Articles

Cation Complexation, Photochromism, and Reversible Ion-Conducting Control of Crowned Spironaphthoxazine

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A spironaphthoxazine derivative incorporating a monaza-12-crown-4 moiety at the 5′-position has been designed as a light-resistant, cation-complexable photochromic compound. Complexation of alkali metal ions by the crown moiety in the crowned spironaphthoxazine allows the spironaphthoxazine skeleton to isomerize to its corresponding open colored form, even under dark conditions. Specifically, Li^+ complexation greatly stabilizes the open colored form due to the intramolecular interaction between its oxo group and crown-complexed cation, as well as the selective Li^+ complexation of its 12-crown-4 moiety. Taking advantage of the high Li^+ selectivity in the cation-induced isomerization of crowned spironaphthoxazine, the thermal stability of the open colored form can be modulated continuously by added Li^+ concentrations. Even in the presence of the metal ion, UV- and visible-light irradiation led to further isomerization to the open form and back-isomerization to the initial closed form, respectively. Photoisomerization of crowned spironaphthoxazine to its open form promoted Li^+ binding due to the additional axial interaction with the crown-complexed Li^+, while that back to the closed form attenuated the cation binding. The photoinduced change in the cation-binding ability of crowned spironaphthoxazine, which possesses high light-fatigue resistance, has led to a highly reversible, photochemical switching system of ionic conduction.

Introduction

Photochromic compounds are convenient tools for controlling physical properties by their photoirradiation. In particular, photochromic compounds that are able to undergo heterolytic bond cleavage, such as spirobenzopyran derivatives,[1] are quite effective for photochemical control of physical properties. A number of attempts were, therefore, made to apply spirobenzopyran derivatives to the photochemical control of membrane transport,[2,3] membrane potential,[4-7] rheology,[8,9] and electrode reactions.[10,11]

We have already designed spirobenzopyran derivatives carrying a monoazacrown ether moiety and aimed at the photochemical control of the cation-binding ability of crown ethers.[12,13] The crowned spirobenzopyran deriv-atives are effective photochromic compounds that strongly complex certain alkali metal ions on photoisomerization to their corresponding merocyanine forms, owing to the efficient additional binding of the phenolate anion. Thus, the photoisomerization-induced change in the cation-binding ability of the crowned spirobenzopyrans effected photoinduced switching of the ionic conductivities of composite membranes containing them. The reversibility of this photochemical ionic conductivity switching system is very limited, however, due to the easy light fatigue of the spirobenzopyran derivatives.[1,14]

Spironaphthoxazine derivatives undergo a photoisomerization similar to that of spirobenzopyran derivatives. Their closed forms isomerize to the corresponding open colored forms upon UV-light irradiation and vice versa on visible-light irradiation or heating. Spironaphthoxazine derivatives, which generally show excellent light-fatigue resistance,[14,15] are expected to be more reliable and durable photochromic control systems than their corresponding spirobenzopyran derivatives. This prompted us to incorporate a crown ether moiety into a spironaphthoxazine skeleton. We have already communicated the extremely high Li^+ selectivity of crowned spironaphthoxazine 1 on the cation-induced isomerization.[16] Here we wish to report the details of the cation complexation and photochromism of crowned spironaphthoxazine 1, especially the highly Li^+-selective coloration and high thermal stability of its open colored form induced by Li^+ complexation and the

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highly reversible photoinduced switching of ionic-conductivity based on the photoisomerization-driven cation-binding-ability change.

