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Photocontrol of ionic conduction by photochromic crown ethers

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Contents

Abstract

Crown ether derivatives carrying a photochromic moiety, photochromic crown ethers, are attractive key materials for photochemical control of ionic conduction in the solid or quasi-solid state. The photochromic crown ethers can modify ionic conduction in two modes. A mode for photocontrol of ionic conduction is based on molecular control in complexation of cations that are ion-conducting carriers by crown ethers incorporating a photochromic moiety such as spirobenzopyran, spironaphthoxazine, and Malachite Green dye. Another mode is based on photoinduced changes in the phase and molecular orientation of the crown moieties

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that are ion-hopping sites by using crowned azobenzene derivatives capable of forming highly-ordered liquid crystal phases such as smectic and cholesteric phases.

Keywords: Photochromic crown ethers; Ionic conduction

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1. Introduction

Ion migration affords electric conduction in media. Specifically, ion conduction in the solid or quasi-solid state is attractive to researchers in the field of material chemistry. Extensive work has so far been devoted to designing organic ionic conductors, so-called polymer electrolytes [1–3]. One of the main aims to design new polymer electrolytes is to attain high ionic conductivities close to those for inorganic ionic conductors. Crown ethers can be utilized to enhance ionic conductivities of polymer electrolytes [4–9], since the addition of crown ethers to polymer electrolytes often allows promotion in salt solubilization, ion separation, and carrier migration.

Only several studies have been reported concerning ion-conducting organic materials whose ionic conductivity can be switched by external stimuli such as light and heat [10–17], although the photoresponsive ion-conducting organic materials are useful for applications in material chemistry such as device fabrications for imaging, memory, and printing. Photochromic compounds, which isomerize reversibly by photoirradiation, are convenient tools for controlling physical properties. This is the case with photochemical control of ionic conductivity. For instance, photoisomerization of spirobenzopyran derivatives causes rheological changes of polymer electrolytes, thus affecting their ionic conductivities [17]. Photochromic compounds that ionize photochemically can bring about photoinduced carrier generation, which in turn increases ionic conductivity in polymers [16,18]. Photoisomerization of azobenzene derivatives between their trans and cis form sometimes leads to a marked phase transition between crystal and liquid states, which can change ion mobilities and thereby ionic conductivities in ion-conducting composite films [13,15].

The design of photochromic compounds incorporating a crown ether moiety that plays an important role in ionic conduction, namely photochromic crown ethers, are expected to provide more sophisticated ways to photochemical control of ionic conduction in media. Here, we describe the design of photochromic crown ethers that can regulate ion migration by their photoisomerization, their photochromism and cation-complexation behavior in solution, and their applications to photoresponsive ion-conducting materials.

2. Photochemical control of ionic conduction based on molecular control of cation complexation by photochromic crown ethers

2.1. Photoinduced changes of cation-complexing ability

2.1.1. Crowned spirobenzopyran

Spirobenzopyran derivatives, which undergo photoisomerization between their electrically-neutral spiropyran and zwitterionic merocyanine forms [19], when equipped with a crown ether moiety, are expected to modulate the cation-complexing property of the crown ether moieties. There are several crowned spirobenzopyrans synthesized so far, in most of which a spirobenzopyran skeleton carries a crown ether moiety at its indoline part, probably due to the ease of synthesis [20–23]. The author has dared to design spirobenzopyrans modified at the 8-position of its benzopyran part, **1** ($n=1$–3), to attain effective cation-complexing control induced by photoisomerization of its spiropyran moiety [24,25]. In other words, in the metal ion complexes of the merocyanine form of **1** ($n=1$–3), its nitrophenolate anion can interact intramolecularly with a metal ion captured by its crown moiety due to the formation of a six-member-ring chelate by the oxy anion of the phenolate and the nitrogen atom of the crown ring. Photoisomerization of the crowned spirobenzopyrans can affect this intramolecular interaction, which in turn results in changes of their cation-complexing ability.

Cation extraction from an aqueous solution of an alkali metal picrate with a 1,2-dichloroethane solution of a crowned spirobenzopyran under dark conditions allows us to estimate cation-complexing abilities of the resulting crowned spirobenzopyrans, **1** ($n=1$–3) [25]. As model compounds of the crowned spirobenzopyrans **1** ($n=1$–3), their corresponding *N*-benzyl monoazacrown ethers were also employed for comparison on the cation extraction. The cation extractabilities for **1** ($n=1$–3) reflect the cation-complexing abilities of their parent crown ethers, i.e. *N*-benzyl-monoaza-12-crown-4, -15-crown-5, and -18-crown-6 (Fig. 1). The order of extractability is $Li^+ > Na^+ > K^+ >$for **1** ($n=1$), $Na^+ > Li^+ > K^+$ for **1** ($n=2$), and $K^+ > Na^+ > Li^+$ for **1** ($n=3$). Thus, the cation-complexing abilities and extractabilities of crowned spirobenzopyrans originate essentially in those for their corresponding crown ether moieties. Extraction of Li^+ is, however, enhanced in all of the crowned spirobenzopyrans compared with their corresponding *N*-benzyl monoazacrown ethers.

The absorption spectrum for the organic phase containing a crowned spirobenzopyran showed a significant peak at 500–600 nm, which can be assigned to its

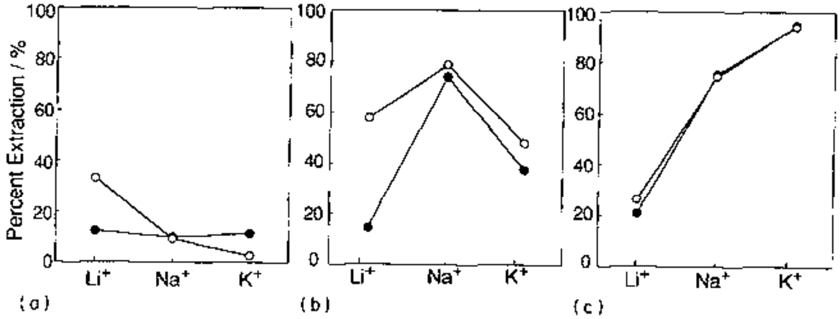


Fig. 1. Cation extraction by crowned spirobenzopyrans **1**($n=1$–3) and comparison with their corresponding model compounds, *N*-benzyl-monoazacrown ethers [25]. Under dark conditions. (a) for 12-crown-4 systems: **1** ($n=1$) (○);, *N*-benzyl-monoaza-12-crown-4 (●); (b) for 15-crown-5 systems: **1** ($n=2$) (○), *N*-benzyl-monoaza-15-crown-5 (●); (c) for 18-crown-6 systems: **1** ($n=3$) (○), *N*-benzyl-monoaza-18-crown-6 (●).

