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Accounts

Molecular Design and Applications of Photochromic Crown Compounds —How Can We Manipulate Metal Ions Photochemically?—

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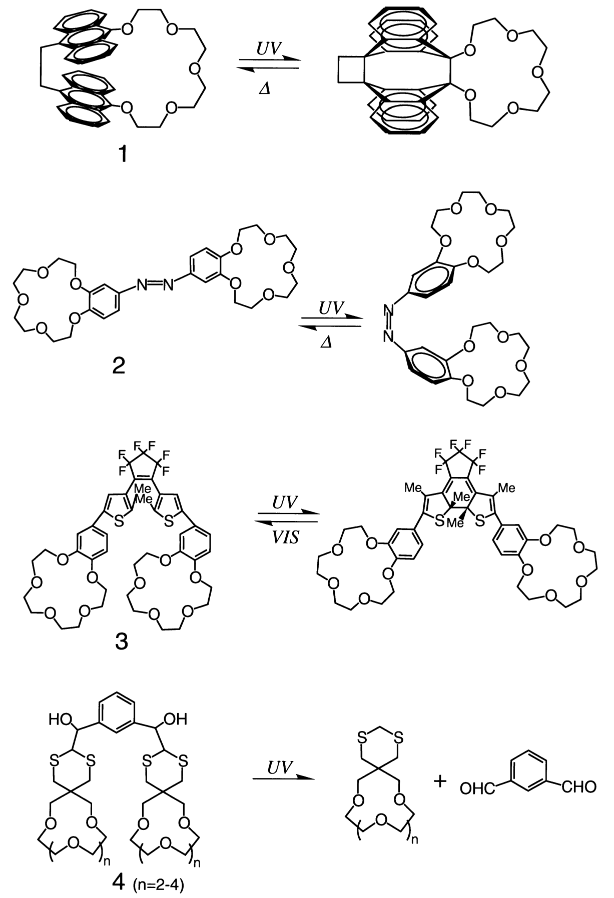
The design and applications of photochromic crown compounds are reviewed here. Such compounds exhibit the possibility of distinct photochemical control of metal-ion complexation, based on the ionic interactions of their photoionized photochromic moieties. Crowned spirobenzopyran derivatives which the authors designed, when isomerized to their corresponding merocyanine form by UV irradiation, can afford an additional binding site for a metal ion complexed by their crown ether moiety in a sophisticated way, i.e., by the six-membered chelate formation with the phenolate oxygen atom and the crown-ether-ring nitrogen atom. The crowned spirobenzopyrans, therefore, have their metal-ion complexing properties modified remarkably by photoirradiation, like the crowned spironaphthoxazines that are more photolabile than the spirobenzopyran derivatives. Crowned spirobenzothiopyrans possess an affinity to softer metal ions such as silver ion, which promotes their photoisomerization to the open form. Crowned bis(spirobenzopyran)s are highly selective for multivalent metal ions in the photochemical control of metal-ion complexation. Photochromic crown compounds such as crowned triphenylmethane dyes, when undergoing intermolecular photoionization, exhibit clear-cut photocontrol systems of metal-ion complexation, which are very attractive for applications, especially in materials chemistry. Polymerization of crowned spirobenzopyran and Malachite Green may make it easier to apply the photochromic crown compounds practically. Remarkable polymer effects also appear in the photochromic crown ether polymers; these include photoinduced switching between precipitation and solubilization in vinyl copolymers of spirobenzopyran and crown ether monomers. Several examples are described of the applications of photochromic crown compounds in materials and analytical chemistry, i.e., photo-responsive ionic conduction and photoenhanced ion sensing and separation.

Photochromism originally means photoinduced color changes of chemical compounds or their solutions based on their absorption-spectral changes. Photochromism of organic compounds is often accompanied by remarkable structural changes.[1] In this case, photochromism may provide photochromic compounds with special functions besides the color (absorption-spectral) changes.