1

2 R: −CH₂·N⟨cyclohexyl⟩

3 R: −H
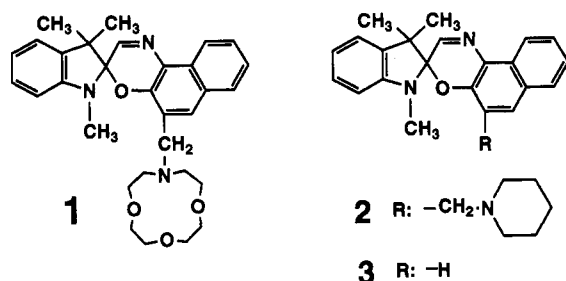
Experimental Section

Synthesis of 1,3,3-Trimethyl-5′-[(1,4,7-trioxa-10-azacyclododec-10-yl)methyl]spiro[indoline-2,3′-3H-naphth[2,1-b]-1,4-oxazine] or 5′-(Monoaza-12-crown-4)ylmethylspironaphthoxazine (1) (Crowned Spironaphthoxazine). An anhydrous chloroform solution (60 mL) of 3-hydroxy-2-naphthoic acid (32 mmol) and thionyl chloride (30 mL) was refluxed for 12 h. The chloroform and excess thionyl chloride were then evaporated off to yield a crude product of the corresponding acid chloride, which was employed for the subsequent reaction without further purification. To the acid chloride dissolved in chloroform (60 mL) was added dropwise a chloroform solution (60 mL) containing 1,4,7-trioxa-10-azacyclodecane (monoaza-12-crown-4, 32 mmol)[17] and triethylamine (35 mmol), and the mixture was then refluxed for 3 h. After the reaction, the chloroform solution was washed successively with 10% citric acid aqueous solution and saturated NaCl aqueous solution and was then dried over MgSO₄. Solvent evaporation yielded N-[(2-hydroxy-3-naphthyl)-carbonyl]monoaza-12-crown-4, which was recrystallized from ethyl acetate. To an anhydrous tetrahydrofuran (THF) solution (30 mL) of LiAlH₄ (13 mmol) was added dropwise a THF solution (20 mL) of N-[(2-hydroxy-3-naphthyl)carbonyl]-monoaza-12-crown-4 (2.3 mmol) over at least 1 h. The mixture was stirred at room temperature for 3 h and then refluxed for 2 h. In order to remove the excess LiAlH₄, ethyl acetate (50 mL) was added dropwise to the mixture over 1 h while the mixture was stirred in a dry ice–acetone bath. The mixture was stirred for an additional 2 h in the cold bath and was then allowed to stand at room temperature. After gradual treatment of the reaction mixture with 7% HCl (aq) (50 mL), followed by the organic solvent evaporation, the aqueous phase was neutralized with Na₂CO₃ and extracted by chloroform. Solvent evaporation from the chloroform layer afforded a crude product of 10-[(2-hydroxy-3-naphthyl)methyl]-1,4,7-trioxa-10-azacyclododecane or N-[(2-hydroxy-3-naphthyl)methyl]monoaza-12-crown-4, which was recrystallized from ethyl acetate (off-white crystal, 57%): mp 96–97 °C; IR (KBr) 3500 cm⁻¹ (OH), 1160 cm⁻¹ (COC); ¹H-NMR (100 MHz, CDCl₃) δ 3.02 (t, 4H), 3.7–4.0 (m, 12H), 4.06 (s, 2H), 7.2–8.0 (m, 7H); MS m/e (relative intensity) 331 (M⁺, 100). Anal. Calcd for C₁₉H₂₅NO₄: C, 68.86; H, 7.60; N, 4.23, O, 19.31. Found: C, 68.61; H, 7.59; N, 4.18.

The condensation of N-[(2-hydroxy-3-naphthyl)methyl]-monoaza-12-crown-4 with 1,3,3-trimethyl-2-methyleneindoline was performed as follows. To N-[(2-hydroxy-3-naphthyl)methyl]-monoaza-12-crown-4 (5.1 mmol) dissolved in 50% acetic acid (9 mL) was added dropwise an aqueous solution (3 mL) of NaNO₂ (26 mmol) with stirring in an ice bath. The mixture was stirred for 1 h at room temperature and was then evaporated to dryness. Anhydrous ethanol (50 mL) was added, and the excess of NaNO₂ was filtered off. After addition of 1,3,3-trimethyl-2-methyleneindoline (2.5 mmol) and triethylamine (ca. 20 mmol, some was consumed for neutralization of the residual acetic acid), the mixture was refluxed for 3 h under an argon atmosphere. Evaporation of the ethanol yielded a crude oil of 1, which was purified successively by column chromatography (silica gel,

chloroform) and preparative HPLC (octadecylsilanized silica, methanol) (greenish brown glass, 35%): IR (neat) 1610 cm⁻¹ (C=N), 1100 cm⁻¹ (COC); ¹H-NMR (100 MHz, CDCl₃) δ 1.33 (d, J = 3 Hz, 6H), 2.8–3.0 (m, 7H), 3.6–3.9 (m, 14H), 6.5–8.1 (m, 9H), 8.67 (d, J = 8 Hz, 1H); MS m/e (relative intensity) 516 (M⁺, 100). Anal. Calcd for C₃₁H₃₇N₃O₄: C, 72.21; H, 7.23; N, 8.15, O, 12.41. Found: C, 71.97; H, 7.50; N, 8.07.

