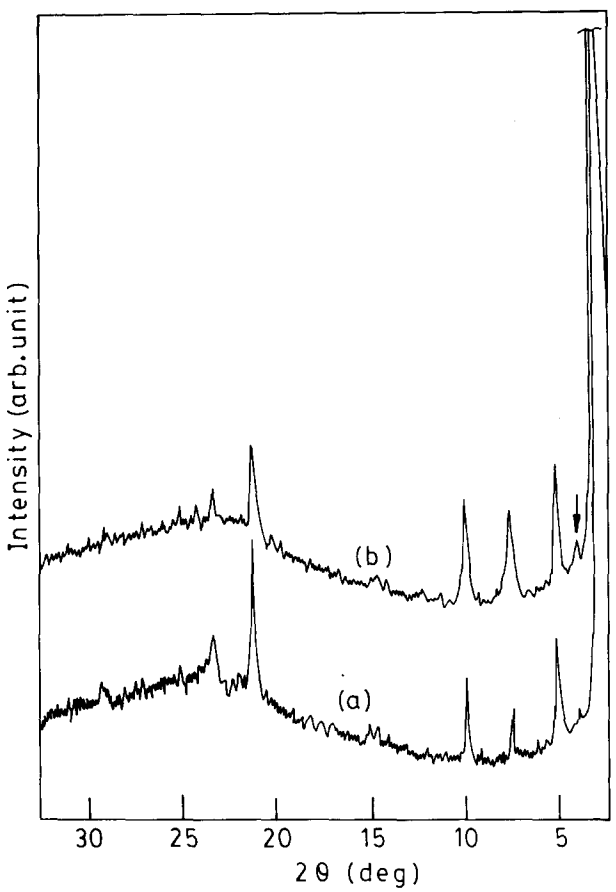

Fig. 3. X-Ray diffractogram of hexadecyl merocyanine dye: (a) at room temperature (~30°C); (b) at 65°C.

with that at 30°C (Fig. 3). Such a variation in the peak intensity, while the number and position of the peaks remained constant, implied a conformational change of the *cis* → *trans* type[3] of the dye molecules within the same crystalline structure. This *cis* → *trans* isomerisation can also be induced by light, which causes proton transport across the membrane giving rise to photovoltage in a similar experimental system.[1–3]

The results indicate that hexadecyl merocyanine dye molecules, when incorporated in a lipid membrane, generate thermovoltage of high magnitude and good storage capacity, due to the heat-induced reversible *cis-trans* isomerisation, as suggested by DTA and X-ray diffraction studies. An H^+ ion is transported from side A to side B, generating an asymmetric charge distribution across the membrane, which gives rise to the observed thermovoltage.

Comparison of the data in Tables 1 and 2 shows that the range through which the thermovoltage is generated coincides with the range through which the endothermic reaction takes place, confirming our hypothesis that the heat-induced conformational change of the dye molecule is responsible for the proton gate action of the dye incorporated in the membrane. The role of the membrane is to prevent the back flow of these protons, thereby causing the voltage difference across the membrane.

A planar lipid membrane is a good model for a biological membrane which is the site for major physical processes taking place in the living world. The experimental process reported here thus not only provides a good model for the study of membrane-based heat-induced charge transfer processes, but can also be used to design an efficient storage cell with good reproducibility.

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