PERKIN 2

Potential photoresponse of membranes containing a lipophilic crowned spirobenzopyran

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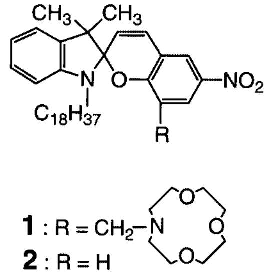
Received (in Cambridge, UK) 21st June 1999, Accepted 1st September 1999

Potential response and its photoresponse for plasticized-poly(vinyl chloride) membranes containing a lipophilic crowned spirobenzopyran were surveyed and compared with those for membrane systems of a spirobenzopyran derivative not carrying any crown ether moiety. On UV-light irradiation, an intriguing type of time-course change was found with the membrane potential for the crowned spirobenzopyran system in the presence of alkali metal ions, *i.e.*, the potential first increases and then decreases. The photoresponse profile for the crowned spirobenzopyran system was affected considerably by the sort of metal ions and the pH conditions of aqueous phases. This phenomenon is explained by an ion-exchange mechanism specific to crowned spirobenzopyran, that is, fast proton exchange followed by slow metal-ion exchange of its merocyanine form. The system for the corresponding spirobenzopyran without crown ether moiety exhibited a steady potential photoresponse that depends on the pH conditions of aqueous phases.

Spirobenzopyran derivatives are typical photochromic compounds that can undergo reversible isomerization between their electrically neutral spiropyran and zwitterionic merocyanine forms.[1] Therefore, they can be utilized as a key material for the photochemical control of physical properties. For instance, extensive research has been devoted to the photocontrol of electromotive force (emf) for membranes containing a spirobenzopyran derivative, taking advantage of the electrical-charge formation derived from photoisomerization to its merocyanine form.[2–11] These photoresponsive membranes are of great importance in membrane technology and science. Also, they may be very interesting from the viewpoint of light sensors and visual sensation in biological systems.[12]

A spirobenzopyran derivative, when a monoazacrown ether moiety is incorporated into its 8-position, displays an attractive phenomenon, which is the photochemical change of metal-ion binding based on intramolecular interaction between a phenolate anion and a metal ion complexed by the crown ether moiety in its merocyanine form.[13] This crowned spirobenzopyran has been successfully applied to photoinduced switching systems of ionic conductivity.[14] What will happen when the crowned spirobenzopyran is incorporated into membranes? Since the crowned spirobenzopyran is electrically neutral in its spiropyran form, its crown ether moiety may exchange cations by ion–dipole interactions. On the other hand, it turns out to be ionic in the merocyanine form and the resulted ionic charges may exchange ions by ion–ion interactions. It is, therefore, of much interest to investigate how membrane potential occurs at the interface between electrolyte solutions and membranes containing a crowned spirobenzopyran and how the potential responds to its photoisomerization. Crowned spirobenzopyran might realize sophisticated ion-sensing systems such as ion sensors whose ion selectivity can be photochemically switched between cations and anions.[15]

Here we report the potential response and photoresponse for plasticized-poly(vinyl chloride) (PVC) membranes containing lipophilic crowned spirobenzopyran **1**. A comparison with membranes of spirobenzopyran not containing any crown ether moiety **2** is also mentioned.



Experimental

Synthesis

1′-Octadecyl-3′,3′-dimethyl-6-nitro-8-[10-(1,4,7-trioxa-10-azacyclododecyl)methyl]spiro[2*H*-1-benzopyran-2,2′-indoline] or crowned spirobenzopyran **1** was synthesized as follows. A dry ethanol solution (15 cm^3) of 1-octadecyl-3,3-dimethyl-2-methyleneindoline[16] (3 mmol) and 2-hydroxy-3-formyl-5-nitrobenzyl monoazacrown ether[13] (3 mmol) was refluxed for 8 h. After the reaction, the ethanol was evaporated off to yield a crude product of the corresponding crowned spirobenzopyran, which was purified by silica-gel column chromatography with solvent-gradient elution (from 0 to 3 vol% CH_3OH in $CHCl_3$) to yield a dark-brown viscous liquid (17%) ($R_f = 0.4$ in silica-gel thin-layer chromatography with elution of $CHCl_3$–CH_3OH (97/3)): ^{1}H-NMR, δ 0.90 (3H, t, $J = 7.5$ Hz, CH_2CH_3) 1.1–1.5 (38H, m, $(CH_2)_{16}CH_3$ and CCH_3), 2.55–2.65 (4H, m, NCH_2CH_2O), 3.0–3.2 (2H, m, $NCH_2(CH_2)_{16}$), 3.4–3.8 (14H, m, OCH_2 and