Other Chemicals. 1,3,3-Trimethyl-5′-(1-piperidinomethyl)-spiro[indoline-2,3′(3H)-naphth[2,1-b]-1,4-oxazine] or 5′-piperidinomethyl spironaphthoxazine (2)[18] was prepared in a way similar to that for the crowned spironaphthoxazine. 1,3,3-Trimethylspiro[indoline-2,3′(3H)-naphth[2,1-b]-1,4-oxazine] or unsubstituted spironaphthoxazine (3) was used as received from Tokyo Kasei. 10-Benzyl-1,4,7-trioxa-10-azacyclodecane or N-benzylmonoaza-12-crown-4 was prepared according to a reported procedure.[17] Unless otherwise specified, all the reagents were the best grade available. The solvents for the spectroscopy were spectrograde from Dojindo. Water was deionized. Poly(vinyl chloride) (PVC, average polymerization degree of 1020) was purified by repeated reprecipitation from tetrahydrofuran (THF) in methanol. Poly(perfluorosulfonic acid) (PPFS, Nafion) was purchased as a 5 wt % alcohol solution from Aldrich, and its Li⁺ salt (PPFS-Li⁺) was obtained by neutralizing the polymer acid with a lithium methoxide methanol solution. A plasticizer for PVC membranes, bis(2-ethylhexyl) sebacate (DOS) was purified by distillation in vacuo. Oligooxyethylene diacetate (OOEAc) was prepared by treating oligooxyethylene (average molecular weight of about 400) with excess acetic anhydride (70 °C, 1 day) and then purified by alumina chromatography. THF and N,N-dimethylformamide (DMF) for the preparation of composite films were distilled over LiAlH₄ and CaH₂, respectively.

Cation-Induced Isomerization. Acetonitrile solutions containing crowned spironaphthoxazine and an alkali metal perchlorate in identical concentrations were allowed to stand for 24 h under dark conditions, and their absorption spectra were then taken. Photoirradiation was made by using UV (300–400 nm) and visible (>490 nm) lights, which were obtained by passing a light from a 500-W Xe lamp through Toshiba UV-D36 and Y-50 color filters, respectively.

Thermal Decoloration Rate. A 4 × 10⁻⁴ mol dm⁻³ spironaphthoxazine acetonitrile solution with and without an alkali metal perchlorate was irradiated by UV light for 2 min. The absorbance for the corresponding open colored form at 615 nm was followed with time at 8 °C, immediately after the photoirradiation. The first-order rate constants of thermal decoloration (k) were determined from the slope in the plots of $\log[(A_t - A_\infty)(A_0 - A_\infty)]$ vs time (t), where A_t, A_0, and A_∞ are the absorbance at 615 nm at t, $t = 0$, and $t = $ infinity, respectively.

Composite Film Fabrication. PVC composite films for absorption spectroscopy and ionic conductivity measurements were prepared on indium–tin oxide-coated (ITO) glasses (2 × 2.5 cm) by a spin coating technique from THF solutions and then dried at 50 °C under a nitrogen stream. In general, 0.1 mL of a THF solution (0.8 mL) containing PVC (60 mg, 49.8 wt %), DOS (50 mg, 41.5 wt %), photochromic compound (10 mg, 8.3 wt %), and LiClO₄ (0.5 mg, 0.4 wt %) was used for each spin coating on an ITO glass, affording a composite film with 5-μm thickness. PPFS-Li⁺ composite films for ionic conductivity measurements were obtained on ITO glasses by casting 0.1 mL of a DMF solution (0.5 mL) containing PPFS-Li⁺ (25 mg, 45.5 wt %), OOEAc (10 mg, 18.2 wt %), photochromic compound (20 mg, 36.4 wt %). The DMF was evaporated in about 2 h under a pressure of 2.7 kPa at 40 °C. The films were dried at 60 °C for 1 day under the reduced pressure, possessing 20-μm thickness. In the PPFS-Li⁺ films for isothermal transient ionic current measurements, about 0.03 cm³ of the DMF solution was used for casting on Pt-sputtered ITO glasses to yield a film of 5-μm thickness. On the composite films for ionic conductivity measurements, gold was evaporated as an electrode (4.7-mm diameter, about 10-nm thickness).