Macrocyclic polyethers, so-called crown ethers, bind cations selectively in their cavities and are therefore useful tools for manipulation, analysis, and separation of cations such as alkali metal ions.[2,3] Incorporation of a crown ether moiety into a photochromic compound can be expected to provide the parent photochromic skeletons with high functionalities. For instance, in a crown ether containing two anthracene moieties in the ring, **1**,[4,5] the anthracene moieties dimerize intramolecularly by photoirradiation (Chart 1). The photoinduced dimerization diminished the cavity size of the crown ether moiety, in turn altering the cation-complexing property based on the size-fit concept. Heating in the dark after the dimerization causes the reverse reaction to the monomeric form and thereby restores the original cation-complexing property. The cation-complexing property of **1** can be thus controlled by repetitive cycles of photoirradiation and heating. An acyclic polyether (podand) carrying an anthracene moiety at both ends, when irradiated by UV light, is cyclized to a crown ether by intramolecular dimerization of the two anthracene moieties.[6] Since the original podand is different from the photoinduced crown ether in its cation-complexing ability, this also turns out to be a photocontrol reagent for cation complexation.

A bis(crown ether) bridging two crown ether rings by an azobenzene moiety, **2**, is also photoresponsive.[7–9] The trans form of azobenzene, which is thermally stable, isomerizes to the corresponding cis form by UV irradiation and vice versa by visible irradiation or heating. Bis(crown ether) derivatives are able to accommodate a cation with their two adjacent crown ether rings if they can assume a conformation suitable for the intramolecular cooperation of the crown ether rings.[10] In this case, bis(crown ether) derivatives show a selectivity for cations that are a little larger in size than the crown-ring cavity and are often superior to their corresponding monocyclic crown ethers



1

2

3

4 (n=2-4)

Chart 1.

in the cation selectivity.[11,12] Thus, the cis bis(crown ether), which can bind a cation by "bis(crown ether) effect", is different from the corresponding trans form in the cation selectivity.[13,14] Photoisomerization of the azobenzene moiety of **2**, therefore, changes its cation selectivity. The conformation of bis(crown ether) can be controlled between cis (parallel) and trans (anti-parallel) forms by photoisomerization of diarylethene moiety that is thermally irreversible and fatigue-resistant.[15–17] That is to say, the open-ring form of a bis(crown ether) bridged by a diarylethene moiety, **3**, captures large cations by bis(crown ether) effect, whereas the corresponding closed-ring form releases the cation.

Photoinduced bond scission is an interesting path to photochemical control of cation complexation of crown ether derivatives such as cryptand[18] and bis(crown ether)s.[19] For instance, photolysis of photolabile bis(crown ether) **4** in the presence of a photosensitizer destroys its bis(crown ether) structure to yield its monomeric analog. The bis(crown ether) can bind methyl viologen efficiently by cooperation of the two adjacent crown ether rings, but the photoinduced monomeric analog cannot do so. A problem in the photocontrol system is its irreversibility, i.e., the monomeric analog cannot be reverted to the initial bis(crown ether) by light or heat.

Photochromism accompanying ionization must bring about a much more remarkable effect than that with a simple structural change on the cation complexation of crown ether derivatives, based on the additional ionic interaction. Typical photochromic compounds undergoing intramolecular ionization are spirobenzopyran derivatives. Since spirobenzopyran derivatives photoisomerize reversibly from the electrically neutral spiropyran form to the corresponding zwitterionic merocyanine isomers, extensive studies have been devoted to their applications to photochemical control of physical properties in solutions. The examples are in photocontrol of membrane transports,[20] membrane potentials,[21–24] and polymer rheology.[25,26] On the other hand, many triphenylmethane dyes like Malachite Green exhibit photochromism accompanying heterolytic bond cleavage, thus undergoing *inter*molecular photoionization.[1] UV light causes photoionization of Malachite Green leuconitrile to its corresponding triphenylmethyl cation and cyanide anion, which are then reverted to the initial electrically neutral molecule by heating in the dark. The Malachite Green dyes have been receiving attention as an attractive tool for photocontrol of appearance and disappearance of ionic environments. Ionic conductivities can be regulated photochemically by using Malachite Green dyes in solution and polymer.[27–29] Photochemical control of polymer rheology is also feasible by using a Malachite green dye.[30] Polymeric membranes containing a Malachite Green moiety can modify membrane transport of anions by photoirradiation.[31]