J. Chem. Soc., Perkin Trans. 2, 1999, 2539–2544

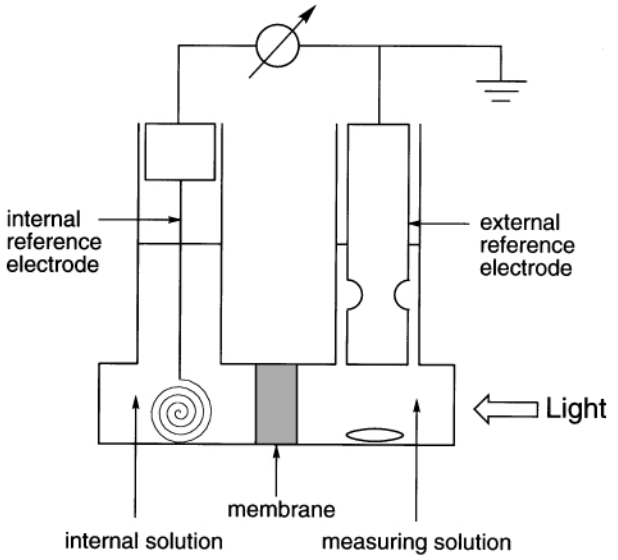


Fig. 1 Schematic diagram for potential measurement cell.

PhCH$_2$), 5.85 (1H, d, $J = 10$ Hz, C*H*=CHPh), 6.60 (1H, d, $J = 8$ Hz, 7′-H of indoline), 6.7–7.3 (4H, m, CH=C*H*Ph and 4′-, 5′-, and 6′-H of indoline), 7.90 (1H, d, $J = 4$ Hz, 5-H of benzopyran), 8.60 (1H, d, $J = 4$ Hz, 7-H of benzopyran); MS, *m*/*z* (% relative intensity) 747 (M$^+$, 100), 573 (62). Anal. Calcd for $C_{45}H_{69}N_3O_6$: C, 72.25; H, 9.30; N, 5.62. Found: C, 72.09; H, 9.28; N, 5.46%.

Other chemicals

1′-Octadecyl-3′,3′-dimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] or uncrowned spirobenzopyran **2** was prepared in a similar way to a procedure in the literature.[16] PVC with an average polymerization degree of 1020 was purified by reprecipitation from tetrahydrofuran (THF) in methanol. Bis(2-ethylhexyl) sebacate (DOS) was purified by vacuum distillation. THF was distilled over Na metal. Alkali and alkaline-earth metal chlorides and ammonium chloride were of analytical reagent grade. Water was deionized. The pH values for the aqueous phases were adjusted with KOH and HCl aqueous solutions. No special buffer solution was used to avoid significant interference by its electrolytes.

Membrane fabrication

PVC membranes were prepared by casting from a solution consisting of PVC (50 mg), DOS (100 mg), a spirobenzopyran derivative (10 mg), and THF (2 cm^3) on a flat Petri dish of 20 mm inner diameter. After air drying for two days, a disk of 15 mm diameter (thickness of 0.1–0.2 mm) was cut out from the membrane and then conditioned by soaking in a 1×10^{-6} mol dm^{-3} Li$^+$ solution overnight before setting in the measurement cell.

