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Benzo-15-crown-5 Linked Spirobenzopyran. I. Photocontrol of Cation-Binding Ability and Photoinduced Membrane Potential Changes

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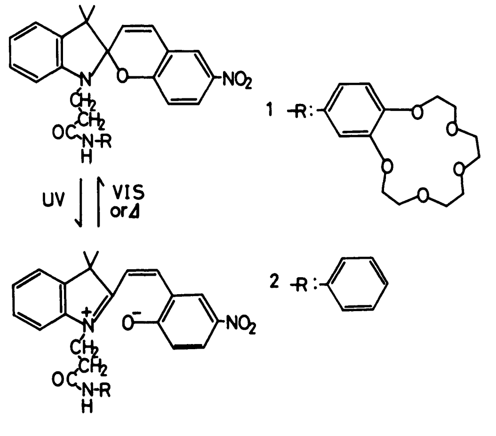
Benzocrown ether-linked spirobenzopyran (**1**) and its analogue (**2**) which has no crown ring were synthesized. The binding abilities of **1** for alkali metal cations (Na^+, K^+, Rb^+, Cs^+) were found to change by UV light irradiation, while **2** did not bind these cations before and after UV light irradiation. The plasticized poly(vinyl chloride) (PVC) membrane entrapping **1** or **2** showed photoinduced potential changes reversibly by UV and visible light irradiation. In the membranes of both **1** and **2** showed normal photochromism of spirobenzopyran. In the case of **1**, the magnitude of the photoinduced potential change depended upon kind and concentration of alkali metal cations. However, the magnitude of photoinduced potential change of the membrane entrapping **2** was hardly affected by kind and concentration of alkali metal cations. The results are explained in terms of cooperative action of both crown ether and spiropyran.

Spirobenzopyran derivatives are well known photoresponsive organic compounds which can be reversibly isomerized by UV and visible light irradiation. This character was utilized to regulate polymer conformation,[1)] viscosity of polymer solution,[2)] enzyme activity,[3)] membrane potential,[4—8)] and ion permeation using liquid membrane,[9)] etc. Crown ether derivatives have cation binding ability, and are widely studied not only in labolatory but also in industry. We have already reported the ion permeability[10,11)] and the membrane potential change[12—17)] which occurs reversibly upon photoirradiation across the poly(vinyl chloride) (PVC) membrane containing azobenzene-modified crown ethers.

In the present study, we synthesized spirobenzopyran derivatives bearing benzo-15-crown-5 and phenyl units (**1** and **2**, respectively), and examined photoresponsive cation binding ability of them by liquid–liquid extraction method, and by measuring membrane potentials across the PVC membranes entrapping **1** (PVC(**1**) membrane) and **2** (PVC(**2**) membrane).

From the different point of view, **1** is regarded as a photoresponsive crown ether. Photoisomerism of azobenzene has been used in many photoresponsive crown ethers.[10—22)] The present system works based on the different isomerism performed by spiropyran, so **1** belongs to a new family of functional molecules showing photoresponsiveness.



Experimental

Materials. Poly(vinyl chloride)(PVC) (polymerization degree of 1100) was purchased from Wako Pure Chemical Industry Ltd. and used without further purification. Dibutyl phthalate (DBP), tetrahydrofuran (THF), and alkali metal chlorides (NaCl, KCl, RbCl, and CsCl) were of extra pure reagent grade. Alkali metal picrates were prepared according to the Fuoss method.[23)] Double-distilled water was used throughout.