Drastic photoinduced changes in cation-complexing property can be expected by incorporation of photoionizable photochromic moiety into crown ether derivatives. Spirobenzopyran derivatives carrying a crown ether moiety at the 1′-position, **5** and **6**,[32,33] were synthesized (Chart 2). In organic solutions of some of the crowned spirobenzopyrans, cation-induced isomerization was observed due to the occurrence of polar circumstance in the periphery of the spirobenzopyran skeleton by cation binding of the crown moiety.[32] In plasticized polymeric membranes containing crowned spirobenzopyran **6**, its photoinduced membrane potential change was found to depend on the kind of alkali metal ions in a measured solution, probably because of the cation-binding effect on the isomerization of its spirobenzopyran skeleton.[33] Nevertheless, the presence of a distinct photoinduced change of cation-complexing property was hard to observe in the previous crowned spirobenzopyrans.

The authors designed crowned spirobenzopyrans that can undergo efficient photocontrol of cation-complexing property based on ionic interaction.[34,35] Triphenylmethane dyes, such as Malachite Green, carrying crown ether moiety, so-called crowned triphenylmethane dyes (or crowned Malachite Green) were also synthesized;[36,37] some of theses can realize all-or-nothing-type photoinduced switching of cation-complexing property.[38,39] The authors thereafter continued to design crown ether derivatives incorporating plural spirobenzopyran moieties,[38,40] a spirobenzothiopyran moiety,[41] and crowned spirobenzopyran polymers.[42] Interesting properties of the photochromic compounds were discovered besides their photoresponsive cation-complexing property. The photochromic crown compounds were already applied to materials chemistry such as photoresponsive ion-conducting materials.[43] The authors are also making applications of the photochromic crown ethers to analytical chemistry.[44,45] The design of photochromic crown ethers, their photochemical control behavior, and their applications to materials and analytical chemistry are de-

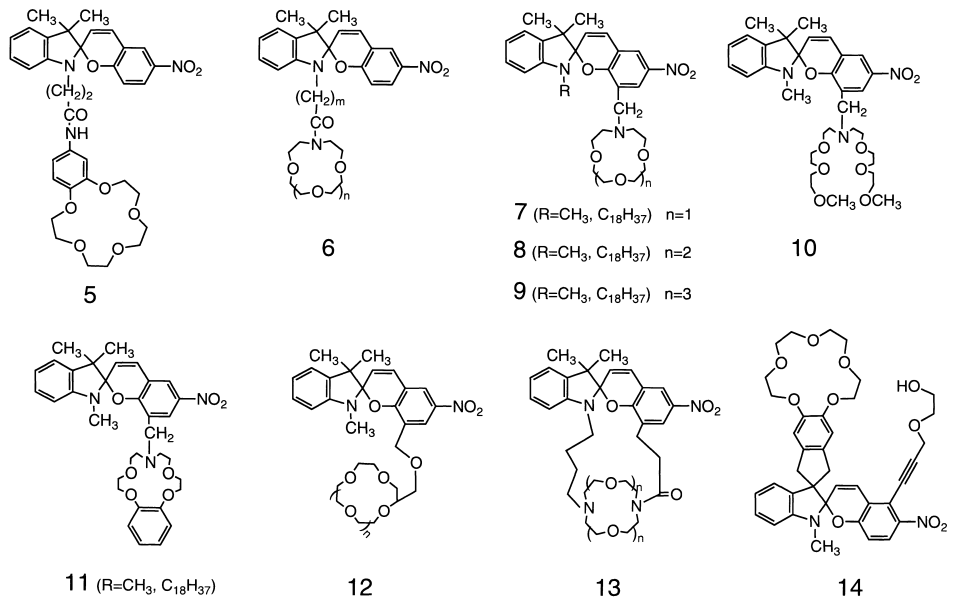


Chart 2.

scribed in this account.