Measurements

The emf measurements were made at room temperature, using a U-type cell equipped with a quartz window for UV-light irradiation as shown schematically in Fig. 1. In the measurement cell, an ion-sensing membrane with 1 cm^2 area separated two aqueous phases. One of the phases contained 1×10^{-3} mol dm^{-3} LiCl and a spiral Ag-AgCl electrode of 1 cm^2 area as the internal reference electrode. The other contained a measuring solution with various LiCl concentrations and an external reference electrode, that is, a double-junction-type electrode with 0.1 mol dm^{-3} NH_4NO_3 and 3 mol dm^{-3} KCl in its outer and inner barrels, respectively. The electrochemical cell was Ag-AgCl | 1×10^{-3} mol dm^{-3} LiCl | membrane | measuring solution || 0.1 mol dm^{-3} NH_4NO_3 || 3 mol dm^{-3} KCl | AgCl-Ag. The internal and double-junction-type reference electrodes were connected to the positive and negative jacks of an electrometer, respectively. The measuring solutions contained appropriate concentrations of alkali metal chloride (MCl) and KOH or HCl for adjusting the pH (1×10^{-3} mol dm^{-3} KOH for pH 9.6, 1×10^{-2} mol dm^{-3} KOH for pH 12.3, 1×10^{-1} mol dm^{-3} KOH for pH 13.3, and 1×10^{-1} mol dm^{-3} HCl for pH 1.3). Photoirradiation of the ion-sensing membrane was achieved from the measuring solution through a quartz window at a distance of 25 cm from the membrane. Unless otherwise noted, UV (300–400 nm) and visible (>500 nm) lights were obtained by passing light of a 500 W xenon lamp through Toshiba UV-D36 and V-Y50 color filters, respectively.

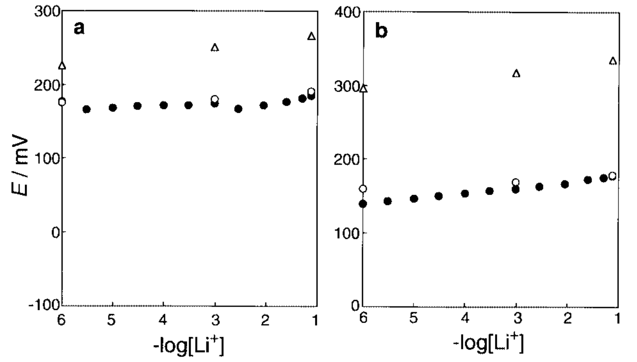


Fig. 2 Potential responses for membranes containing crowned spirobenzopyran **1** (**a**) and uncrowned derivative **2** (**b**) under medium-pH conditions. (●) In the dark; (○) on visible-light irradiation; (△) on UV-light irradiation after turning off the visible light. The emf values for the **1** system on UV-light irradiation are maximal ones.

Results and discussion

Potential response under medium-pH conditions

Potential response and its photoresponse for plasticized-PVC membranes containing crowned spirobenzopyran **1** were first studied under medium-pH conditions, where both of the aqueous phases did not contain any acid or base (Fig. 2). The corresponding spirobenzopyran without any crown ether moiety **2** was also employed for comparison. The potential measurements for each LiCl aqueous solution were made successively in the dark, on visible-light irradiation, and then on UV-light irradiation. On UV-light irradiation, anomalous time-course changes of membrane potential were observed in the membrane of crowned spirobenzopyran **1**, whereas steady emf readings were attained within 1 min in those of uncrowned derivative **2**. The maximal values are, therefore, plotted in the case of the **1** system on UV-light irradiation. Since a protonated merocyanine isomer of **1** may be formed to some extent at the membrane interface, visible light irradiation might isomerize it back to its corresponding spiropyran form. However, visible-light irradiation hardly changed the membrane potential of the crowned spirobenzopyran system established under dark conditions. On the contrary, UV-light increased the potential significantly due to the photoisomerization from the spiropyran to merocyanine forms. Under either dark or photoirradiated conditions, the LiCl concentration in the measured solution does not seem to affect the membrane potential very much. This indicates that the membrane of crowned spirobenzopyran responds neither to the cation nor the anion. A similar potential response was found for the PVC membranes containing uncrowned spirobenzopyran **2**, although the UV-light-induced potential increase did not accompany such time-course changes as seen in the **1** system.

