Photoinduced Extraction and Active Transport of Anions by a Triphenyl Methane Derivative

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Triphenylmethane derivative leukobase (**1**) was converted to its cation form **2** by UV irradiation. This lipophilic cation form was stable in dichloromethane with green color (λ_{max}=634 nm), and returns to the original colorless form of **1** when shaked with an alkaline solution. Compound **2** exhibited excellent anion extraction ability (from aqueous solution into dichloromethane) under the conditions of appropriate pH, but **1** has no anion extraction ability. Photoinduced active transport of anions across a liquid (dichloromethane) membrane was achieved by using the difference in the extraction ability between **1** and **2** together with the difference in pH between the source and receiving phases.

Many photoresponsive systems are widely studied for the purposes of developing excellent photosensors, photomemories, and molecular devices for efficient energy conversion. Among many chromophores, which can be used as photoswitches of these systems,[1,2] azobenzene and spirobenzopyran have most frequently been employed. We have already shown that photoinduced changes of ion permeability[3,4] and of membrane potential,[5–15] can be attained with poly(vinyl chloride) (PVC) membranes containing azobenzene or spirobenzopyran derivatives. The photoresponsiveness of triphenylmethane derivatives is very different from that of azobenzene and spirobenzopyran since it is dissociated into two species, one is an organic cation and another is a hydroxide anion, and consequently triphenylmethane derivatives have been used to change solution properties[16–18] or ionic features of materials[19,20] by light. The present study deals with the use of a triphenylmethane derivative leukobase (**1**) as a photocontrollable anion carrier, and the active transport performed here may be compared with the similar phenomena achieved in the systems where spirobenzopyran[21] and azobenzene[22] derivatives act as photoresponsive carrier.

Experimental

Materials. Sodium picrate was prepared according to the Fuoss method.[23] Methyl Orange purchased as extra pure reagent grade was purified by recrystallization. The pH values of the aqueous solutions used in liquid-liquid extraction and active transport experiments were adjusted by using NaOH and HCl solutions. Dichloromethane was of spectral grade.

Bis[4-(dibutylamino)phenyl]phenylmethanol (1). *N,N*-Dibutylaniline (6 g, 29.2 mmol) and benzaldehyde (1 g, 9.4 mmol) were dissolved in a mixture of ethanol (8 ml) and 35% HCl (3 ml). The mixture was refluxed for 48 h, and cooled and alkalized with 2 mol dm^{-3} NaOH. The solution was extracted with dichloromethane, and the organic layer was dried over K_2CO_3 and evaporated. Purification by silica-gel column chromatography (eluted by hexane until *N,N*-dibutylaniline was completely removed and subsequently by a mixed solvent of hexane and ether (50:1 by volume)) afforded 3 g (62%) of **1** as pale yellow oil. Found: C, 81.83; H, 10.01; N, 5.15%. Calcd for $C_{35}H_{50}N_2O$: C, 81.66; H, 9.79; N, 5.44%. ^{1}H NMR ($CDCl_3$) δ=0.7—1.7 (28H, m, $N(CH_2C_3H_7)_2$), 3.1—3.6 (8H, m, $N(CH_2C_3H_7)_2$), 5.3 (1H, s, OH), 6.4—7.4 (13H, m, aromatic ring).

Liquid-Liquid Extraction. At 25 °C, a 2 ml of aqueous solution containing sodium picrate or Methyl Orange (1.0×10^{-5} mol dm^{-3}) and sodium hydroxide (various concentrations) was vigorously shaken with an equal volume of dichloromethane solution containing **1** or **2** (1.0×10^{-5} mol dm^{-3}). After sufficient agitation, the picrate concentration in aqueous layer was determined by absorbance change at 354 nm. The Methyl Orange concentration was also determined in a similar manner at 462 nm.

Method of Anion Transport across a Liquid Membrane. All measurements were carried out at 25 °C with a cylindrical U-tube (diameter: 17 mm) having a plain area (2.0 cm^2) in the center of the tube, which allows effective UV irradiation. The composition of the system is as follows: phase A: Methyl Orange (1.0×10^{-5} mol dm^{-3}) solution (5 ml of water); phase B: dichloromethane solution (20 ml) containing 5.0×10^{-6} mol dm^{-3} of **1**; phase C: Methyl Orange (1.0×10^{-5} mol dm^{-3}) solution containing various concentrations of NaOH (5 ml of water). During transport experiments the phase B (liquid membrane) was stirred gently.

Photoirradiation Conditions. Photoirradiation was performed with a 500 W xenon lamp (Ushio Electric Inc.) using a Toshiba cut-off filter UV D-35 for isolating UV light (320 nm$<\lambda<$400 nm).