1. Photochromic Crown Compounds Photoionizing Intramolecularly

Crowned Spirobenzopyran. In the previous spirobenzopyran derivatives possessing a crown ether moiety, such as **5** and **6**, the crown ether moiety was incorporated at the 1′(*N*)-position of spirobenzopyran skeleton, probably due to the synthetic convenience. A general synthetic procedure for spirobenzopyran derivatives is in the condensation reaction of an indolenine and a nitrosalicylaldehyde derivative. Each of the previous crowned spirobenzopyrans was obtained by the reaction of nitrosalicylaldehyde with an indolenine carrying a crown ether moiety at the 1-position that is easily accessible. It was, however, anticipated that efficient photochemical control of cation complexation might be realized with crowned spirobenzopyrans where a crown ether moiety is incorporated at the 8-position of the spirobenzopyran skeleton. This is because a phenolate anion in the metal-ion complex of the merocyanine form of crowned spirobenzopyran is most likely to interact axially with a cation captured by its crown ether moiety. Spirobenzopyran derivatives carrying a monoazacrown ether moiety at the 8-position, crowned spirobenzopyrans **7–10**, were thus designed.

Cation complexation-induced isomerization of the crowned spirobenzopyrans proceeds as illustrated by absorption spectra in Fig. 1, when an alkali metal ion is dissolved in an organic solution of a crowned spirobenzopyran under dark conditions. The absorption spectra for acetonitrile solutions containing an equimolar amount of a crowned spirobenzopyran and an alkali metal perchlorate showed significant peaks assigned to the merocyanine form of crowned spirobenzopyran between 500 and 550 nm. The addition effect of Li^+, a high-charge-density metal ion, on the isomerization of crowned spirobenzopyrans is remarkable, although the cation-complexing selectivities of the crown ether moieties themselves naturally contribute to the isomerization. Specifically in the **7**(R = CH_3) and **8**(R = CH_3) systems, Li^+ addition causes a pronounced absorption peak based on their corresponding merocyanine isomers. Even in the acyclic analog **10** system, Li^+ addition allows the isomerization to its merocyanine isomer more or less, while Na^+ and K^+ affect the isomerization only with great difficulty. Spirobenzopyran derivatives carrying a benzomonoaza-15-crown-5 moiety **11**[46] and an oxymethylcrown ether moiety **12**,[47] and cryptand spirobenzopyran **13**[48] show a similar behavior to **8** on the metal-ion addition. In the systems of spirobenzopyran derivatives containing a piperidinomethyl group and no substituent at the 8-position, however, no significant isomerization can be detected spectrophotometrically by the addition of an equimolar amount of alkali metal salt under dark

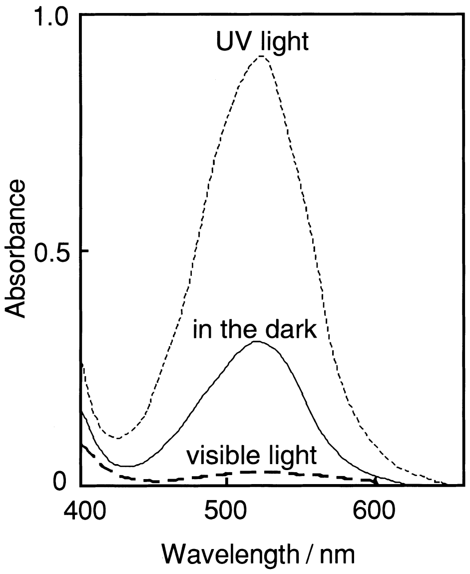


Fig. 1. Photoisomerization of crowned spirobenzopyran **7**(R = CH_3) in THF in the presence of Li^+.[35] [**7**(R = CH_3)] and [$LiClO_4$]: 2×10^{-4} mol dm^{-3}.

conditions.