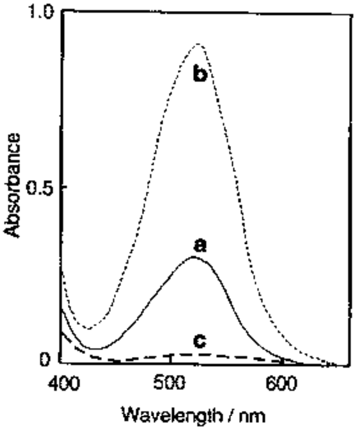


Fig. 2. Photoisomerization of crowned spirobenzopyran **1** ($n=1$) in THF in the presence of Li^+ [25]. [**1** ($n=1$)] and [$LiClO_4$]: 2×10^{-4} mol dm^{-3}, (a) under dark conditions; (b) UV-light irradiation; (c) visible-light irradiation.

corresponding merocyanine isomer, indicating isomerization induced by the cation complexation of its crown moiety. Thus, cation complexation by the crown moiety makes the spirobenzopyran molecule more polar, promoting the formation of their corresponding merocyanine isomers.

Cation-complexation-induced isomerization of the crowned spirobenzopyrans also occurs when an alkali metal ion is added directly to an organic solution of a crowned spirobenzopyran under dark conditions, as shown in Fig. 2.

^{7}Li-NMR spectroscopy under dark conditions explains the distinct difference in the environment of the Li^+ between the metal ion complexes of spiropyran and merocyanine forms of the crowned spirobenzopyran **1** ($n=1$) (Fig. 3). When spirobenzopyran of 12-crown-4 **1** ($n=1$) was added to a $LiClO_4$ acetonitrile solution, a strong peak was observed at a higher frequency in addition to the peak assigned to crown-complexed Li^+. The high frequency peak in the crowned spirobenzopyran **1** system was not observed in a 1:1 mixture system of *N*-benzyl-monoaza-12-crown-4 and a spirobenzopyran not carrying any crown moiety. The ^{7}Li-NMR results, therefore, suggest that the crown-complexed Li^+ interacts intramolecularly with its phenolate anion in the Li^+-complexation-induced isomerization of crowned spirobenzopyran **1**, as demonstrated in Scheme 1. The intramolecular interaction is remarkable, especially in the merocyanine isomers of crowned spirobenzopyrans where the crown ring fits Li^+ very well.

Furthermore, UV-light irradiation on a tetrahydrofuran solution containing a 1:1 mixture of crowned spirobenzopyran **1** ($n=1$) and $LiClO_4$ enhances the isomerization from the spiropyran to merocyanine forms (Fig. 2). On the contrary, visible-light irradiation brings about isomerization back to the spiropyran form. The isomerization of crowned spirobenzopyrans is quite reversible even in the presence of Li^+. Visible-light irradiation of an acetonitrile solution containing **1** ($n=1$) and $LiClO_4$ increases the high frequency peak in the ^{7}Li-NMR spectrum while decreasing the

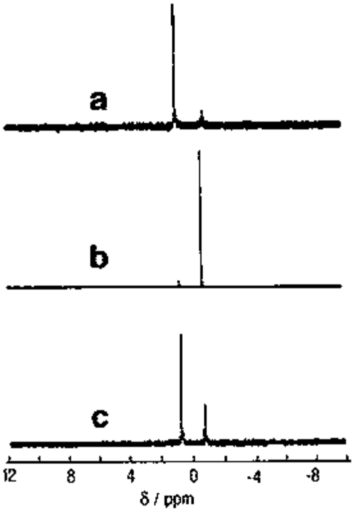
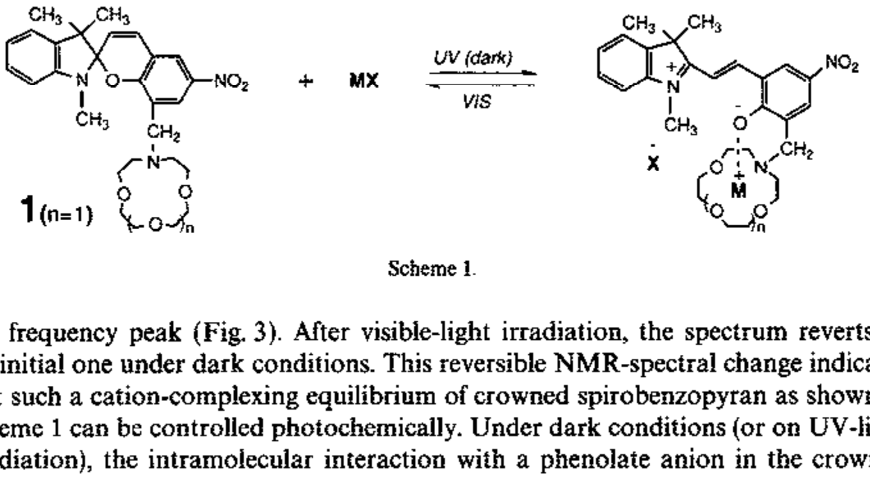


Fig. 3. ^{7}Li-NMR spectral changes for $LiClO_4$ acetonitrile solution in the presence of crowned spirobenzopyrans 1 ($n=1$) under dark and photoirradiated conditions[25]. 2×10^{-2} mol dm^{-3} $LiClO_4$ and 1.6×10^{-2} mol dm^{-3} 1 ($n=1$) in CH_3CN–CD_3CN(7/3): (a) under dark conditions; (b) on visible-light irradiation; (c) on UV-light irradiation.



Scheme 1.

low frequency peak (Fig. 3). After visible-light irradiation, the spectrum reverts to the initial one under dark conditions. This reversible NMR-spectral change indicates that such a cation-complexing equilibrium of crowned spirobenzopyran as shown in Scheme 1 can be controlled photochemically. Under dark conditions (or on UV-light irradiation), the intramolecular interaction with a phenolate anion in the crowned merocyanine promotes Li^+ complexation by an additional-binding-site effect such as with the 'lariat ether effect' [26] and the 'chelate effect' [27]. Visible-light irradiation, however, induces the isomerization to the spiropyran form and thereby attenuates the additional-binding-site effect, thus decreasing the Li^+-complexing ability.