Ionic Conductivity Measurements. Ac impedance of com-

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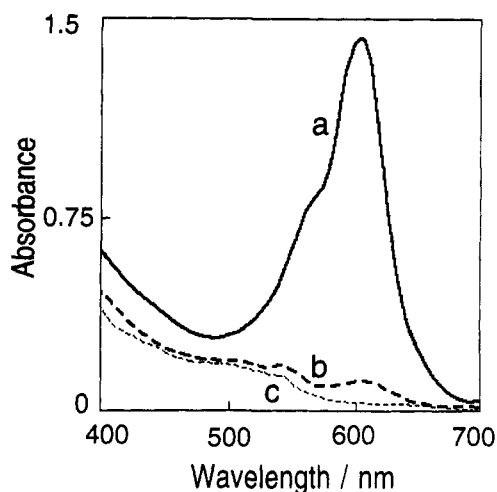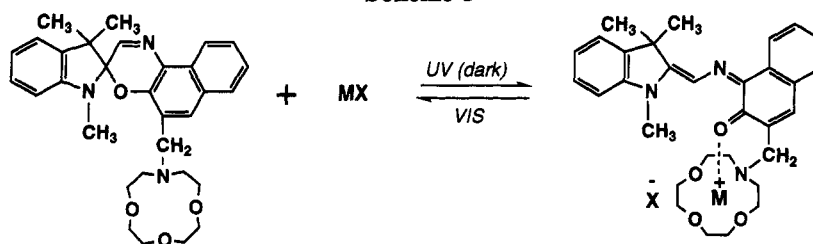(18) Taylor, L. D.; Nicholson, J.; Davis, R. B. *Tetrahedron Lett.* 1967, 1585–1588.

Scheme 1

Figure 1. Absorption–spectral changes of crowned spironaphthoxazine acetonitrile solutions on addition of alkali metal salts under dark conditions. [1] and [$MClO_4$]: 4×10^{-4} mol dm^{-3}. a: Li^+. b: Na^+. c: K^+.

posite films was measured as reported previously.[19] Ionic conductivity was calculated by the Cole–Cole plots method. Isothermal transient ionic currents were measured in a manner similar to a procedure in the literature,[20,21] using a cell setup for the ionic conductivity measurements. After an appropriate dc voltage was applied across a composite film for 3 h, its polarity was rapidly switched, and the resulting transient current was then monitored every second.

Results and Discussion

Alkali Metal Ion Complexation and Isomerization. Equimolar addition of an alkali metal perchlorate to an acetonitrile solution of crowned spironaphthoxazine 1 caused significant spectral changes (Figure 1). Specifically, when $LiClO_4$ was added, a strong absorption peak appeared at 615 nm and was assigned to the open form of crowned spironaphthoxazine. Na^+ addition brought about a slight absorption–spectral change, but K^+ addition hardly changed the visible spectrum of the crowned spironaphthoxazine solution. In acetonitrile solutions of spironaphthoxazine containing a piperidine moiety 2 and unsubstituted spironaphthoxazine 3, no significant absorption–spectral change was observed on alkali metal ion addition, under identical conditions. This suggests that the isomerizations of 1 to its open colored form is induced by cation complexation of its crown ether moiety. Alkali metal picrate extraction by N-benzylmonoaza-12-crown-4[12] indicated that just the monoaza-12-crown-4 moiety of 1 can bind alkali metal cations with a selectivity order of $Li^+ \sim$
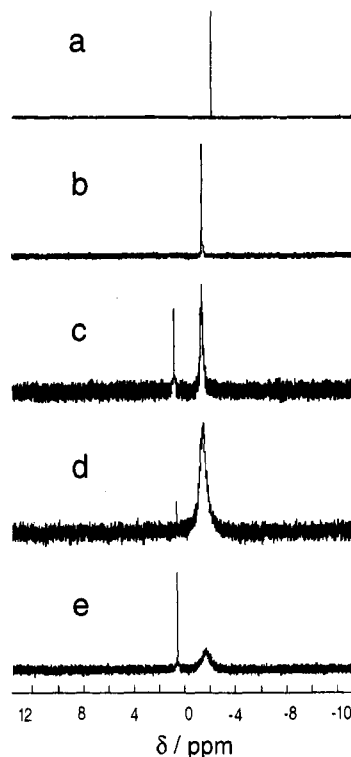
Figure 2. ⁷Li-NMR spectra of $LiClO_4$ acetonitrile solutions in the presence of crowned spironaphthoxazine. External standard: 2×10^{-2} mol dm^{-3} $LiClO_4$ in D_2O. a: $LiClO_4$ only (2×10^{-2} mol dm^{-3} in $CD_3CN/CH_3CN(3/7)$). b: a + 2×10^{-2} mol dm^{-3} N-benzylmonoaza-12-crown-4. c: a + 2×10^{-2} mol dm^{-3} 1, under dark conditions. d: c, on visible-light irradiation. e: c, on following UV-light irradiation.