3′,3′-Dimethyl-6-nitro-1′-[2-[3,4-(1,4,7,10,13-pentaoxatridecane-1,13-diyl)phenylcarbamoyl]ethyl]spiro[2*H*-1-benzopyran-2,2′-indoline] (1). 1′-(2-Carboxyethyl)-3′,3′-dimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline][24)] (1 g, 2.62 mmol) and 4′-aminobenzo-15-crown-5[25)] (0.75 g, 2.65 mmol) were dissoloved in 50 ml of the mixed solvent of chloroform and DMF (9:1 in volume). After dicyclohexylcarbodiimide (DCC) (0.54 g, 2.62 mmol) was added to the mixture at −5 °C, the mixture was stirred for 24 h, and then the formed *N,N′*-dicyclohexylurea was filtered off. The filtrate was subjected to silica-gel column chromatography (dichloromethane:EtOH=15:1 in volume). The obtained crude product was recrystallized from methanol to give 0.64 g (38%) of **1**. Mp 114 °C. Found: C, 64,49; H, 6.22; N, 6.47%. Calcd for $C_{35}H_{39}N_3O_9$: C, 65.10; H, 6.09; N, 6.51%. ^{1}H NMR ($CDCl_3$) δ=1.1, 1.25 (6H, s, CH_3 of pirrole ring), 1.5—1.9 (2H, broad, $-NCH_2-$), 2.4—2.8 (2H, m, $-CH_2-CO-$), 3.3—4.2 (16H, m, $-CH_2-$ crown ether), 5.75 (1H, d, *J*=16 Hz C$\underline{H}$=CH-nitrobenzene), 6.3—7.2 (9H, m, aromatic H of 3$\underline{H}$-indole and benzocrown, -NH-, and CH=C$\underline{H}$-nitrobenzene), 7.7—8.1 (3H, m, aromatic of nitrobenzene). IR (KBr) $\delta_{C=O}$ 1655 cm^{-1} (amide I), ν_{N-H} 1610 cm^{-1} (amide II).

3′,3′-Dimethyl-6-nitro-1′-[2-(phenylcarbamoyl)ethyl]spiro[2*H*-1-benzopyran-2,2′-indoline] (2). Compound **2** was synthesized from 1′-(2-carboxyethyl)-3′,3′-dimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] (0.5 g, 1.31 mmol) and aniline (0.12 g, 1.29 mmol) using a method analogous to that used for **1**. Purification of **2** was performed by recrystallization from isobutyl alcohol to give 0.40 g (68%) of **2**. Mp 120 °C. Found: C, 70.85; H, 5.93; N, 9.10%. Calcd for $C_{27}H_{25}N_3O_4$: C, 71.19; H, 5.53; N, 9.22%. ^{1}H NMR ($CDCl_3$) δ=1.1, 1.25 (6H, s, CH_3 of pirrole ring), 1.5—1.9 (2H, broad, NCH_2-), 2.4—2.9 (2H, m, $-CH_2-CO-$), 5.75 (1H, d, *J*=16 Hz -C$\underline{H}$=CH-nitrobenzene), 6.5—7.3 (10H, m, aromatic H of 3*H*-indole and aniline, -NH-, and -CH=C$\underline{H}$-nitrobenzene), 7.7—8.1

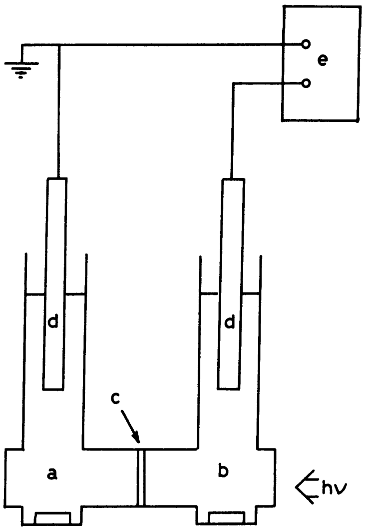


Fig. 1. Schematic sketch of the cell for membrane potential measurements.
a and b: Electrolyte solution, c: Membrane, d: Double junction type S.C.E.s, e: Potentiometer.

(3H, m, aromatic of nitrobenzene). IR (KBr) $\delta_{C=O}$ 1650 cm^{-1} (amide I), ν_{N-H} 1605 cm^{-1} (amide II).

Benzo-15-crown-5(**3**) was synthesised according to the Pedersen's method.[26]

Preparation of Membranes. (PVC(**1**)) or (PVC(**2**)) membrane was prepared by pouring the mixture of PVC (235 mg), DBP (0.54 ml), **1** (24.8 mg) or **2** (17.7 mg), and THF (20 ml) onto a flat Petri dish (9.2 cm diameter) and allowing the solvent to evaporate. The prepared membranes have a thickness of ca. 0.1 mm, and their mechanical strength was satisfactory for the spectroscopic and electrochemical measurements. The membrane entrapping both **2** and **3** was prepared in the same manner as that of PVC(**2**) membrane, except for addition of **3** (10.5 mg).