Absorption spectra were taken for 1,2-dichloroethane solutions of spirobenzopyran derivatives **1** and **2**, to know what the membrane-potential photoresponse originates from. Even

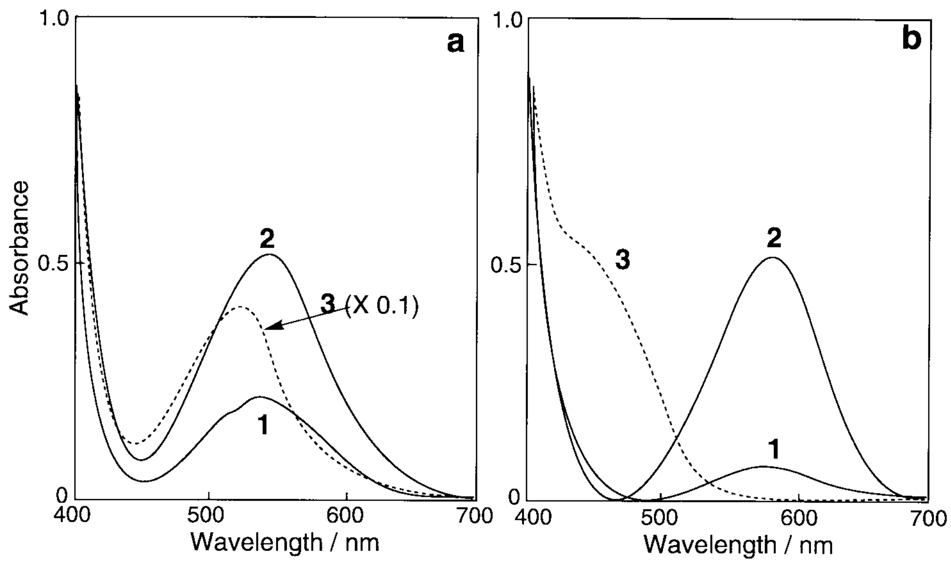
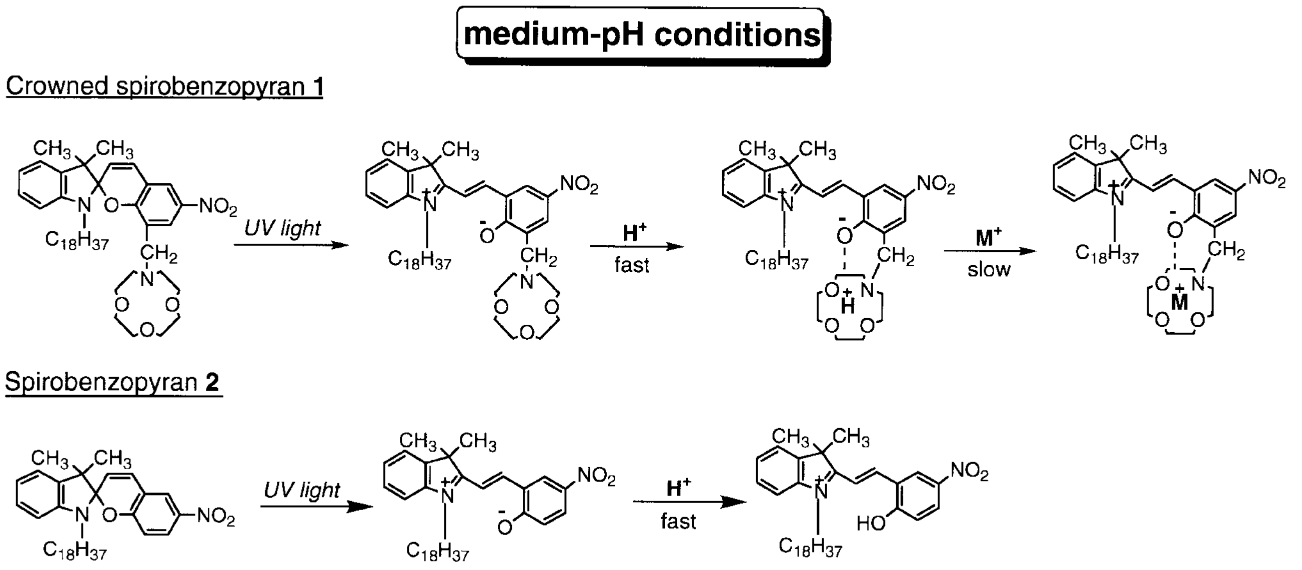


Fig. 3 Absorption-spectral changes of crowned spirobenzopyran **1** (**a**) and uncrowned derivative **2** (**b**). [spirobenzopyran]: 2 × 10^{-3} mol dm^{-3} in 1,2-dichloroethane. (**1**) In the dark; (**2**) on UV-light irradiation; (**3**) on addition of a drop of HCl aqueous solution.