2.1.2. Crowned spironaphthoxazine

Crowned spironaphthoxazine **2** shows similar behavior to the corresponding spirobenzopyran in cation-induced isomerization [28]. Equimolar addition of an alkali metal perchlorate to an acetonitrile solution of crowned spironaphthoxazine **2** causes

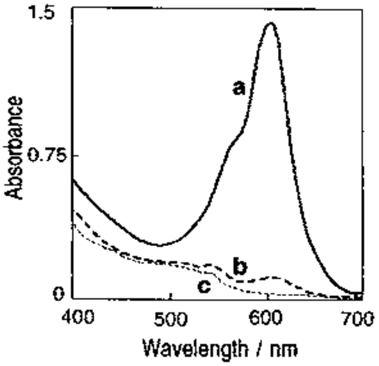
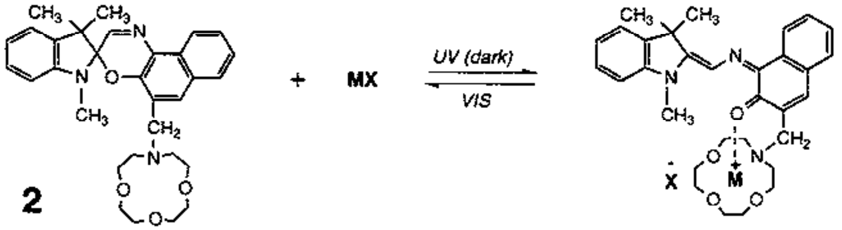


Fig. 4. Absorption-spectral changes of crowned spironaphthoxazine acetonitrile solutions on addition of alkali metal salts under dark conditions [28]. [**2**] and [$MClO_4$], each 4×10^{-4} mol dm^{-3}: (a) Li^+; (b) Na^+; (c) K^+.

significant spectral changes (Fig. 4). Specifically on Li^+ addition, a strong absorption peak appears at 615 nm, which can be assigned to the open form of crowned spironaphthoxazine. Na^+ brings about a small change in the absorption spectrum, but K^+ hardly has any effect on the visible spectrum of the crowned spironaphthoxazine solution. An acetonitrile solution of an uncrowned spironaphthoxazine does not show any significant absorption spectrum change following the alkali metal ion addition under identical conditions. This indicates that the isomerization of **2** to its open colored form is induced by cation complexation of its crown ether moiety, as is the case with the crowned spirobenzopyrans. Also, the effective intramolecular interaction between the oxo group and crown-complexed metal ion in the metal ion complex of the open form of the crowned spironaphthoxazine **2** (Scheme 2) appears to contribute considerably to this cation-induced isomerization. This means that the position into which the crown moiety is incorporated is quite crucial for effective intramolecular interaction. Any significant cation-induced enhancement in the isomerization of the spironaphthoxazine moiety to its open form was not found in a spironaphthoxazine derivative carrying a benzocrown ether moiety at the 9′-position, which is relatively remote from the oxo group [29]. Photoisomerization of the crowned spironaphthoxazine **2** proceeds reversibly even in the presence of Li^+. The subsequent thermal decoloration of the crowned spironaphthoxazine in acetonitrile,



Scheme 2.

in the presence of an alkali metal perchlorate, allows us to elucidate the cation-binding effect on the thermal stability of the crowned spironaphthoxazine open form. Li^+ complexation remarkably stabilizes the open colored form of the crowned spironaphthoxazine, the thermal decoloration rate constant of which (5.3×10^{-4} s^{-1}) is decreased by two orders of magnitude in the presence of equimolar Li^+ compared with that in the absence of any metal ion (3.0×10^{-2} s^{-1}). Na^+ addition also decreases the rate constant by about an order of magnitude (6.0×10^{-3} s^{-1}), but K^+ hardly changes the rate constant (2.1×10^{-2} s^{-1}). The Li^+ selectivity for the thermal stability enhancement of the open colored form of **1** is as anticipated from that for the cation-complexation-induced isomerization under dark conditions. The thermal stability enhancement of the open colored form of **2** by Li^+ addition is derived from the intramolecular interaction between the oxo group and Li^+, combined with the selective cation binding of its crown moiety. Interestingly, the thermal stability of the open colored form of **2** can be regulated by the added Li^+ concentration. In most of the well-known spironaphthoxazine derivatives, their open colored forms are not very thermally stable; their open colored forms isomerize back to their corresponding closed forms immediately after turning off the UV light [19,30]. Thus, the crowned spironaphthoxazine–Li^+ system has a large advantage over conventional spironaphthoxazines for practical applications as a photochromic compound [31].

The photoirradiation of crowned spironaphthoxazine in the presence of Li^+ can alter the complexation equilibrium established between **2** and Li^+ under dark conditions. When UV light enhances the isomerization of **2** to the corresponding open form, the participation of its oxo group as an additional binding site augments its cation-binding ability, as also illustrated in Scheme 2. The intramolecular interaction was supported by ^{7}Li-NMR spectroscopy of a mixed system of **2** and $LiClO_4$ under dark and photoirradiated conditions.

2.1.3. *Crowned Malachite Green*

Many triphenylmethane dyes such as Malachite Green exhibit photochromism accompanying heterolytic bond cleavage, thus undergoing photoionization [19]. For instance, UV light causes isomerization of Malachite Green leuconitrile to its corresponding triphenylmethyl cation (and quinoid cation) and cyanide anion, which then revert to the initial electrically-neutral molecule by heating in the dark. In a Malachite Green leuconitrile carrying a crown ether moiety **3**, photochromism of its Malachite Green moiety between the electrically neutral and ionic forms can affect cation complexation of its crown ether moiety [32]. Potentiometry using a Na^+-selective glass electrode supports the cation-complexation equilibrium changes of the crowned Malachite Green leuconitrile induced by its photochromism. Under dark conditions, the crown ether moiety of **3** can complex Na^+ even in an aqueous MeOH solution. UV-light irradiation of the **3** solution raises the electrode potential (Fig. 5). This means that photoionization of crowned Malachite Green leuconitrile **3** to its corresponding cation releases Na^+ from its crown ether moiety due to the intramolecular electrostatic repulsion between the resulting two cations (Scheme 3). The subsequent heating of the solution under dark conditions, which causes a thermal