Absorption Spectra. Photoisomerization of **1** and **2**, which proceeds in solution or in the membranes, was monitored by measuring the absorption spectra.

Liquid–Liquid Extraction. At 25 °C, a 2 ml aqueous solution containing alkali metal picrate (1×10^{-5} mol dm^{-3}) and alkali metal chloride (1 mol dm^{-3}) was vigorously shaken in quartz UV cell with the equal volume of dichloromethane solution containing **1**, **2**, or **3**. After sufficient agitation, the picrate concentration in the aqueous layer was determined by the absorbance change at 354 nm. To obtain the data after UV irradiation, the liquid–liquid extraction was carried out under UV light.

Membrane Potential Measurements. All measurements were carried out at 25 °C with a U-shaped glass cell illustrated in Fig. 1. Double junction type of saturated calomel electrodes were employed. Both solutions were stirred vigorously. The effective membrane area of the cell was 2.54 cm^2. The composition of the electrochemical cell for the membrane potential measurements was as follows; Hg_2Cl_2 (s), Hg | KCl (sat.) | 0.1 mol dm^{-3} $(CH_3)_4NCl$ | electrolyte solution (c) | membrane | electrolyte solution (c) | 0.1 mol dm^{-3} $(CH_3)_4NCl$ | KCl (sat.) | Hg_2Cl_2 (s), Hg. The electrolyte solution of the left side was earthed. Photoirradiation was performed with 500 W xenon lamp (Ushio Electric Inc.) using cut off filters Toshiba UV D-35 and Y-45 for isolating UV (320 nm$<\lambda<$400 nm) and visible (450 nm$<\lambda$) light, respectively. Photoirradiation was done from the right side.

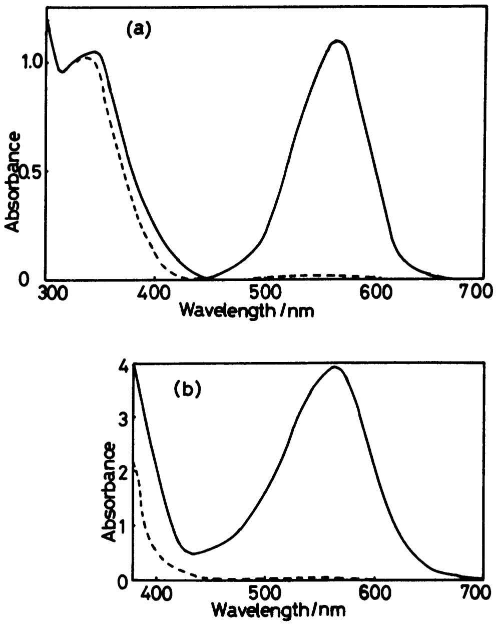


Fig. 2. (a) Absorption spectra of **1** in dichloromethane solution (1×10^{-4} mol dm^{-3}) before (---) and after (——) UV irradiation. (b) Absorption spectra of **1** in PVC membrane before (---) and after (——) UV irradiation.

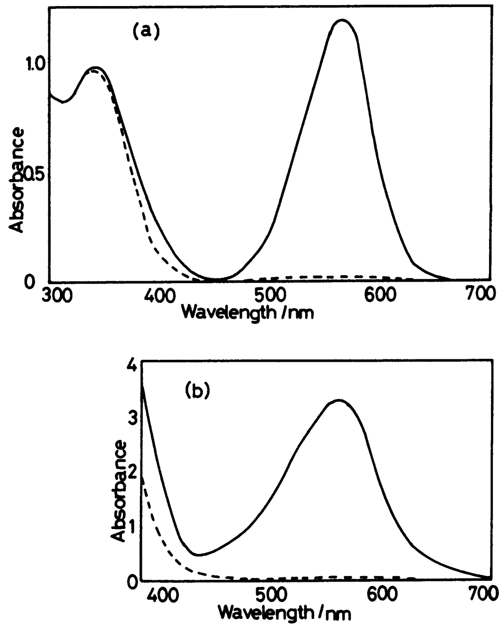


Fig. 3. (a) Absorption spectra of **2** in dichloromethane solution (1×10^{-4} mol dm^{-3}) before (---) and after (——) UV irradiation. (b) Absorption spectra of **2** in PVC membrane before (---) and after (——) UV irradiation.