Scheme 1

under dark conditions, the isomerization from spiropyran to merocyanine proceeds to some extent in both of the systems **1** and **2**, as evidenced by the absorption in the visible region that can be assigned to their corresponding zwitterionic merocyanine forms (Fig. 3). UV-light irradiation enhanced the isomerization to merocyanine forms with an increased absorption between 500 and 600 nm in both of the spirobenzopyran derivatives. Existence of some acid modified the absorption spectra for the spirobenzopyran derivatives drastically even under dark conditions. In the system of uncrowned spirobenzopyran **2**, addition of a small quantity of HCl caused a dramatic blue shift in the visible absorption from 580 to 460 nm. This clearly shows that the isomerization from the spiropyran to protonated merocyanine forms of **2**, which is a quaternary ammonium cation, occurs under acidic conditions, either in the dark or on UV-light-irradiation (Scheme 1). Since the aqueous phases without addition of any acid or base are weakly acidic at a pH value of a little lower than 6, the protonated merocyanine form of **2** is also formed in the membrane phase. On the other hand, such a drastic blue shift of the merocyanine absorption as seen in the system of **2** was not found on the acid addition for the system of crowned spirobenzopyran **1**. The slight blue shift suggests that a proton is not added directly to the phenolate anion of the merocyanine form of **1** but is bound to both the phenolate anion and crown ether ring (mainly its nitrogen atom) by their cooperative action. The protonated merocyanine form of crowned spirobenzopyran may easily exchange a metal ion with its proton. In any event, the protonation of merocyanine forms of spirobenzopyran derivatives **1** and **2** is promoted on UV-light irradiation under the medium-pH conditions.

A great difference in the potential response under medium-pH conditions between the membranes of crowned and uncrowned spirobenzopyrans **1** and **2**, is in the UV-light-induced response. That is to say, the membrane potential for the crowned spirobenzopyran system changes with time on photoirradiation, as demonstrated in Fig. 4a, *i.e.*, UV light increased the potential at first and then decreased it. On visible-light irradiation after the UV-light irradiation, the membrane potential was firstly decreased and was then increased. For the membranes of uncrowned spirobenzopyran **2**, on the other hand, the membrane potential was increased by UV light to level off within 1 min, and *vice versa* by visible light (Fig. 4b). Probably, the time-course changes of membrane potential for the **1** system under the medium-pH conditions can be explained as shown in Scheme 1. The merocyanine form of crowned spirobenzo-

