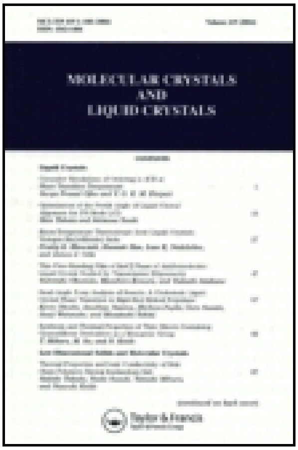

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Photoinduced Potential Change by Crowned Triphenylmethane Dye Derivatives in Poly(vinyl chloride)-Based Liquid Membranes

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Photoinduced Potential Change by Crowned Triphenylmethane Dye Derivatives in Poly(vinyl chloride)-Based Liquid Membranes

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Photoirradiation effect on potential response to sodium ion concentrations and photoinduced potential change were investigated with plasticized poly(vinyl chloride) membranes based on triphenylmethane dye derivatives carrying a bis(monoaza-15-crown-5) moiety and a tris(monoaza-15-crown-5) moiety. A drastic photoinduced switching in potential response to sodium ion concentrations was realized by membranes containing crowned triphenylmethane dye derivatives. The photoinduced potential change was affected by complexing species such as a multinuclear complex.

Keywords: crown ether; metal-ion complexation; photoionization; poly(vinyl chloride) membrane; potential response; triphenylmethane dye

INTRODUCTION

We had already proposed the photochemical control of cation complexation by triphenylmethane dye derivative carrying a bis (monoaza-15-crown-5) moiety [1,2] **1** (Scheme 1) and a tris(monoaza-15-crown-5) moiety [3,4] **2** (Scheme 2) which realized so called all-or-none type photochemical control of cation complexation by the

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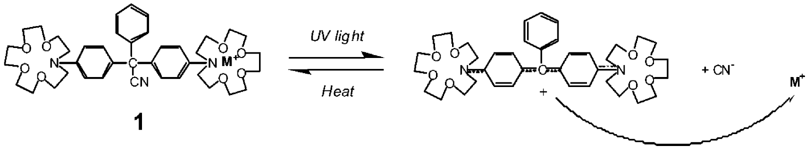


SCHEME 1

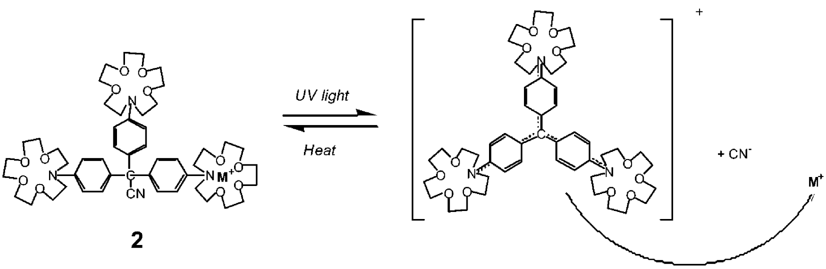
complete release of a crown-ether-complexed metal ion after UV irradiation. It is very interesting to see how the drastic change in the cation-complexing ability of them is reflected in potential response of membranes incorporating the photosensitive compound and if photochemical switching of ion selectivity for the membrane ion sensor is feasible. Since the crown ether ring in photosensitive compounds plays an important role in complexing, it is also interesting to investigate the effect of the number of crown ether ring in **1** and **2** upon the potential response. Here we report photoinduced switching of potential response for poly(vinyl chloride) (PVC) membranes containing **1** and **2**. Furthermore, the potential photoresponse is discussed by comparing **1** with **2**.

EXPERIMENTAL

Measurements

Preparation of Membrane

PVC membranes were prepared by pouring the mixture of PVC (50 mg), bis(2-ethylhexyl)sebacate (200 mg), a crowned triphenylmethane dye derivative (5 mg), and tetrahydrofuran (2 cm^3) onto a flat Petri dish of 3-cm inner diameter. After allowing the solution to evaporate for three days, the membrane was conditioned by soaking in sodium chloride solution (1×10^{-6} mol dm^{-3}) overnight.