The cation effect on the isomerization of crowned spirobenzopyrans to their merocyanine isomers under dark conditions can be explained by ^{7}Li-NMR spectroscopy (Fig. 2). An acetonitrile solution containing only $LiClO_4$ shows a peak assigned to Li^+ solvated simply by acetonitrile in the ^{7}Li-NMR spectrum (top). The peak is shifted continuously to higher frequencies by addition of *N*-benzylmonoaza-12-crown-4 due to the Li^+ complexation by the crown ether (middle). On addition of crowned spirobenzopyran **7**(R = CH_3) instead of the crown ether, another peak is observed at an even higher frequency besides the peak based on crown-ether-complexed Li^+ (bottom). The highest-frequency peak indicates that a powerful additional interaction with Li^+ complexed by a crown ether moiety occurs on the Li^+ binding of crowned spirobenzopyran, followed by isomerization to its merocyanine isomer. The ^{7}Li-NMR results, therefore, suggest strongly that the crown-complexed Li^+ interacts intramolecularly with its phenolate anion in the Li^+ complex of crowned spirobenzopyran **7**(R = CH_3), as demonstrated in Scheme 1. This intramolecular interaction is probably stabilized by the six-membered chelate formation of the crown-ether-ring-nitrogen and phenolate-oxygen atoms with Li^+. A tendency similar to that of the **7**(R = CH_3) system is seen in ^{7}Li-NMR spectra of crowned spirobenzopyran **8**(R = CH_3), suggesting the intramolecular interaction between a complexed Li^+ and a phenolate anion also takes place in the merocyanine isomer complex of **8**(R = CH_3). A peak based on the phenolate-interacting Li^+ is, however, difficult to find in the NMR spectra of either spirobenzopyran derivatives of 18-crown-6, **9**(R = CH_3) or its acyclic analog **10**, which themselves cannot bind Li^+ very powerfully. The powerful intramolecular interaction, therefore, seems to occur only in the merocyanine isomers of crowned spirobenzopyrans of which the crown ether ring fits Li^+ well.

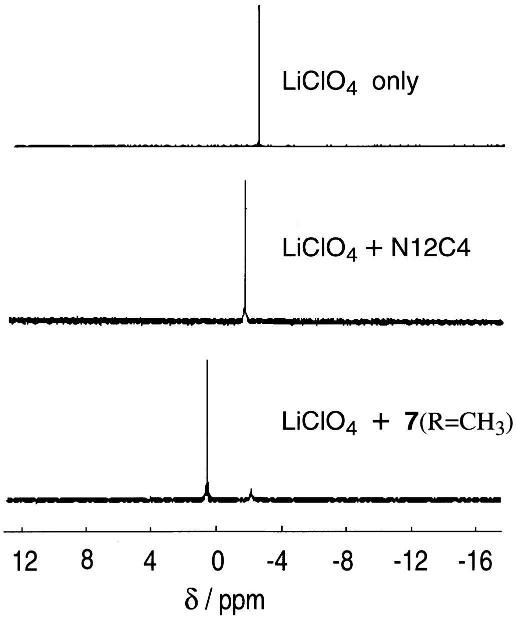
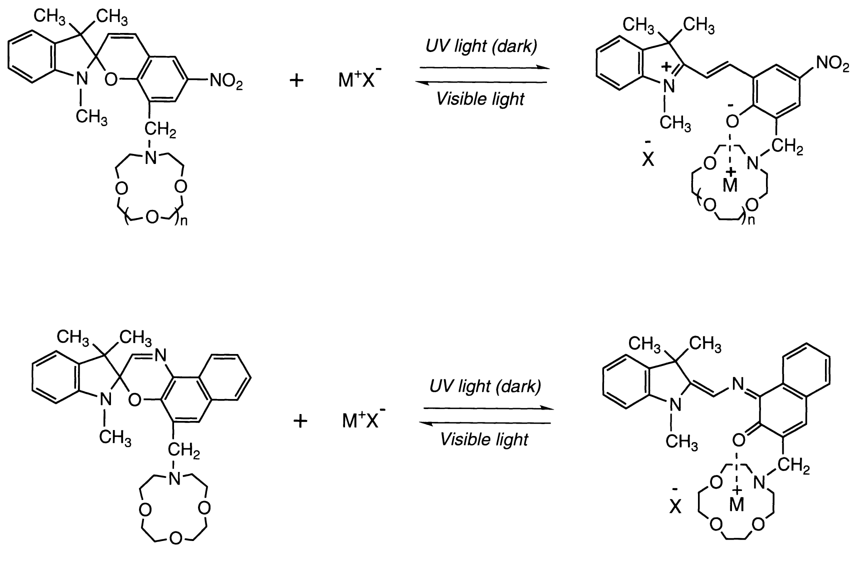


Fig. 2. ^{7}Li-NMR spectra for $LiClO_4$ acetonitrile solution in the absence and presence of *N*-benzyl-monoaza-12-crown-4 (N12C4) and crowned spirobenzopyran **7**(R = CH_3) under dark conditions.[35] [$LiClO_4$]: 2×10^{-2} mol dm^{-3}, [N12C4]: 2×10^{-2} mol dm^{-3}, [**7**(R = CH_3)]: 1.6×10^{-2} mol dm^{-3}.