Results and Discussion

Photochemical and pH-Dependent Interconversion between 1 and 2. Absorption spectra of **1** before and after UV irradiation in dichloromethane are shown in Fig. 1. Compound **1** before UV irradiation showed an absorption band at 270 nm (ε=35000) and the solution was colorless. After UV irradiation (ca. 6 min), the absorption band at 270 nm was decreased and a new absorption band was observed at 634 nm (ε=55000), the color of the solution being green. This spectral change indicates that **1** was converted to **2**.[16] The time course of the reaction monitored by the absorbance change at 634 nm is shown in Fig. 2. The reaction was completed within 6 min. The cation form **2** was very stable as shown by no change in the

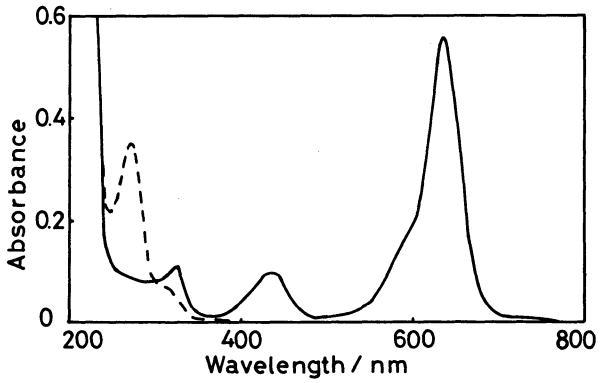


Fig. 1. Absorption spectra of **1** in dichloromethane (1.0×10^{-5} mol dm^{-3}) before (---) and after (——) UV irradiation.

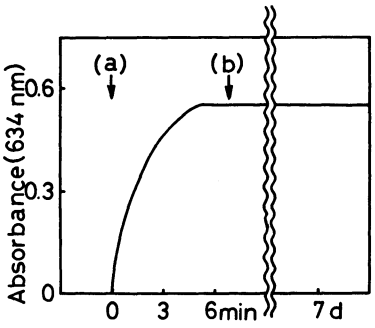
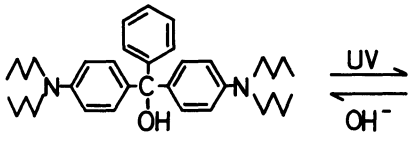
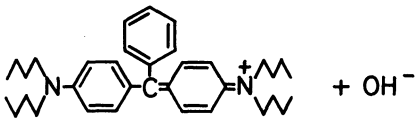


Fig. 2. The change of the absorbance at 634 nm of **1** (1.0×10^{-5} mol dm^{-3}) in dichloromethane induced by UV irradiation.
(a) On the set of UV irradiation. (b) End of UV irradiation.

absorbance at 634 nm even after 7 d. The extent of the reversal of **2** to **1** was examined at 25 °C by shaking a 2 ml of dichloromethane solution of **2** (1.0×10^{-5} mol dm^{-3}) with the equal volume of the aqueous solutions of different pHs. The concentration of **2** depended upon the pH of the aqueous solutions (line (a) in Fig. 3); the cation form **2** was transformed into the original form of **1** by the addition reaction of hydroxide ions to the tertiary carbon in **2** when shaked with alkaline solutions. On the contrary, **2** was not transformed to **1** when shaked with acidic solutions of pH>1.



1



2

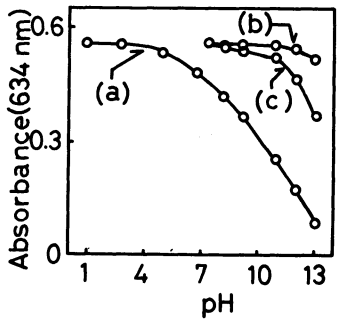


Fig. 3. The change of the absorbance at 634 nm of **2** (1.0×10^{-5} mol dm^{-3}) in dichloromethane induced by shaking with aqueous solutions with different pHs. (a) Shaked with aqueous solution without organic anions. (b) Shaked with aqueous solution containing sodium picrate (1.0×10^{-5} mol dm^{-3}). (c) Shaked with aqueous solution containing Methyl Orange (1.0×10^{-5} mol dm^{-3}).

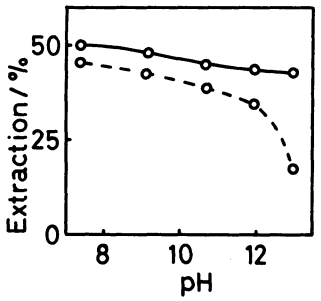


Fig. 4. Effect of pH on extraction by **2**.
——; Sodium picrate. ---; Methyl Orange. The conditions are same as those in Fig. 3.