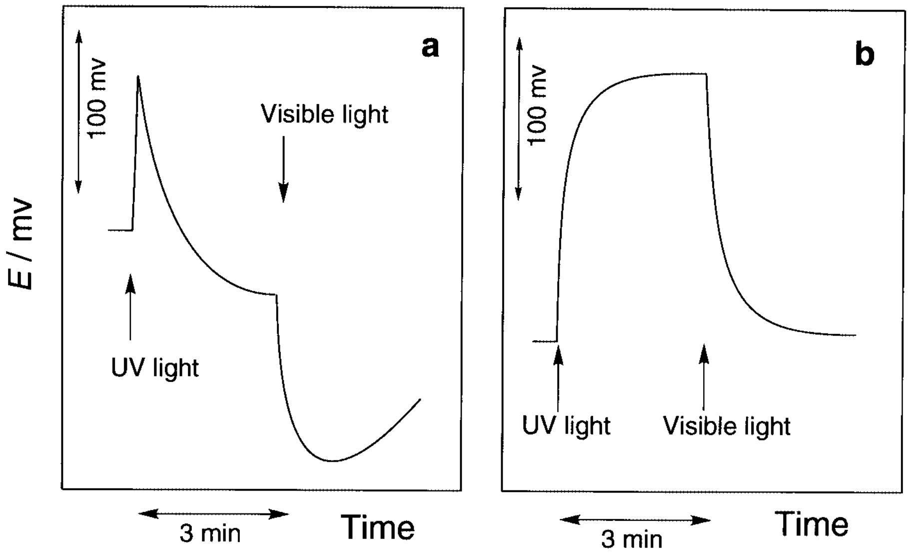


Fig. 4 Time-course changes of membrane potentials for systems of crowned spirobenzopyran **1** (**a**) and uncrowned derivative **2** (**b**) on photo-irradiation. Aqueous phase: 1×10^{-3} mol dm^{-3} LiCl, at pH 5.9.

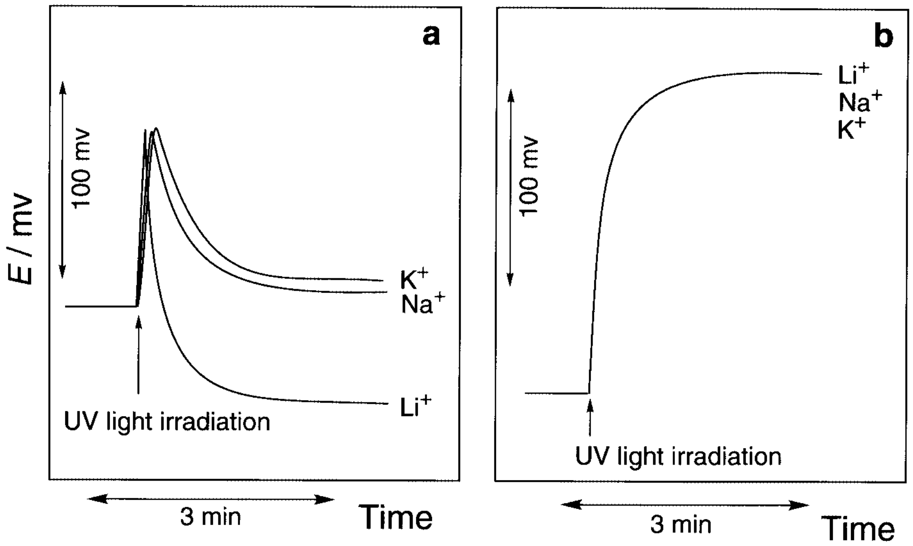


Fig. 5 Metal-ion dependence of potential photoresponse for membranes containing crowned spirobenzopyran **1** (**a**) and uncrowned derivative **2** (**b**) under medium-pH conditions. Aqueous phase: 1×10^{-3} mol dm^{-3} MCl, at pH 5.9.

pyran which results from UV-light-induced isomerization is protonated immediately by protons in the membrane phase to yield a quaternary ammonium cation.[2,8,9] Thus, the UV-light-irradiated membrane containing a spirobenzopyran derivative **1** or **2** is proton-sensitive at the early stage. Thereafter, the protonated merocyanine in the **1** membrane binds metal cations in the aqueous phase by its crown ether moiety with some time lag, which may be due to the electrostatic repulsion. The metal-ion binding of the protonated merocyanine accompanies a proton release to yield a phenolate anion that in turn interacts with the crown-complexed metal ion. In other words, the time-course potential change in the membrane of crowned spirobenzopyran **1** may be attributed to a fast proton response followed by the slow metal-ion response of its protonated merocyanine form. The metal-ion binding by crowned merocyanine at the interface between the membrane and aqueous phases leads to some extrusion of the metal-ion-bound merocyanine moiety into the measuring aqueous phase. Actually, on UV-light irradiation at high metal-ion concentrations of the aqueous phase, a detectable amount of crowned merocyanine dissolved out from the membrane to aqueous phases. This extrusion of the merocyanine moiety to the aqueous phase in turn alleviates the charge separation established at the interface between the membrane and aqueous phases, thus decreasing the membrane potential.