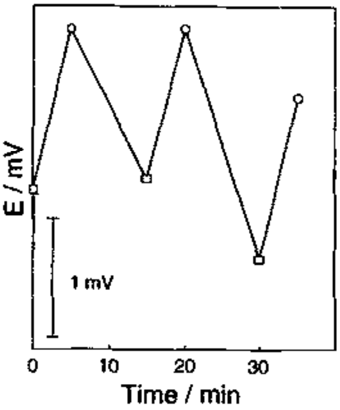
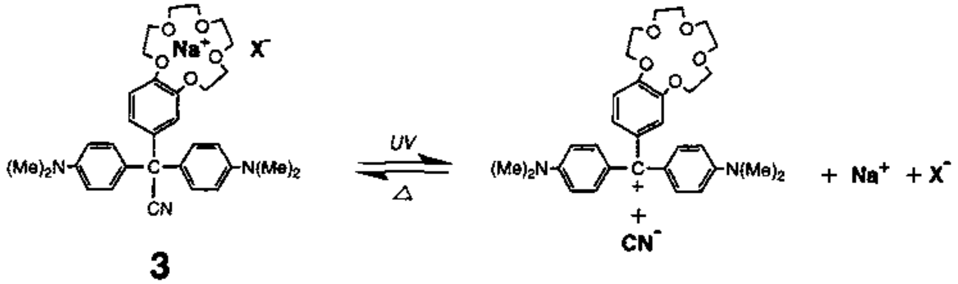


Fig. 5. Cation-binding switching of crowned Malachite Green leuconitrile 3 by alternating UV-light irradiation and heating [32]. Photoirradiation started at each point of □ and then finished at the point of ○, and vice versa for heating in the dark.



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Scheme 3.

back reaction from the ionic to electrically-neutral molecules, promotes cation binding by the crown ether moiety owing to the disappearance of the inter-cationic interaction. On the contrary, hardly any potential change can be found on photoirradiation in the system of an uncrowned Malachite Green. Molecular orbital calculations of crowned Malachite Green 3 and its quinoid cation by the MNDO–PM3 method [33] show that the crown ether oxygen atoms, especially in the aromatic oxygen atoms for the electrically-neutral derivative 3, generally have lower negative point charges than those of its corresponding quinoid cation. Photochemical control of the cation-complexing ability in the crowned Malachite Green 3 can therefore be attributed to the changes in the electric charges of crown ether oxygen atoms between the electrically-neutral species and its cationic species as well as the intramolecular electrostatic repulsion.

2.2. Applications to photoinduced switching of ionic conductivity

The photocontrol of ionic conductivity in ion-conducting composite films can be realized, taking advantage of the photochemical control of cation complexation mentioned above. Crowned spirobenzopyran **1** ($n=1$) was applied to an ion-conducting system consisting of poly(vinyl chloride) (PVC), 2-ethylhexyl sebacate (DOS) and $LiClO_4$ [34,35]. Absorption spectra showed that crowned spirobenzopyran **1** ($n=1$) isomerizes substantially to its corresponding merocyanine, form even under dark conditions, in the ion-conducting composite film of the PVC–DOS–$LiClO_4$–**1** system. Visible-light irradiation promotes isomerization to its spiropyran form, decreasing the absorption at 510 nm. UV light, then, allows significant isomerization back to the merocyanine form. Therefore, the photoisomerization of the crowned spirobenzopyran is quite reversible in the composite film. The ionic-conductivity photoresponse for the PVC-based ion-conducting composite film on alternate irradiation of visible and UV light was synchronized with the photoisomerization of the crowned spirobenzopyran, as expected. Conceivably, the merocyanine isomer of **1**, which strongly binds Li^+ due to the formation of an intramolecularly phenolate-interacting Li^+ complex, retards Li^+ conduction in the film, as illustrated in Scheme 1. Visible-light-induced isomerization to the corresponding spiropyran form releases some Li^+, thus promoting Li^+ conduction. However, since not only Li^+ but also its counteranion takes part in ion conduction in the bi-ionic conducting system of PVC–DOS–$LiClO_4$–**1** ($n=1$) films, the contribution of the photoinduced cation-complexing control to the ionic-conductivity change might be compensated for by that of the counteranion conduction.

In a single-ionic conducting system containing crowned spirobenzopyran **1** ($n=1$), where only a cation participates in ion conduction, the ionic conductivity can be switched more remarkably by photoirradiation. Fig. 6 demonstrates a typical photoresponse of ionic conductivity for lithium poly(perfluorosulfonate) (PPFS-Li^+)–oligooxyethylene diacetate (OOEAc)–**1** ($n=1$) composite films while turning visible light on and off and being heated under dark conditions. The magnitude of the photoinduced ionic-conductivity switching for the PPFS-Li^+–OOEAc–**1** composite film (twentyfold) is much greater than that of the previously mentioned

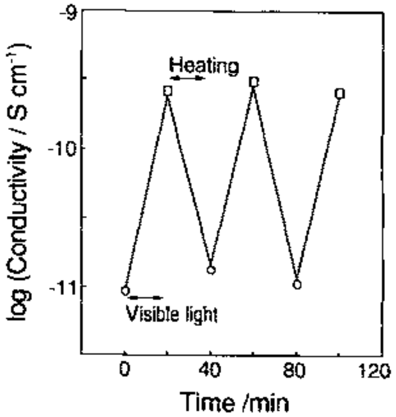


Fig. 6. Photoinduced ionic-conductivity changes in composite film of PPFS-Li^+–OOEAc–1 ($n=1$) on turning visible light on and off while being heated at 70°C under dark conditions [35].

bi-ionic conducting system, i.e. the PVC–DOS–$LiClO_4$–**1** composite film (twofold). Obviously, the cation-binding control based on the mechanism in Scheme 1 contributes much more efficiently to the photoinduced switching of ionic conductivity in the single-ionic conducting system than in the bi-ionic system.