$Na^+ > K^+$. Nevertheless, the Li^+ selectivity in the cation-induced isomerization appears to be much higher than expected from the cation-binding ability of monoaza-12-crown-4 itself. This metal ion complexation-induced isomerization of 1 to the corresponding open colored form is likely to be related to an intramolecular interaction of its oxo group with its crown-complexed metal ion, especially with a high-charge-density metal ion such as Li^+, as is shown schematically in Scheme 1. ⁷Li-NMR spectroscopy of an acetonitrile solution containing 1 and $LiClO_4$ supports the intramolecular interaction in the Li^+ complex of the crowned spironaphthoxazine open form (Figure 2). Equimolar addition of N-benzylmonoaza-12-crown-4 to a $LiClO_4$ acetonitrile solution caused a slight shift of its Li^+ peak to higher frequency, which is probably due to the metal ion complexation by the crown compound. When crowned spironaphthoxazine 1 was added instead of the N-benzylmonoazacrown ether, another peak was found at much higher frequency, in addition to that resulting from Li^+ complexation by the crown moiety. The new peak might possibly result from the Li^+ complex of the corresponding open form. The appearance of the much

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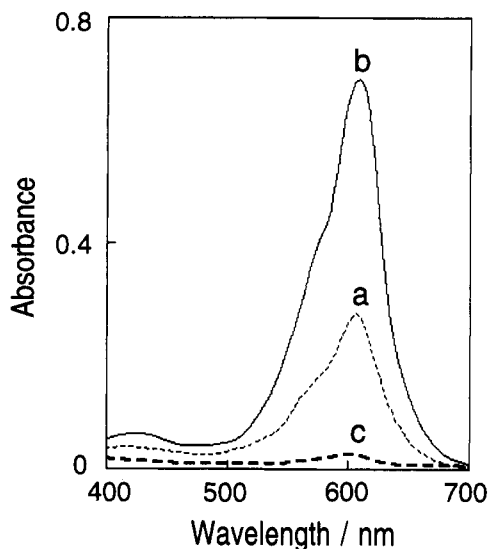**Figure 3.** Photoinduced spectral changes of crowned spironaphthoxazine acetonitrile solution in the presence of LiClO₄. [1] and [LiClO₄]: 8 × 10⁻⁵ mol dm⁻³. a: Under dark conditions. b: On UV-light irradiation. c: On visible-light irradiation (1 min).

Figure 4. First-order plots of thermal decoloration for crowned spironaphthoxazine acetonitrile solutions in the presence of alkali metal perchlorate. [1] and [MClO₄]: 4 × 10⁻⁴ mol dm⁻³, at 8 °C. (○) Li⁺. (□) Na⁺. (△) K⁺. (●) without salt.

higher frequency peak in the ⁷Li-NMR suggests an intramolecular interaction between the oxo group and Li⁺ in the complex of the crowned spironaphthoxazine open form. Thus, the formation of a stable six-membered-ring chelate of the oxo oxygen atom and crown-ring nitrogen atom with Li⁺,[22] induced by selective cation binding of the crown moiety, stabilizes the open colored form of 1 substantially. Additionally, the highly Li⁺-selective, color-inducing isomerization of crowned spironaphthoxazine will be useful for spectrophotometric Li⁺ determination in alkali metal ion mixtures.

Photoisomerization. As mentioned above, the Li⁺ complexation of crowned spironaphthoxazine induced considerable isomerization to its open colored form. Irradiation of UV light further enhanced the isomerization to the open colored form, as seen in Figure 3. Visible light, on the other hand, reversed the isomerization to the closed colorless (spironaphthoxazine) form. Only slight absorption based on the crowned spironaphthoxazine open form was seen around 615 nm during visible-light irradiation. This means that visible-light irradiation can restore "open" 1, which is formed by cation complexation under dark conditions, to its closed form. That is to say, the photoisomerization of crowned spironaphthoxazine is ready to proceed even in the presence of Li⁺. Of course, upon removal of the UV or visible light, the isomerization equilibrium of the 1 – Li⁺ acetonitrile solution reverted smoothly to that initially established under dark conditions.