Since crowned spirobenzopyran **1** possesses a metal-ion selectivity,[13] the potential photoresponse for the membranes of **1** should be governed by the sort of alkali metal ions in the measuring solution. Marked difference in the UV-light-induced potential response among alkali metal ions was observed in the crowned spirobenzopyran system (Fig. 5). The crowned spirobenzopyran possessing a monoaza-12-crown-4 moiety is capable of binding Li^+ more powerfully than Na^+ and K^+ due to the intramolecular electrostatic interaction of its phenolate anion with a crown-complexed Li^+,[13] undergoing effective exchange of H^+ with Li^+. This brought about a speedy potential decrease, which is preceded by its increase based on the proton binding in the membrane of **1**. At extremely low pH (*e.g.*, pH 1.3), there was no significant UV-induced change of membrane potential as shown in Fig. 6a. At such a low pH, the crowned spirobenzopyran is protonated to a considerable degree. It was considered that UV-light irradiation did not lead to further isomerization to the merocyanine form and thereby the membrane potential change.

On the contrary, the PVC membrane based on the spirobenzopyran not containing any crown ether moiety, **2**, is sensitive

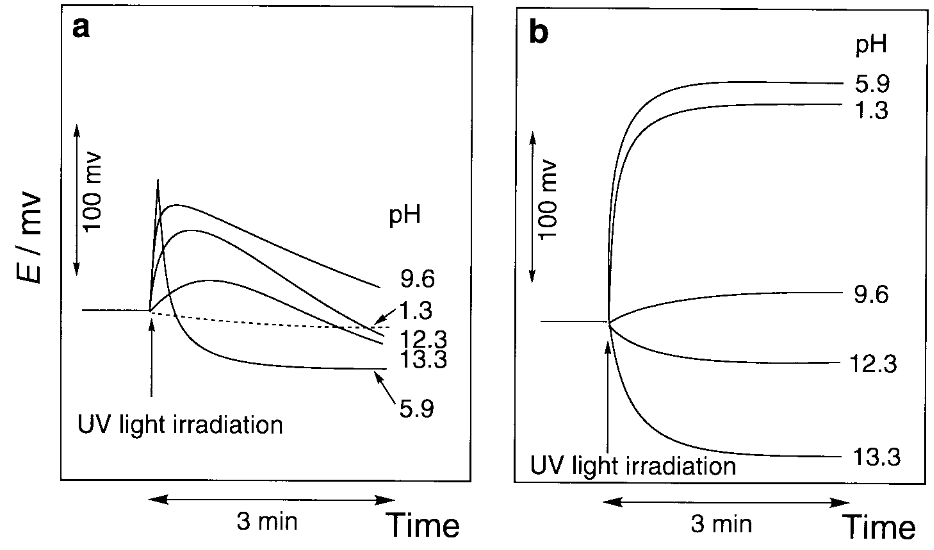
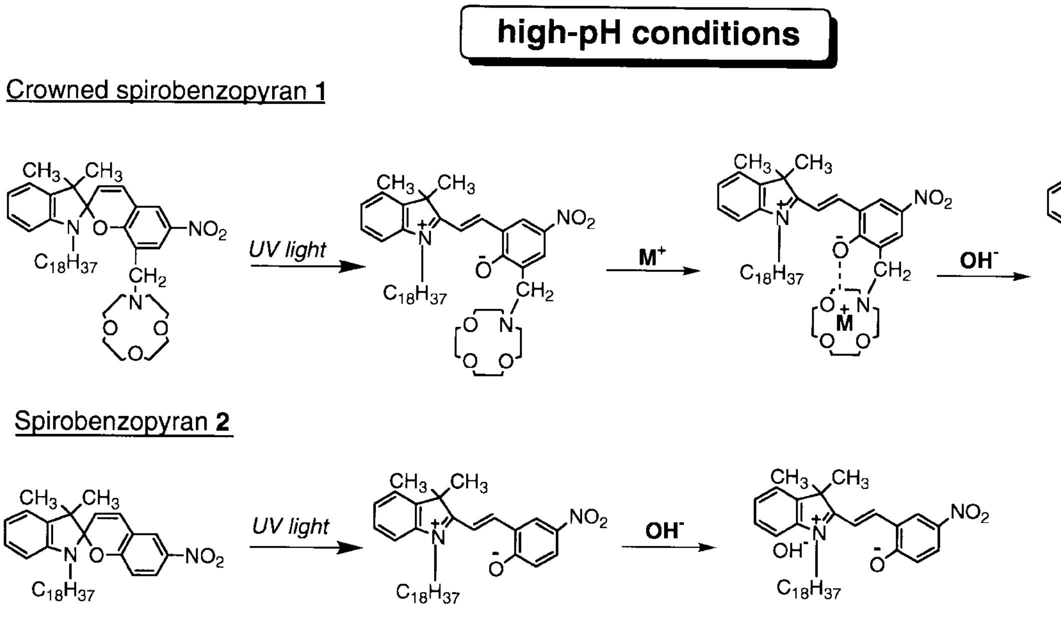