Isothermal transient ionic current measurements offer useful information about the significant photoinduced change in ionic conductivity of the PPFS-Li^+–OOEAc–**1** composite film (Fig. 7). The ionic current peaks in the curves are definitely derived from Li^+ conduction in the single-ionic conducting composite film. The current peak appears at an earlier stage under visible-light-irradiated conditions than under dark conditions. This is indicative of a higher Li^+ mobility under visible-light-irradiated (i.e. the spiropyran-rich) conditions than under dark (i.e. the merocyanine-rich) conditions. The drift mobility μ of Li^+ in the composite film, which can be calculated from the transient time, is 2.8×10^{-11} cm^2 s^{-1} V^{-1} under dark conditions. The mobility is increased by tenfold on visible-light irradiation. Turning off the visible light restores the ion mobility almost to the initial value. Ionic conductivity σ is generally defined by the equation $\sigma = qn\mu$, where q, n, and μ denote ionic charge, carrier density, and ion mobility respectively. The ionic conductivity is about twenty-fold greater under visible-light-irradiated conditions than under dark conditions, while the ion mobility is about tenfold greater in the former than in the latter. The results suggest that the photoinduced ionic-conductivity change for the composite film of PPFS-Li^+–OOEAc–**1** ($n=1$) is ascribed to the change in the Li^+ mobility rather than in the carrier density.

Spironaphthoxazine derivatives undergo a similar photoisomerization to the spirobenzopyran derivatives; their closed forms isomerize to the corresponding open colored forms on UV-light irradiation, and vice versa on visible-light irradiation or heating [19]. Spironaphthoxazine derivatives, which generally show excellent light-fatigue resistance [30,36], are expected to be more reliable and durable photochromic material than their corresponding spirobenzopyran derivatives. Marked photochemical switching of ionic conductivity can also be realized with both of the PVC– and PPFS-Li^+-based composite films containing crowned spironaphthoxazine **2** [28]. By visible-light irradiation, Li^+, the ionic carrier in films, tends to be released from

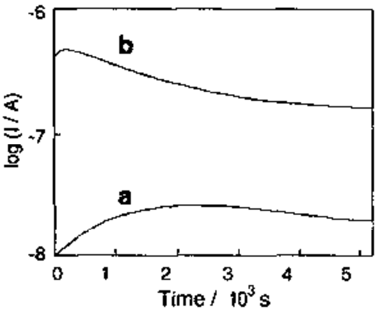


Fig. 7. Isothermal transient ionic currents for composite film of PPFS-Li^+–OOEAc–**1** ($n=1$) [35]: (a) under dark conditions; (b) under visible-light-irradiated conditions.

the crowned spironaphthoxazine molecules. The ionic conductivity of the composite film is thus increased as anticipated from Scheme 2. The subsequent UV-light irradiation allows the open colored form of crowned spironaphthoxazine to bind Li^+ strongly, therefore decreasing the ionic conductivity.

It should be noted that the photochemical ionic-conductivity switching in the composite films containing crowned spironaphthoxazine **2** is excellently reversible and reproducible, as demonstrated in Fig. 8. Even after a 30-cycle irradiation of UV and visible light, the magnitude of the ionic-conductivity change was almost constant in the PPFS-Li^+-based composite films. In similar composite films containing a crowned spirobenzopyran instead of the crowned spironaphthoxazine [35], some light fatigue or deterioration was observed after several photoirradiation cycles; the magnitude of the photochemical ionic-conductivity change decreased. The high durability of the photochemical ionic-conductivity switching system containing crowned spironaphthoxazine **2** as the key compound is definitely ascribable to the excellent light-fatigue resistance of the spironaphthoxazine derivative.

Photoinduced switching of ionic conductivity was also attempted in PVC- and PPFS-Na^+-based composite films containing crowned Malachite Green **3**. The photoionization of the Malachite Green leuconitrile moiety of **3** causes generation of two ion-conducting carriers, i.e. a cyanide anion and a triphenyl or quinoid cation, which themselves in turn raise the ionic conductivity of the composite films. In the photochromism of crowned Malachite Green in the presence of a crown-complexable metal ion, Na^+, as shown in Scheme 3, photoionization brings about release of Na^+ complexed by the crown moiety of **3**. The resulting free Na^+ is also able to participate in ionic conduction. In other words, the photoionization of Na^+-complexed crowned Malachite Green **3** results in synergistic generation of ion-conducting carriers. The ion-conducting system of the crowned Malachite Green, therefore, exhibits remarkable photoinduced changes in the ionic conductivity, i.e. the ionic conductivity is increased by UV-light irradiation and vice versa by heating without photoirradiation.

Other photochromic crown ethers that can control their cation-binding abilities

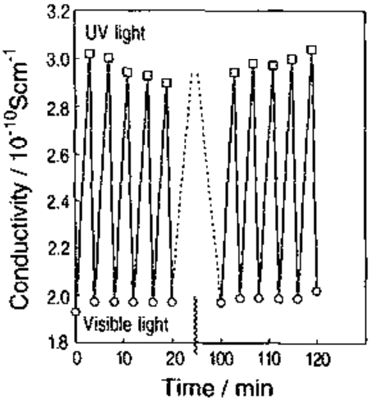


Fig. 8. Photoinduced ionic-conductivity changes for single-ionic conducting composite film of PPFS-Li^+-crowned spironaphthoxazine **2** [28].

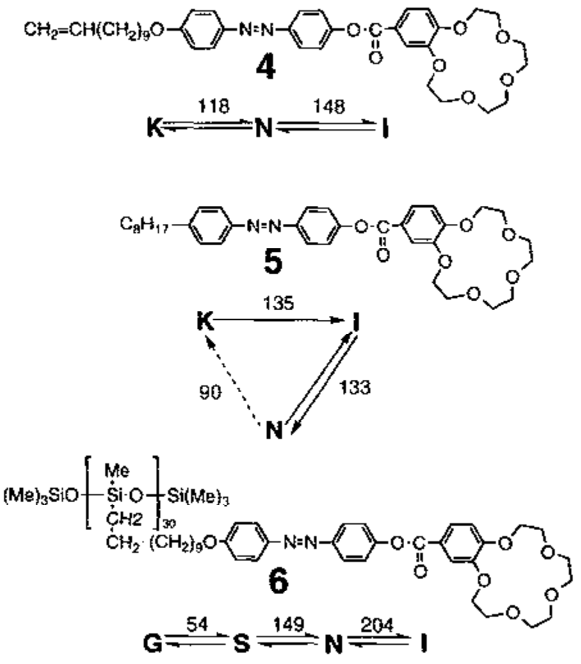
by photoisomerization of their photochromic moieties are also candidates for key materials of photoinduced ionic-conductivity switching. The examples are in anthraceno crown ethers where two anthracene nuclei are incorporated into a monocyclic crown ring [37] and azobenzene bis(crown ether)s where two crown rings are connected by an azobenzene unit [38]. Further examples for photochromic crown ethers with potentially ionic groups are merocyanine azacrown ethers which undergo photoejection of metal cations [39] and styryl dye crown ethers in which additional binding by an ionic site is feasible on their photoisomerization [40].