Thermal decoloration of the crowned spironaphthoxazine was followed in acetonitrile in the presence of an alkali metal perchlorate, in order to elucidate the cation-binding effect on the thermal stability of the crowned spironaphthoxazine open form. Typical first-order plots of thermal decoloration of 1 are shown in Figure 4, indicating that the cation complexation of its crown moiety increases the thermal stability of the open colored form of 1. In particular, it should be noted that Li⁺ complexation markedly stabilizes the open colored form of crowned
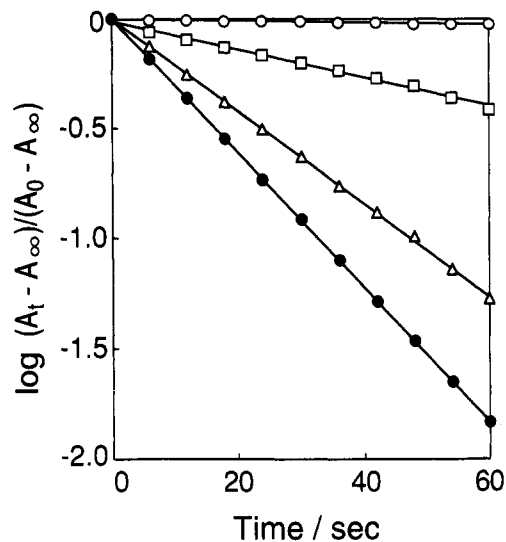
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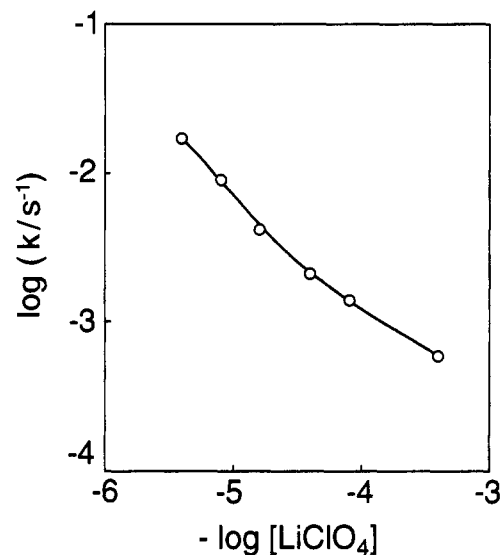**Figure 5.** Dependence of Li⁺ concentration on thermal stability of crowned spironaphthoxazine open colored form. [1]: 4 × 10⁻⁴ mol dm⁻³ in CH₃CN, at 8 °C.

Table 1. First-Order Rate Constants of Thermal Decoloration of Crowned Spironaphthoxazine and Its Analogs[a]

	k, 10⁻² s⁻¹			
	no metal ion	Li⁺	Na⁺	K⁺
1	3.0	0.053	0.60	2.1
2	9.0	3.9	7.9	8.3
3	14	11	11	11

[a] [Spironaphthoxazine] and [MClO₄]: 4 × 10⁻⁴ mol dm⁻³ each in CH₃CN, at 8 °C.

spironaphthoxazine, the stability of which is enhanced by 2 orders of magnitude in the presence of equimolar Li⁺ relative to the absence of any metal ion (Table 1). Na⁺ addition also enhanced the thermal stability of the crowned spironaphthoxazine open colored form by about 1 order of magnitude, but K⁺ hardly modifies its stability. The selective thermal stability enhancement of the open colored form of 1 by Li⁺ is as expected from that of the cation complexation-induced isomerization under dark condi-
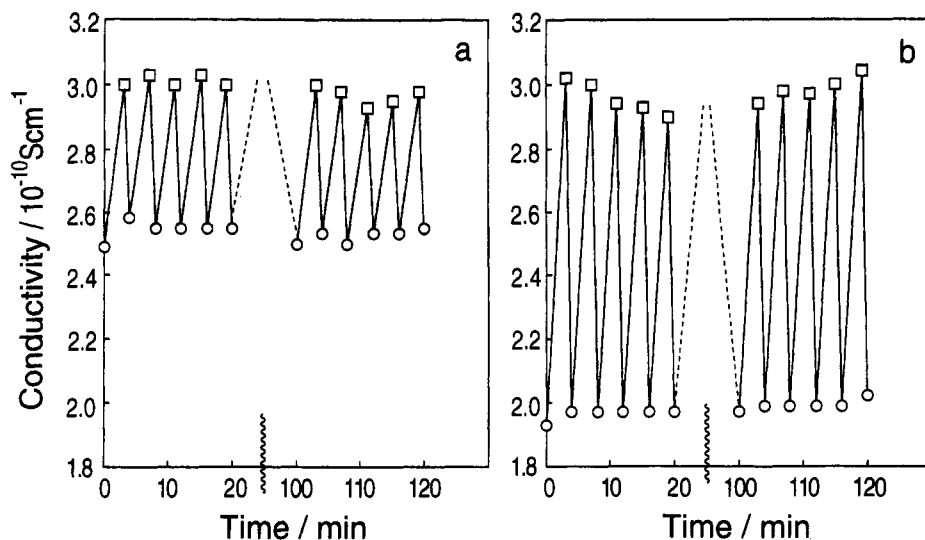
Figure 6. Photoinduced ionic-conductivity changes for crowned spironaphthoxazine-containing composite films. a: Bi-ionic conducting system based on PVC. b: Single-ionic conducting system based on PPFS–Li⁺. Photoirradiation started at each point of O and then finished at the point of □ for visible light and vice versa for UV light.