Fig. 6 pH dependence of potential photoresponse for membranes containing crowned spirobenzopyran **1** (**a**) and uncrowned derivative **2** (**b**). Aqueous phase: 1 × 10^{-3} mol dm^{-3} LiCl and an appropriate concentration of KOH or HCl.



Scheme 2

only to proton and did not show such a delayed cation response dependent on the sort of metal ions.

Potential response under high-pH conditions

Under medium-pH (weakly acidic) conditions, the PVC membranes of spirobenzopyran derivatives **1** and **2** are highly sensitive to proton. In order to alleviate the proton effect, the membrane-potential response of the spirobenzopyran derivatives was surveyed at low H^+-concentrations, that is, with basic aqueous phases. Even under high-pH conditions, photoinduced time-course changes of membrane potential were still found in the crowned spirobenzopyran system, although the potential did not change with time so drastically as under medium-pH conditions (Fig. 6a). The photoinduced merocyanine isomer of **1** can pick up a metal ion immediately from the aqueous phases at low H^+ concentrations, as demonstrated in Scheme 2. The UV-light-induced merocyanine form of crowned spirobenzopyran **1** is, therefore, metal-ion sensitive at the early stage, increasing its membrane potential. The following charge counterbalance of the N^+ part in the metal-ion-bound merocyanine of **1** by OH^- transferred from the aqueous phase results in marked diminution of the charge separation in the membrane interface, thus decreasing the membrane potential. Under the higher pH conditions, some extrusion (or dissolution out) of the proton- and metal-ion-bound merocyanines might occur, also leading to some decrease in the membrane potential. Fig. 6b shows the pH dependence in the membrane potential photoresponse for the system of uncrowned spirobenzopyran **2**. The membranes of **2** are proton-sensitive on UV-light irradiation under low- and medium-pH conditions of the measuring aqueous phase, as already mentioned. Naturally, the proton response of the UV-light-induced merocyanine form of **2** diminished with increasing pH. The potential photoresponse for the system of **2** almost disappeared around pH 10. Finally, the zwitterionic merocyanine is even sensitive to OH^- under extremely high pH conditions. At any pH of the measuring aqueous phase, the membranes based on uncrowned spirobenzopyran **2** underwent the steady potential photoresponse.

In conclusion, the plasticized-PVC membranes based on crowned spirobenzopyran **1** exhibited anomalous time-course potential changes on photoirradiation, which are based on the combination of proton and metal-ion responses by its merocyanine form. The phenomenon is very different from that in the membrane system for the corresponding spirobenzopyran derivative not possessing any crown ether moiety **2**. The photoresponsive membrane system based on crowned spirobenzopyran **1** may be quite difficult to apply to conventional ion sensors in which stable readings in the membrane potential are required for ion assay. However, since the potential photoresponse depends remarkably upon the sort of metal ion and pH, the present system may be a promising candidate for ion sensors based on non-linear response.[17] Furthermore, the membrane-potential photoresponse in the system of crowned spirobenzopyran **1** resembles so-called "active potential" in the pattern of potential changes.[18] In the active potential, Na^+ flow is gated by K^+ flow, the quickly-increased potential being restored. In the present membrane system of **1**, the subsequent metal-ion flow can gate H^+ flow on photo-excitation. Our photoresponsive membrane system might give a clue to the information transmission in biological systems.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture. We also acknowledge Yamada Science Foundation for financial support.

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Paper 9/04897I