SCHEME 2

Membrane Potential Measurement

Membrane potential measurements were done by using a U-type cell equipped with a quartz window for photoirradiation at 25. In a measurement cell, a membrane with an effective area of 0.785 cm^2 separated two aqueous phases. The electrochemical cell was Ag|AgCl| 1×10^{-3} mol dm^{-3} sodium chloride | membrane | measuring solution ($0-1 \times 10^{-1}$ mol dm^{-3} sodium chloride) || 0.1 mol dm^{-3} NH_4NO_3 || 3 mol dm^{-3} KCl | AgCl | Ag. The pH of measuring solution was adjusted by NH_3 or HCl solution. Photoirradiation of the membrane was achieved from the side of the measuring solution through the quartz window. UV light source (< 330 nm) was a xenon lamp (500 W) equipped with a photoguide tube and a Toshiba UV-D33S filter.

RESULT AND DISCUSSION

Potential Response to Sodium Ion Under Dark and UV Irradiated Conditions

Figure 1 shows typical potential responses to sodium ion concentration of membranes containing **1** under dark condition. Under acidic condition at pH 6, the sensitivity to sodium ion was low because the nitrogen atoms of monoaza-15-crown-5 of **1** underwent protonation which resulted in poor cation-complexing ability of **1**. When the crown ether ring was free from protonation (pH 8–12), the potential response of

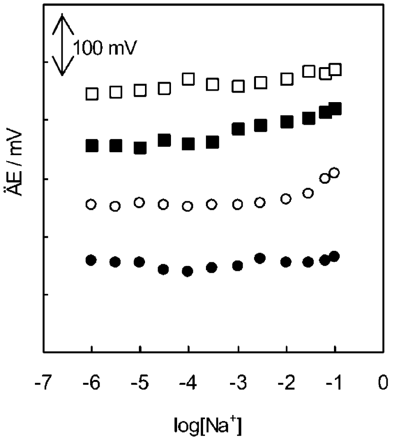


FIGURE 1 Potential response for membrane containing triphenylmethane dye derivative **1** under dark condition at pH 6 (●), pH 8 (○), pH 10 (■), and pH 12 (□).

membranes **1** was increased with the concentration of sodium ion, which can be complexed by its crown ether moiety. The potential increase with the concentration of sodium ion was also observed in the system of **2** (data not shown). On the other hand, under UV irradiation, the addition of sodium ion did not cause any potential change in the membrane **1**, exhibiting no potential response to changes in the concentration of sodium ion. The potential responses to sodium ion at pH 10 and the slope for calibration plots under UV irradiation was 0 mV/decade for the membrane **1**, while the responses were 16 mV/decade and 27 mV/decade under dark condition for the membranes **1** and **2**, respectively (Fig. 2). The 0 mV/decade for membrane **1** was observed at any pH under UV irradiated condition. This significant difference in the photoinduced changes of membrane potential response arises from the photoinduced changes of cation-binding ability of the ion carriers, i.e. once **1** is UV irradiated, the photogenerated positive charge results in the effective release of a crown-complexed cation in the system of **1** owing to the electrostatic repulsion (Scheme 1). In contrast to the system of biscrowned Malachite Green **1**, a triphenylmethane derivative carrying one benzocrown ether moiety, as we have reported previously, does not exhibit any drastic change of potential response to cation because it binds a metal ion under either dark or UV irradiated conditions [1].

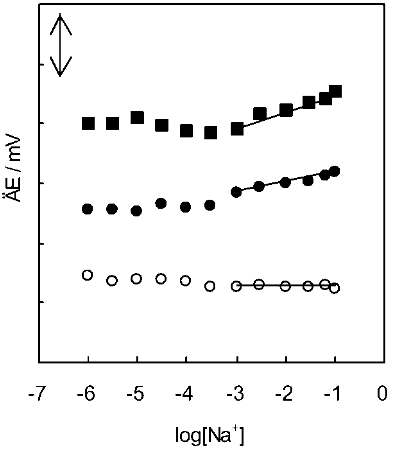


FIGURE 2 Potential response for membranes containing **1** (●) and **2** (■) under dark condition and UV-irradiated condition (○) for the system of **1**. The pH of the measuring solution was 10 and the slopes of calibration plots were obtained in the range of sodium ion concentration higher than 1×10^{-3} mol dm^{-3}.

Consequently, the photochemical switching of potential response to cation was accomplished by the **1** and **2** undergoing so called all-or-none type photochemical switching of cation-complexing ability.