Liquid-Liquid Extraction. The results of liquid-liquid extraction with **1** and **2** are shown in Fig. 4. The extraction ability of **2** decreased with increasing pH value. In the case of Methyl Orange, an abrupt drop of the extraction ability was observed around pH 12. The absorbances of the dichloromethane solutions measured after the extraction are shown as lines (b) and (c) in Fig. 3. The results indicate that electrostatic interaction of **2** with picrate or Methyl Orange enables **2** to be hardly affected by hydroxide ion. This effect has not been seen with benzoate anion or 1- or 2-naphthaleneacetate anion, the pH profiles being the same as shown in Fig. 3-(a). It is interesting that there are significant differences between picrate and Methyl Orange anions in extraction facility and in the ability of stabilizing the cation form **2** against the attack of hydroxide ion. These results also imply that various anions may be selectively extracted by **2** under appropriate conditions (the selectivity for the picrate anion is most remarkable around pH 13 in this study).

Photoinduced Active Transport. Based on the anion extraction ability of **2**, photoinduced active transport has been attempted. Figure 5 illustrates time response of the concentration of Methyl Orange in phases A and C. The pHs of phases A (without

NaOH) and C (containing 0.10 mol dm^{-3} of NaOH) were initially set to be 7.3 and 13.0, respectively. In the dark the concentration changes of Methyl Orange in both phases A and C were negligible. After UV irradiation for 10 min onto phase B,[24] the concentration of Methyl Orange began to decrease in phase A, and increase in phase C with time. After 10 h, the concentrations of Methyl Orange in phases A and C became ca. 30% and ca. 150%, respectively, of the initial concentration.[25] After 72 h, the concentrations in phases A and C became ca. 1% and ca. 196%, respectively, and at this point 90% of compound **2** was found to be changed to **1**. The result also indicates that the system can be used for transporting various organic salts against the gradient of hydroxide ion. When the pH of phase C is 11.9, active transport still proceeds, but the rate of the Methyl Orange transportation is smaller than the case of pH 13.0. When the pH in phase C was 10.6, active transport was not attained, the concentration of Methyl Orange in phase C decreasing as in phase A (Fig. 6). When the pH in phase C was 8.8, the rate of Methyl Orange diminution in phase C was almost equal to in phase A. Table 1 lists the concentrations of Methyl Orange in phases A and C, at the time of 8 and 72 h after UV irradiation in the above mentioned pH runs. In any case the concentration in phase A decreases with time. On the contrary, the profile of concentration change of Methyl Orange in phase C is affected by the pH in the phase.

The mechanism of the active transport is shown in

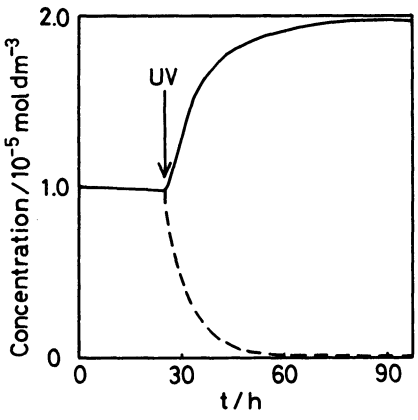


Fig. 5. Time response of the concentration of Methyl Orange in phases A (---) and C (——).
pH values in phases A and C were 7.3 and 13.0, respectively. The concentration of **1** in phases A and C was 1.0×10^{-5} mol dm^{-3}. UV means UV irradiation for 10 min.

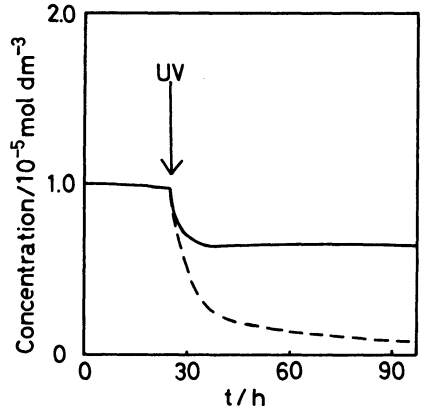
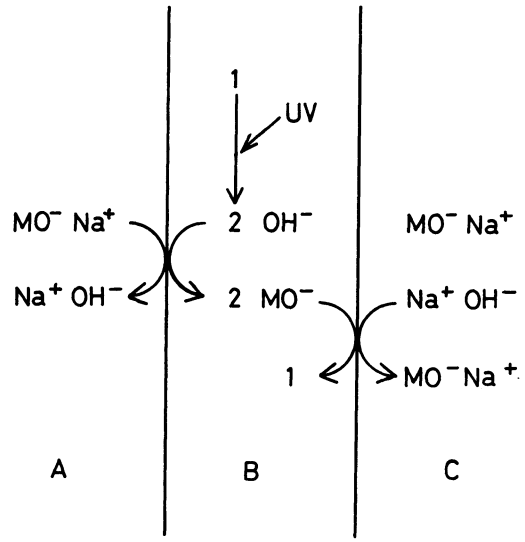


Fig. 6. Time response of the concentration of Methyl Orange in phases A (---) and C (——).
pH values in phases A and C were 7.3 and 10.6, respectively. The concentration of **1** in phases A and C was 1.0×10^{-5} mol dm^{-3}. UV means UV irradiation for 10 min.