Crowned spirobenzopyrans **7**–**9** can be isomerized reversibly to the corresponding crowned merocyanines by photoirradiation even in the presence of alkali metal ions, as exemplified by the **7**(R = CH_3) system (Fig. 1). A ^{7}Li-NMR spectrum of an acetonitrile solution of **7**(R = CH_3) and $LiClO_4$ is also modified by photoirradiation. Without photoirradiation, the solution exhibits a strong peak at the higher frequency and a tiny peak at the lower frequency, as mentioned above. Visible irradiation prior to the NMR measurement intensifies the lower-frequency peak while it weakens the higher-frequency peak (Fig. 3). The spectrum almost reverts to the initial spectrum if one removes the visible light, gradually at room temperature and immediately by heating. The NMR-spectral change is also attained by UV irradiation to some extent. The photoinduced



Scheme 1. Photocontrol of metal ion complexation by crowned spirobenzopyran **7**(R = CH_3) and spironaphthoxazine **15**.

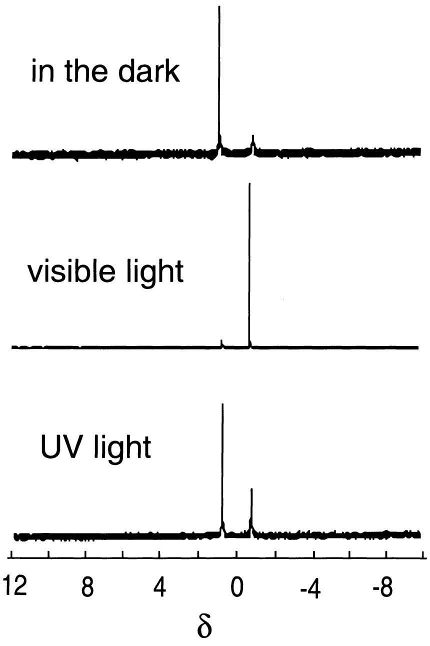


Fig. 3. ^{7}Li-NMR spectra for $LiClO_4$ acetonitrile solution in the presence of crowned spirobenzopyran **7**(R = CH_3) under dark and photoirradiated conditions.[35] [**7**(R = CH_3)]: 1.6×10^{-2} mol dm^{-3}, [$LiClO_4$]: 2×10^{-2} mol dm^{-3} in CH_3CN/CD_3CN (7/3).

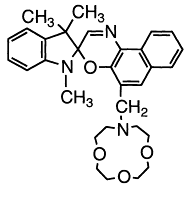
NMR-spectral changes indicate clearly that such cation-complexing equilibrium of crowned spirobenzopyran as shown in Scheme 1 (top) can be controlled photochemically. Under dark conditions (or on UV irradiation), the intramolecular interaction with a phenolate anion in the crowned merocyanine promotes Li$^+$ binding due to the additional-binding-site effect, which resembles the "lariat ether effect".[49] Visible irradiation, on the other hand, induces the isomerization to the spiropyran isomer and thereby attenuates the additional-binding-site effect, thus diminishing the Li$^+$-complexing ability. As a result, photochemical control of metal-ion complexation is definitely realized in the crowned spirobenzopyrans.

The photochromic behavior of crowned spirobenzopyrans is governed both by the metal-ion complexing ability of the crown ether moiety and by the kind of solvents. UV irradiation enhances or depresses the isomerization of the spiropyran moiety to the corresponding merocyanine form, showing positive or negative photochromism, respectively. For instance, in spirobenzopyran derivatives bearing an oxymethylcrown ether moiety **12**, the metal-ion complexing ability of the crown ether moiety affects both thermal isomerization and photoisomerization of their spirobenzopyran moiety to a great extent.[47] When the interaction of the crown ether moiety with a metal ion is strong enough to cause thermal isomerization of the spirobenzopyran moiety to the corresponding merocyanine form and to suppress UV-induced isomerization to the merocyanine form, a negative photochromism appears. On the other hand, a relatively weak interaction of the crown ether moiety with a metal ion affords a positive photochromism. This phenomenon enables us to switch the photochromic behavior between positive and negative photochromism of crowned spirobenzopyrans by changing the kind of metal ion added.