tions. In spironaphthoxazine systems containing a piperidine moiety 2, and in unsubstituted 3, alkali metal ions, even Li⁺, exhibited only slight or no effect on the stability of their open colored forms. These results again suggest that the thermal stability enhancement of the open colored form of 1 by Li⁺ addition originates in the intramolecular interaction between the oxo group and Li⁺, combined with the selective cation binding of its crown moiety. More noticeable is that the thermal stability (or thermal decoloration rate constant) of the crowned spironaphthoxazine open form depends upon the added Li⁺ concentration, as demonstrated in Figure 5. In other words, the thermal stability of the open colored form of 1 can be regulated continuously by the Li⁺ concentration. In most well-known spironaphthoxazine derivatives, the open colored forms are not very thermally stable; they isomerize quickly back to their corresponding closed forms after a UV light is turned off.[1,14] Thus, the crowned spironaphthoxazine-Li⁺ system has a significant advantage over the conventional spironaphthoxazines for practical applications as photochromic compounds.[23]

Photochemical Switching of Ionic Conductivity. It is expected from the above observation of the photoirradiation of crowned spironaphthoxazine in the presence of Li⁺ that the complexation equilibrium between 1 and Li⁺, established under dark conditions, can be altered by photoirradiation. That is to say, when UV light enhances the isomerization of 1 to the corresponding open form, the participation of its oxo group as an additional binding site augments its cation-binding ability, as is illustrated in Scheme 1. However, to the contrary, visible light causes isomerization back to the closed form, resulting in disappearance of the additional binding site and, thereby diminution in the cation-binding ability. If this is the case, alteration of the cation-binding ability, that is, the cation trapping and releasing by crowned spironaphthoxazine, should greatly affect ionic conduction in systems containing 1 and a Li⁺ salt.

We have designed photochemical ionic conductivity switching systems that are composed of a polymer support, a plasticizer, a Li⁺ salt, and crowned spironaphthoxazine.

Two types of ion-conducting composite films were fabricated: one is a bi-ionic conducting film consisting of PVC, DOS, LiClO₄, and 1, where both the cation and anion take part in the ionic conduction, and the other is a single-ionic conducting film consisting of PPFS–Li⁺, OOEAc, and 1, where only the cation can migrate, due to the extremely low mobility of the polymer anion. Absorption spectra for a PVC-based composite film showed that crowned spironaphthoxazine isomerizes to its corresponding open form to some extent under dark conditions, as is the case with the acetonitrile solutions containing 1 and LiClO₄. Also, irradiation with UV and visible lights, respectively, caused the isomerization of 1 to its open colored form and its back-isomerization, even in composite films. Profiles of photoinduced ionic conductivity change for the two types of composite films are depicted in Figure 6. Marked photochemical switching of ionic conductivity was realized with both the PVC- and PPFS–Li⁺-based composite films. With visible-light irradiation, Li⁺, the ionic carrier in films, tends to be released from crowned spironaphthoxazine molecules. The ionic conductivity of the composite film thus increased as anticipated from Scheme 1. Subsequent UV-light irradiation allowed the open colored form of crowned spironaphthoxazine to trap Li⁺, thereby decreasing the ionic conductivity.