3. Photochemical control of ionic conduction based on phase transition and molecular orientation

3.1. *Effective photocontrol based on phase transition*

The isomerization of azobenzene derivatives from their trans to cis forms is caused by UV-light irradiation and vice versa by visible-light irradiation or heating. Azobenzene isomers of cis and trans forms often experience different thermal phase transition. If the isomers of an azobenzene derivative show different phases at a constant temperature, the photoisomerization of the azobenzene causes a distinct phase transition at the temperature. Such a photoinduced phase transition of the azobenzene liquid crystals allows designing of photoresponsive ion-conducting composite films containing an azobenzene liquid crystal [13,15]. Crown ethers, on the contrary, can be expected to play an important role in ionic conduction, since they complex alkali metal ions to form separated ion-pairs. Therefore, combination of a crown ether moiety for the cation-binding part with an azobenzene moiety for the photochromic part affords efficient photoinduced switching of ionic conductivity in ion-conducting composite films containing a crowned azobenzene. That is to say, the crowned azobenzene derivatives contain both a crown moiety facilitating the formation of ion-conducting carriers and an azobenzene moiety forming a domain for the photoinduced phase transition. In that case, ion-conducting carriers are almost always in the domain participating in the change in photoinduced ionic-conductivity. Significant ionic-conductivity switching is, therefore, expected to occur in the crowned azobenzene system. On the contrary, for a system containing a 1:1 mixture of an azobenzene derivative without crown ether moiety and a crown ether, where crown-separated ions (the ion-conducting carrier) are not necessarily in the azobenzene domain, the photoinduced change in ionic-conductivity becomes less intensive.

Crowned azobenzene **4** undergoes a distinct phase transition from its crystal to isotropic liquid phases on UV-light irradiation at room temperature (Scheme 4) [41]. The photoinduced phase transition is indicated by differential scanning calorimetry (DSC) of **4** under photoirradiated conditions, i.e. a broad endothermic peak in the temperature range from room temperature to 100 °C is seen for the photochemical DSC thermogram (Fig. 9). The UV-light-induced phase transition of crowned azobenzene **4** from its solid to liquid states in composite films of polyester–$LiClO_4$–**4**



G: glass, K: crystalline, S: smectic, N: nematic,
I: isotropic. The temperatures are shown in °C.

Scheme 4.

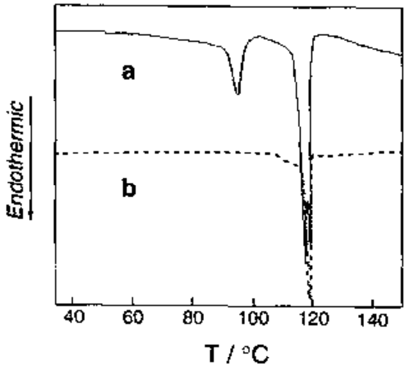


Fig. 9. Photochemical DSC thermogram of **4** and a comparison with dark conditions [41]: (a) while irradiating UV light; (b) under dark conditions.

raises the mobility and/or density of the ion-conducting carriers in the composite film, and thereby enhances the ionic conductivity. The subsequent visible-light irradiation restores the ionic conductivity to the initial value by isomerization of the crowned azobenzene back to its crystal phase.

A similar crowned azobenzene **5** is a monotropic liquid crystalline compound, exhibiting a nematic liquid crystal phase only on decreasing temperature (Scheme 4) [42]. In composite films of polycarbonate–$LiClO_4$–**5**, the ionic conductivity is too low to measure up to 120 °C in the temperature-ascending process due to the low mobility of ion-conducting carrier in the crystal phase of the crowned azobenzene and is increased over 130 °C by the phase transition of **5** to its isotropic liquid phase. In the temperature-descending process, the ionic conductivity is still high down to 90 °C, since the nematic phase still affords good ionic conduction. The ionic conductivity is abruptly diminished around 90 °C due to the phase transition of the crowned azobenzene from nematic liquid crystal to crystal phase. Thus the composite films containing the monotropic liquid crystal possess thermally-bistable ionic conductivity, the difference of which is by more than three orders of magnitude, in the temperature range 90–120 °C. This thermal bistability as well as the photoinduced switching of ionic conductivity is attractive for device applications.

3.2. Photoisomerization-induced changes of molecular orientation

Ion carriers such as crown ethers, when arranged in a highly ordered orientation, are expected to form ion channels that are very similar to efficient ion-transporting channels in biological systems. Several attempts have been made to construct ion-channel models by designing stereoregular polymers or oligomers carrying a crown ether moiety [43,44] and other stacked crown compounds [45,46]. The liquid crystal formation of crown ether derivatives may be another way to make ion-channel mimics. Specifically, highly-oriented liquid crystals carrying a crown ether moiety such as smectic and cholesteric liquid crystals are more likely to realize close stacking of the crown ether moiety.

3.2.1. Crowned azobenzene polymer

Crowned azobenzene polymer **6** can form a smectic liquid crystal phase by the cooperative action of its adjacent crowned azobenzene moiety (Scheme 4) [47]. It is probable that the crown ether moiety of the crowned azobenzene polymer **6** is arranged in the ordered orientation in its smectic phase. Composite films of polyester–$LiClO_4$–crowned azobenzene polymer **6** exhibit intriguing behavior in the photoinduced switching of ionic conductivity. The composite films containing crowned azobenzene polymer **6** and $LiClO_4$ can undergo a marked photochemical switching of their ionic conductivity (Fig. 10). UV-light irradiation decreases the ionic conductivity of the composite films and the subsequent visible-light irradiation increases it to the initial value. Such significant photoinduced changes of ionic conductivity can be seen with high reversibility in the temperature range from 40 to 100 °C. Most interestingly, the tendency in the present crowned azobenzene polymer system is the opposite to that in the photochemical ionic-conductivity switching system of the corresponding crowned azobenzene derivative **4**. A plausible mechanism for the photoinduced ionic-conductivity switching in composite films containing the crowned azobenzene polymer **6** and $LiClO_4$ is as follows. In the smectic liquid crystal state of the crowned azobenzene polymer in the composite film, under dark conditions,