Results and Discussion

Photochemical and Thermal Isomerization of 1 and

2. The absorption spectra of **1** and **2** in dichloromethane are shown in Fig. 2 (a) and Fig. 3 (a), respectively. In dichloromethane, the closed form of **1** showed an absorption band at 340 nm ($\varepsilon=10200$) and the solution was colorless. After UV irradiation (ca. 2 min), the absorption band at 340 nm was shifted to 345 nm ($\varepsilon=10500$) and a new absorption band was observed at 567 nm ($\varepsilon=11000$), the color of the solution being purple. This spectral change indicates that **1** was isomerized from closed form (closed-**1**) to opened form (opened-**1**).[4–7] By visible light irradiation of the solution of opened-**1**, the original spectral pattern of closed-**1** was recovered quickly (ca. 20 s). Opened-**1** was also isomerized thermally with the half life of ca. 80 s in the dark (at 25 °C). The compound **2** showed similar spectral changes to those of **1**. As shown by the absorption changes from 340 nm ($\varepsilon=9700$) of closed **1** to 345 nm ($\varepsilon=10000$) and 567 nm ($\varepsilon=12000$) of opened **2**. The photoinduced absorption changes of **2** in dichloromethane also occurred reversibly by alternate UV and visible light irradiation. The half life of opened **2** was ca. 80 s in the dark (at 25 °C).

The photoisomerization of **1** and **2** occurred also in PVC membranes. The absorption spectra of PVC(**1**) membrane and PVC(**2**) membrane were shown in Fig. 2 (b) and Fig. 3 (b), respectively. These membranes were soaked in 10 mmol dm^{-3} NaCl solutions. The closed forms of **1** and **2** showed no absorption in the wavelength region between 480 and 700 nm, so the membranes were colorless. After UV irradiation, the membranes turned purple, and a new absorption band appeared at 560 nm for PVC(**1**) and at 557 nm for PVC(**2**) membrane, respectively. These changes of the absorption spectra mean clearly that isomerization of **1** and **2** from closed form to opened one was achieved in the membranes. By visible light irradiation of the UV irradiated membranes, the colorless membranes were again obtained. The spectral changes completed within ca. 30 s. Opened **1** and **2** in PVC membranes were also isomerized thermally, with the half lives of ca. 4 and 3 min in the dark, respectively. The UV induced absorption changes of PVC(**2** and **3**) membrane were similar to those of PVC(**2**) membrane with a slightly different half life of ca. 6 min.

Liquid–Liquid Extraction. The results of liquid-liquid extraction with **1**, **2**, and **3** were shown in Table 1. In the dark, **1** showed different binding abilities for alkali metal ions, the magnitude of binding ability lying in the order of $K^+>Na^+>Rb^+>Cs^+$. In contrast, **2** showed no cation-binding ability. The binding ability of the compound **3** was in the order of $K^+>Na^+>Rb^+>Cs^+$, which was the same as that of **1** The cation-binding ability of **1** slightly diminished for all alkali metal cations by UV irradiation. The depressed cation-binding ability of opened **1** might be explained in terms of the electrorepulsive interaction between a positive charge of the nitrogen atom of the spiropyran part and the alkali metal cation trapped by benzo-15-crown-5 moiety in **1**.

Table 1. Effect of UV Irradiation on Liquid–Liquid Extraction

	Condition	Picrate extracted/%			
		Na^+	K^+	Rb^+	Cs^+
1	Dark	38	58	31	24
1	UV irradiated	35	52	28	18
2	Dark	0	0	0	0
2	UV irradiated	0	0	0	0
3		23	36	17	13

a) Organic phase (2 ml of dichloromethane): [**1**], [**2**], or [**3**]=1×10^{-4} mol dm^{-3}. Aqueous phase (2 ml of water): [Alkali metal picrate]=1×10^{-5} mol dm^{-3}, [Alkali metal chloride]=1 mol dm^{-3}.

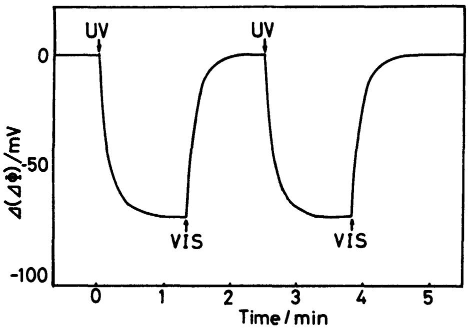


Fig. 4. Photoresponse of the membrane potential to alternate UV and VIS irradiation. PVC(**2**) membrane was used. Electrolyte was NaCl solution (1000 mmol dm^{-3}).