Time-Course Change of Photoinduced Membrane Potential

Crowned triphenylmethane dye derivatives **1** and **2** afford the generation of a positive charge and thereby photocontrol of cation complexation. Therefore, it is interesting to investigate photoinduced potential change for the membranes containing **1** and **2**. Figure 3a shows time-course potential changes for membrane **1**. UV irradiation increased the potential change for membrane **1**, which was induced by the ionized **1**. Interestingly, contrary to membrane **1**, the potential change was decreased by UV irradiation in membrane **2**, as shown in Figure 3b. The discussion in this section will focus on the photoinduced potential decrease in membrane **2**. We designate the photoinduced potential difference (ΔE_{photo}) by the potential after irradiation minus the potential before irradiation ($\Delta E_{photo} = E_2 – E_1$ in Fig. 3) to clarify the dependence of ΔE_{photo} on sodium ion concentration. The values of ΔE_{photo} for membranes **1** and **2**, shown in Figure 4, decreased with an increase in the concentration of sodium ion. The complexation with sodium ion induces positive charges on the membrane interface under dark condition and thereby it increased E_1 resulting in the smaller value for ΔE_{photo}. Though the value for ΔE_{photo} was positive for membrane **2** at low concentration of sodium ion ($0–1 \times 10^{-3}$ mol dm^{-3}), it turned into negative at high concentration (0.1 mol dm^{-3}) as shown in Figure 4b. This fact means that, at high sodium ion concentration, the positive charges caused by crown-ether-complexed sodium ion overcomes the

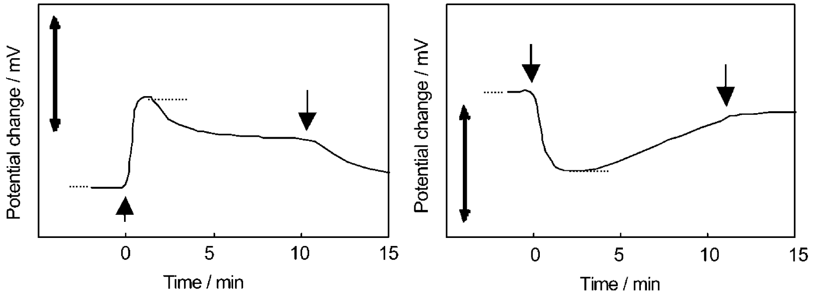


FIGURE 3 Time-course changes of membrane potentials for the system of triphenylmethane dye derivative **1** (a) and **2** (b) on photoirradiation in 0.1 mol dm^{-3} NaCl aqueous solution at pH10. E_1 and E_2 are potential before irradiation and after irradiation, respectively.

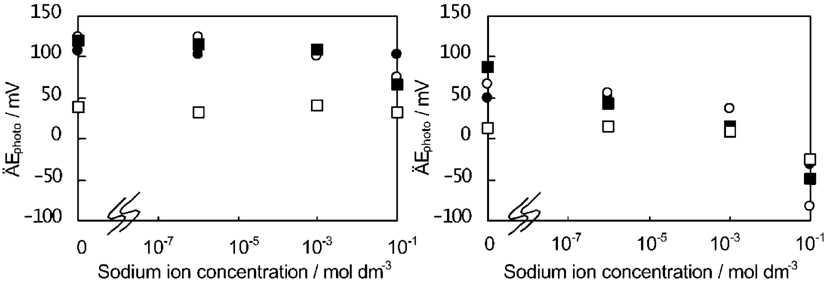


FIGURE 4 Photoinduced potential difference (ΔE_{photo}) for membranes containing triphenylmethane dye derivative **1** (a) and **2** (b) in the presence of 0–1 × 10^{-1} mol dm^{-3} sodium chloride. ΔE_{photo} is obtained by E_2 minus E_1 in Figure 2. The symbols used are the same as Figure 1.

photogenerated positive charges in the system of **2**, even though membrane **1** exhibits positive values for ΔE_{photo} at high concentration of sodium ion (Fig. 4a). Therefore, the difference between **1** and **2** in the complexation with sodium ion at high concentration can be attributable to the different complexing species between them. The three crown ether rings of **2** are likely to form the multinuclear complex with sodium ion which fits into the ring of monoaza-15-crown-5. Electrospray ionization mass spectroscopy is an attractive technique for investigating complexed ions in solution, affording information about complexing species. The system of **2** has three crown ether rings occupied by sodium ion(s), providing 1:3 complex of **2** and sodium ion, besides 1:1 and 1:2 complexes of **2** and sodium ion (data not shown). The 1:3 complex of **2** and sodium ion agrees with the increased E_1 resulting in negative ΔE_{photo}. Though the binuclear complex with sodium ion was also formed in the system of **1**, we speculate that it hardly brought about the greater E_1 than E_2, which in turn induces negative ΔE_{photo}. As a consequence, the multinuclear complexing species for **2** are responsible for the negative ΔE_{photo} by increasing positive charges on the membrane interface under dark condition.

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