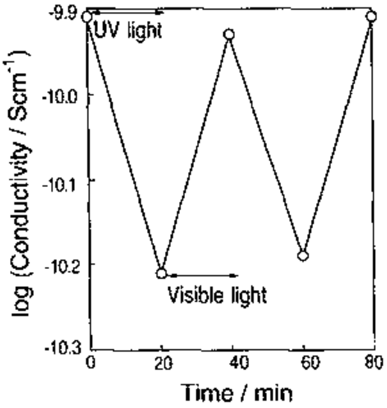
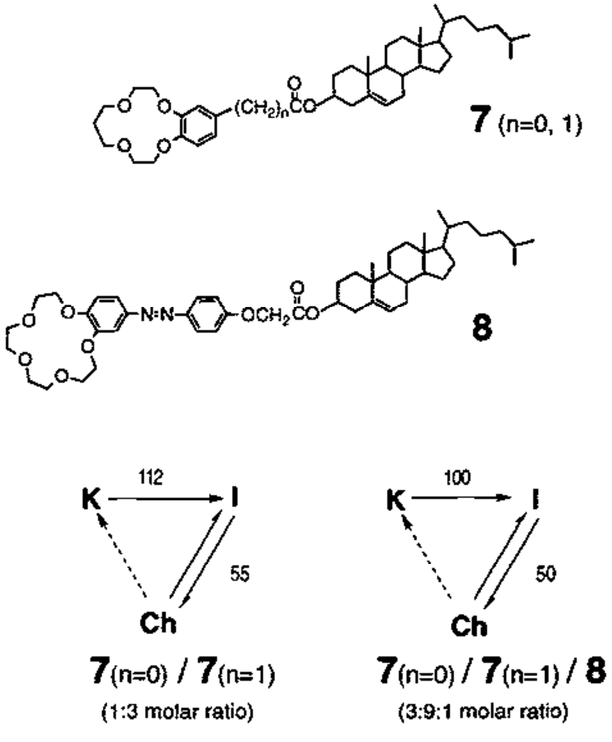


Fig. 10. Photoinduced switching of ionic conductivity for **6**-containing composite film at 60°C [47]. Each point indicates ionic conductivity of saturated level after 20 min photoirradiation.

its adjacent crown moieties at the end of the azobenzene side chain tend to get close to one another due to their highly ordered orientation. As a result, ion-conducting carriers easily migrate on crown ether-based hopping sites, which are the crown moieties themselves for cations and the crown-complexed cations for anions. Photochemical DSC suggests that the UV-light-induced isomerization of the azobenzene moiety decreases the smectic property due to the formation of bulky *cis*-azobenzene moiety, thus resulting in orientation disorder of the side chains. In that case, the adjacent crown moieties are more distant from one another than in the highly-oriented state under dark conditions. The ion-conducting carriers, therefore, cannot so readily hop on the crown moieties under UV-light-irradiated conditions as under dark conditions. The photoisomerization-induced disorder in the highly-oriented smectic state of the crowned azobenzene polymer diminishes the ionic conductivity of the ion-conducting composite films. Such disorder in the smectic state is recovered by visible-light-induced isomerization of the azobenzene moiety back to its trans form and the ionic conductivity is then restored to the initial value.

3.2.2. Crowned cholesterol

Cholesteric liquid-crystalline crown ethers can be employed for mimicking ion channels. Cholesterol derivatives incorporating a crown ether moiety, **7** ($n=0$) and **7**($n=1$), are capable of forming cholesteric liquid crystal phases in mixtures of appropriate molar ratios [48]. Polymeric membranes containing the crowned cholesterol mixtures can undergo efficient ion transport, which resembles more or less that of ion channels in biological cell membranes. In ion-conducting polyester-based composite films containing the crowned cholesterols, therefore, specific ionic conduction can be expected under their cholesteric liquid crystal conditions [49]. A 1:3 mixture of crowned cholesterols **7** ($n=0$) and **7** ($n=1$) shows a monotropic liquid crystal phase transition as shown in Scheme 5 and the mixture is in the cholesteric liquid crystal state below 55°C, even at room temperature, after heating up to the phase transition temperature from crystal to isotropic states. In ion-conducting composite films consisting of a polyester elastomer, the **7** ($n=0$)–**7** ($n=1$) mixture, and $LiClO_4$, the activation energy for ionic conduction changes significantly at around 60 °C; this is very close to the phase transition temperature of the crowned cholesterol mixture from its cholesteric to isotropic states, i.e. the activation energy for ionic conduction in the cholesteric state is lower than that in the isotropic state. If the ionic conduction in the composite film is based primarily on a free diffusion mechanism, the activation energy for the ionic conduction should be lower in the isotropic state than in the cholesteric state. This reverse in the activation energy suggests facilitated ion migration in the cholesteric state compared with the isotropic state, implying that the crown-ether-ring orientation induced by the cholesteric liquid crystal formation promotes ion migration among the crown ether rings. In the composite films containing $KClO_4$ as the ionic species, however, ionic conduction in the cholesteric state possesses a higher activation energy than in the isotropic



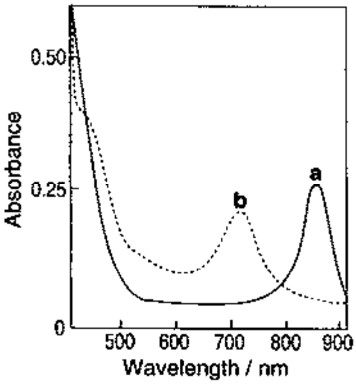
K: crystalline, Ch: cholesteric, I: isotropic.
The temperatures are shown in °C.

Scheme 5.

state. Thus cation complexation by the crown moiety of crowned cholesterols seems to be essential for effective ionic conduction in the cholesteric state.