Photoinduced Potential Change. Figure 4 illustrates time response of the membrane potential change induced by alternate UV and visible light irradiation, which was obtained with the PVC(**2**) membrane. A negative shift of membrane potential was induced by UV irradiation. The membrane potential reached to a steady state under UV light within 30 s, and then returned to the initial potential by visible light irradiation within 30 s. It was reported in other membranes containing spirobenzopyran derivatives[4–8] that photoinduced potential changes occurred synchronously with photoisomerization between closed and opened forms. Since we also observed the purple-colorless change of the PVC(**2**) membrane associated with UV and visible light irradiation, the present photoinduced potential change should occur on the same basis. Table 2 shows the effects of the kind and concentration of alkali metal salts on the photoinduced potential change ($\Delta(\Delta\Phi)$) across the PVC(**2**) membrane. The $\Delta(\Delta\Phi)$ value was not dependent upon the kind of alkali metals except for Na^+, and was hardly affected by the alkali metal concentrations. Table 3 shows the photoinduced potential change $\Delta(\Delta\Phi)$ across the PVC(**1**) membrane. The $\Delta(\Delta\Phi)$ value remarkably depended upon both the kind and concentration of the alkali metals. With increasing concentration, the $\Delta(\Delta\Phi)$ value became less negative or more positive. The tendency for shifting toward more positive poten-

Table 2. Photoinduced Potential Changes, $\Delta(\Delta\Phi)$/mV, across PVC(**2**) Membrane

Electrolyte	Electrolyte concentration/mmol dm^{-3}		
	10	100	1000
NaCl	−78	−76	−71
KCl	−58	−59	−50
RbCl	−57	−59	−51
CsCl	−58	−56	−51

Photoirradiation was conducted from the compatment b side.

Table 3. Photoinduced Potential Changes, $\Delta(\Delta\Phi)$/mV, across PVC(**1**) Membrane

Electrolyte	Electrolyte concentration/mmol dm^{-3}		
	10	100	1000
NaCl	−33	−10	17
KCl	4	10	39
RbCl	2	3	19
CsCl	−21	−4	2

Photoirradiation was conducted from the compartment b side.

Table 4. Photoinduced Potential Changes, $\Delta(\Delta\Phi)$/mV, across PVC(**2** and **3**) Membrane

Electrolyte	Electrolyte concentration (mmol dm^{-3})		
	10	100	1000
NaCl	−74	−71	−61
KCl	−48	−44	−37
RbCl	−57	−53	−34
CsCl	−52	−39	−30

Photoirradiation was conducted from the compartment b side.

tial lay in the order of $K^+ > Rb^+ > Na^+ > Cs^+$. In the case of PVC membrane entrapping azobenzene-linked (bis crown ethers),[3–8] which had stronger binding ability for alkali metal ions after UV irradiation, the $\Delta(\Delta\Phi)$ value was reported to be negatively shifted by photoinduced enhancement of cation-binding ability. The opposite shifts observed here therefore seem reasonable since cation-binding ability of **1** decreases by UV irradiation. Table 4 shows the photoinduced potential changes $\Delta(\Delta\Phi)$ across PVC(**2** and **3**) membrane. Although the extent was smaller than that for PVC(**1**) membrane, the $\Delta(\Delta\Phi)$ value was affected by both the kind and concentration of alkali metals, the absolute value of the negative potential change becoming smaller with increasing alkali metal concentration. This phenomenon may be due to the decreased contribution of the photoinduced charge density to total charge density on the membrane surfaces, which was caused by the amount of alkali metal cations trapped by crown ether **3**.

Conclusion

We have shown by liquid–liquid extraction that the cation selectivity of spirobenzopyran **1** changes by photoirradiation. When **1** was entrapped in PVC membrane, the membrane exhibited marked photoinduced membrane potential changes, which were dependent upon the alkali metal species. This kind of photoexcitable membranes will be useful for construction of new photosensors, with which alkali metal concentrations can be measured.

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