However, since cation complexation by crowned spironaphthoxazine can assist ion-pair separation and, thereby, anion migration in the bi-ionic conducting PVC composite film, the ionic conductivity change due to the photoinduced cation-binding enhancement (or alleviation) may be fully or partially canceled by the resulting anion contribution. The magnitude of the photoinduced ionic conductivity change (ratio of visible-light-enhanced and UV-light-attenuated ionic conductivities) is not very great in the bi-ionic conducting system, being no more than 1.2. In the single-ionic conducting PPFS–Li⁺ composite film, on the other hand, the change in cation-binding ability of crowned spironaphthoxazine in composite films is considered to be reflected straightforwardly in the ionic conductivity change because the contribution of the polymer anion to the ionic conductivity is negligible. The single-ionic conducting system, in fact, afforded more
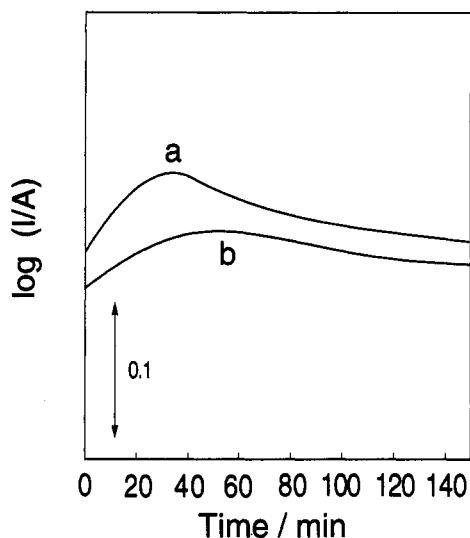
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Figure 7. Isothermal transient ionic current curves for PPFS–Li+-based composite film containing crowned spironaphthoxazine under photoirradiated conditions. a: On visible-light irradiation. b: On UV-light irradiation.

remarkable photochemical switching of ionic conductivity (with an ionic conductivity change of about 1.5) than did the bi-ionic conducting system, as seen from a comparison of the two systems in Figure 6. Measurements of isothermal transient ionic currents in the single-ionic conducting composite film gave useful information about the change in ion mobility induced by photoirradiation (Figure 7). The transient ionic current curves in the PPFS–Li+-based composite film exhibited only a peak that is attributable to Li+ migration across the film. Definitely, visible-light irradiation accelerates the Li+ migration, while UV-light irradiation retards it. The ion mobility, which can be calculated from the transient time, is 2.1×10^{-10} and 1.4×10^{-10} cm^2 s^{-1} V^{-1} upon irradiation by visible and UV lights, respectively, the ratio being 1.5. One can compare the magnitude of the photoinduced ionic conductivity change with that of the ion mobility change, taking account of the relationship $\sigma = qn\mu$, where q, n, and μ refer to ionic charge (a constant), carrier density (or concentration), and ion mobility, respectively. Obviously, the ion mobility change is a primary governing factor in the photoinduced ionic conductivity switching in the

single-ionic PPFS–Li+-based composite film. This verifies that the photochemical ionic conductivity change in the crowned spironaphthoxazine-containing composite films is driven by the Li+ mobility change, consistent with the change in cation-binding ability of the key compound, as seen in Scheme 1.

It should also be noted that the photochemical ionic conductivity switching in the composite films containing crowned spironaphthoxazine 1 is fully reversible and reproducible, as demonstrated in Figure 6. Even after 30 cycles of irradiation by UV light followed by visible light, each of the visible-light-enhanced and UV-light-attenuated ionic conductivities and the magnitude of change were almost constant, in both the PVC- and PPFS–Li+-based composite films. In similar composite films containing a crowned spirobenzopyran instead of the crowned spironaphthoxazine,[13] some light fatigue or deterioration began after several photoirradiation cycles; the magnitude in the photochemical ionic conductivity change decreased with the variation in each of the photoinduced ionic conductivities. Conceivably, the high durability of the photochemical ionic conductivity switching system containing crowned spironaphthoxazine 1 can be ascribed to the excellent light-fatigue resistance of the spironaphthoxazine derivative.[14,15]

In conclusion, the cation-binding ability of crowned spironaphthoxazine in the presence of a Li+ salt can be modulated by photoisomerization due to the presence of an additional binding-site effect in its open colored form. The photoinduced change in the cation-binding ability of 1 has been substantiated by photochemical switching of ionic conductivity in composite films containing 1 and Li+. This photochemical cation-binding control system with crowned spironaphthoxazine as a highly light-resistant key compound is promising not only for its present application to ionic-conductivity switching but also for a variety of applications entailing ion transfer, such as photoinduced membrane transport of ionic species.