A mixture (1:3) of crowned cholesterols **7** ($n=0$) and **7** ($n=1$) containing a small quantity of an azobenzene derivative **8** shows a phase transition behavior similar to the original mixture of **7** ($n=0$) and **7** ($n=1$), as also illustrated in Scheme 5. UV-light irradiation on composite films containing a crowned cholesterol mixture of **7** ($n=0$)–**7** ($n=1$)–**8** and $LiClO_4$ decreases the ionic conductivity, and the subsequent visible-light irradiation again increases the ionic conductivity almost to the initial value. The photoinduced absorption-spectral change in a thin film consisting of **7** ($n=0$), **7** ($n=1$), **8**, and cholesteryl chloride **9** indicates that the helical pitch length of the cholesteric liquid crystal is decreased by the UV-light-induced isomerization of the azobenzene moiety from its trans to cis forms, and is then restored by the back isomerization (Fig. 11). Conceivably, such change in helical-pitch of the cholesteric state also occurs in the mixed system of **7** ($n=0$)–**7** ($n=1$)–**8**. The photoisomerization of the azobenzene moiety of **8** from its trans to cis form allows the **8** molecule to be bent and thereby be more bulky, which in turn augments the twist angle for the cholesteric liquid crystal [50]. The increase in the twist-angle possibly enlarges the distance between its adjacent crown ether rings in the cholesteric liquid crystal. Thus ionic conduction by hopping on the crown moiety or cation-complexed crown moiety is suppressed by the distance extension between the adjacent crown moieties. The subsequent visible-light irradiation again decreases the twist-angle for the cholesteric liquid crystal and thereby facilitates ion hopping on the adjacent crown ether moieties.

Specific ionic conduction was also observed in composite films consisting of polyester, crowned azobenzene **10**, and $LiClO_4$ (or $NaClO_4$), i.e. cation and anion



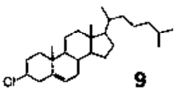


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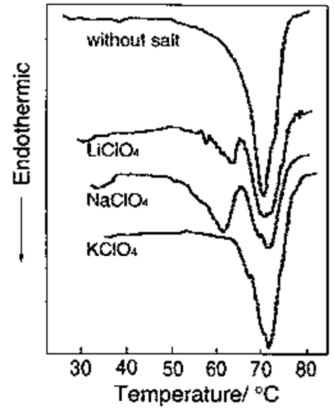
Fig. 11. Absorption-spectral changes of thin films consisting of crowned cholesterols **7** ($n=0$), **7** ($n=1$), and **8**, and cholesteryl chloride **9** on photoirradiation [49]: (a) in the dark or after visible-light irradiation; (b) after UV-light irradiation.

conduction predominate in the $LiClO_4$ and $NaClO_4$ systems respectively [51]. DSC studies indicate that the composite films without any alkali metal perchlorate and with $KClO_4$ possess a single endothermic peak at around 70 °C, which corresponds to the melting point of **10**, while the films containing $LiClO_4$ and $NaClO_4$ give another endothermic peak at around 60 °C in addition to the 70 °C peak (Fig. 12). Microscopic observation shows that significant domains, which actually melt around 60 °C, exist in both of the $LiClO_4$ and $NaClO_4$ systems. Increasing the content of $LiClO_4$ or $NaClO_4$ in the composite films, intensifies the 60 °C peak in the DSC thermogram. This implies that complexation of the crowned azobenzene **10** with $LiClO_4$ and $NaClO_4$ is responsible for domain formation in the composite films. The cation complexation of **10** in the composite films is supported by the mass spectroscopy of extracts of composite films simultaneously containing the three alkali metal perchlorates. The relative peak intensities for the complex cations confirm the cation-complexing selectivity of crowned azobenzene **10**, i.e. $Na^+ > Li^+ > K^+$. Nevertheless, the domains in composite films containing **10** and $NaClO_4$ (or $LiClO_4$), do not seem to consist of 1:1 **10**–M^+ ($M = Li$, Na) complexes. Composite films of polyester and the **10**–$NaClO_4$ (1:1) complex, which melts at around 120 °C, however, do not have any 60 °C peak for the domains but do have a weak 70 °C peak for the crowned azobenzene itself. Possibly, the domains in composite films containing **10** and $NaClO_4$ (or $LiClO_4$) consist of a crown-complexation-induced aggregate of the crowned azobenzene. In X-ray diffraction photographs of the domains in a composite film **10** and $NaClO_4$, the Debye–Scherrer rings have non-uniform diffraction intensities with Bragg spacings of about 4 and 7 Å. Such non-uniformity in the X-ray diffraction was only found in the 'domains' of the composite film which can undergo the photoinduced phase transition. The non-uniform diffraction suggests that the



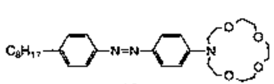


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Fig. 12. DSC thermograms for composite films of polyester-crowned azobenzene **10**–$MClO_4$ [51].

domains form ordered structures. The Bragg spacings of 4 Å and 7 Å may be derived from the ordered aggregation of the long alkyl chains and the crown moieties of crowned azobenzene **10** respectively. The domain formation might explain the predominant cation and anion conduction in the **10**-containing composite films with $LiClO_4$ and $NaClO_4$ respectively. Li^+ easily migrates through the crowned azobenzene aggregate in the **10**–$LiClO_4$ system. In the **10**–$NaClO_4$ system, however, Na^+ is bound so powerfully by the crown moiety that the cation cannot migrate. Instead, the counteranion ClO_4^- is able to move efficiently along the cations fixed in the aggregate. Unfortunately, photoisomerization of crowned azobenzene **10** hardly proceeds in the composite films. So, photoinduced changes of ionic conductivity, based on significant changes in the ordered structure, could not be found in composite films of **10**.

Tubular or columnar mesophases possessing crown ether moieties such as azamacrocycles [52,53] and oligooxyethylenes [54] may be candidates for efficient ionic conductors mimicking ion channels. Their ionic conduction might be controlled photochemically by their corresponding photochromic compounds. Incorporation of a photochromic moiety into ion-conducting systems containing other ion channel mimics would also afford photoinduced switching of ionic conductivity.

4. Conclusions

This review has shown that photochromic crown ethers are quite promising key materials for photoresponsive ion-conducting systems, based on molecular control of cation complexation and transition of ion-conducting phases containing crown ether moieties, especially highly-oriented crown ether phases. Much more drastic photoinduced switching of ionic conductivity with a large difference in conductivity between the two states is possible by designing ion-conducting systems of photochromic crown ethers, especially ion channel mimics. Also, switching systems of ionic conductivity to higher levels of ionic conductivity might be desired in the future. Ion-conducting composite films containing photochromic crown compounds are useful for device applications for memory, display, and printing. One of the applications is in electrostatic image storage [55]. Other applications of photoresponsive ion-conducting materials might be in photo-writable electrochromic display and photorefractive imaging.

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