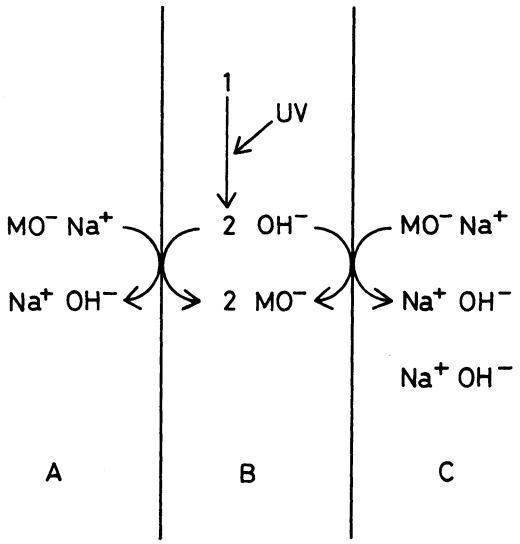


Scheme 1. Schematic sketch of the photoinduced active transport mechanism (the pH in phase C was higher than 11). MO$^-$; Methyl Orange anion.

Table 1. Methyl Orange Concentrations in Phases A and C after UV Irradiation for 10 min

pH in phase C	Methyl Orange concentration/10^{-5} mol dm^{-3}			
	a)		b)	
	Phase A	Phase C	Phase A	Phase C
13.0	0.39	1.40	0.01	1.96
11.9	0.39	1.29	0.04	1.49
10.6	0.36	0.65	0.08	0.64
8.8	0.56	0.55	0.53	0.59

pH in phase A was 7.3. Initial concentration of Methyl Orange in phases A and C was 1.0×10^{-5} mol dm^{-3}. a) 8 h after UV irradiation. b) 72 h after UV irradiation.



Scheme 2. Schematic sketch of the photoinduced transport mechanism (the pH in phase C was lower than 11). MO^-; Methyl Orange anion.

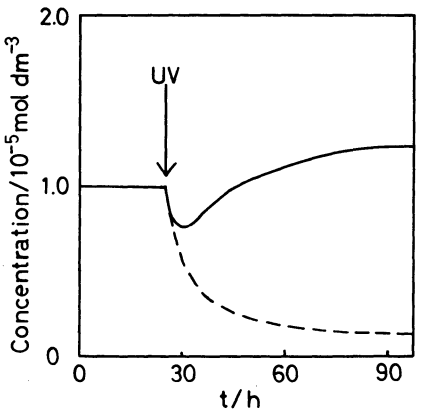


Fig. 7. Time response of the concentration of sodium picrate in phases A (---) and C (——).
pH values in phases A and C were 7.0 and 12.9, respectively. The concentration of **1** in phases A and C was 1.0×10^{-5} mol dm^{-3}. UV means UV irradiation for 10 min.

Scheme 1. At first compound **1** is converted to **2** by UV irradiation, and then **2** binds Methyl Orange at the interface between A and B, releasing hydroxide ion toward phase A. The complex of Methyl Orange anion and **2** is attacked by excess hydroxide ion at the interface between phases B and C, and **2** is converted to **1** releasing Methyl Orange anion toward phase C. When the pH in phase C was less than 11, the concentration of Methyl Orange in phase C decreased as in phase A. The proposed mechanism of the phenomenon is shown in Scheme 2. In this case, the conversion from **2** to **1** does not occur and Methyl Orange is extracted into phase B from both phases of A and C.

We also examined active transport of sodium picrate. The result is shown in Fig. 7. According to the extraction data (Figs. 3 and 4), the anion binding ability of **2** for sodium picrate was stronger than for Methyl Orange, and the ability for sodium picrate was depended upon the pH value to a lesser extent than for Methyl Orange. Therefore, the concentration in phase C (cf. Fig. 5) decreased at an early stage of UV irradiation as in phase A. After 72 h the concentration in phase C slightly increased as the subsequent phenomenon of efficient extraction of picrate anion from phase A to phase B.

Conclusion

The results of extraction data indicate that compound **2** has excellent anion binding ability which depends upon pH value and anion species. Photoinduced active transport of anions through a liquid membrane was achieved on this basis. This photochromic compound works without host–guest complexation and may be regarded as a new system for photoregulated transportation.

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24) After UV light irradiation for 10 min, **1** in phase B was converted to **2** perfectly in this condition.
25) The remained Methyl Orange is present in phase B.