In spirobenzopyran derivatives incorporating a monoazatrithia-12-crown-4 moiety, an analog of **7** where the monoaza-12-crown-4 moiety is replaced with a monoazathiacrown ether moiety, the photochromism reflects the metal-ion complexing property of their thiacrown ether moiety.[50] Each of the thiacrowned spirobenzopyrans showed complexation selective for Mg^{2+} and Ag$^+$ with negative and positive photochromism, respectively. Silver ion, which has high affinity to the thiacrown moiety, facilitates photoisomerization to their corresponding merocyanine form, in which the phenolate anion does not interact with an Ag$^+$ in the thiacrown moiety. This leads to a positive photochromism of thiacrowned spirobenzopyran on UV irradiation. On the other hand, Mg^{2+} in the thiacrown ether can interact with the phenolate anion powerfully, resulting in a negative photochromism on UV irradiation.

A spirobenzopyran carrying a benzocrown ether moiety at 3'-position and a 3-(2-hydroxyethoxy)-1-propynyl group at the 5-position, **14**,[51] can switch metal-ion complexation in a different way from crowned spirobenzopyrans **7**–**9**. When **14** is photoisomerized to its corresponding merocyanine form, a metal ion complexed by the crown ether moiety is capped by the oxyethylene group instead of the phenolate anion of the merocyanine.

Crowned Spironaphthoxazine. Crowned spironaphthoxazine **15**[52] shows a similar behavior to the corresponding spirobenzopyran in the cation-induced isomerization (Chart 3). Equimolar addition of an alkali metal perchlorate to an acetonitrile solution of crowned spironaphthoxazine **15** causes 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. Sodium ion brings about a slight absorption-spectral change, but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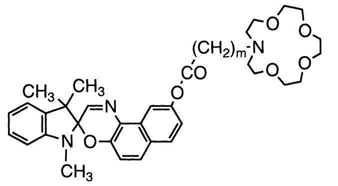
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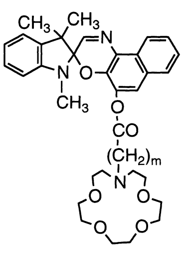
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Chart 3.

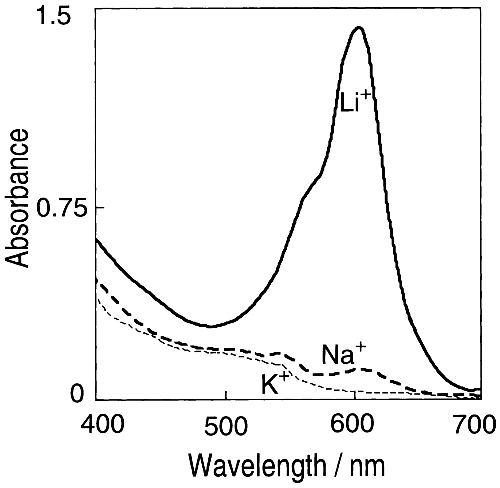


Fig. 4. Absorption-spectral changes of crowned spironaphthoxazine acetonitrile solutions on addition of alkali metal salts under dark conditions.[52] [**15**] and [$MClO_4$]: 4×10^{-4} mol dm^{-3} each.

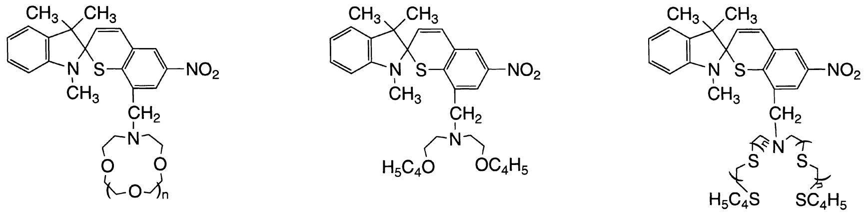
K^+ can change the visible spectrum of the crowned spironaphthoxazine solution hardly at all. An acetonitrile solution of an uncrowned spironaphthoxazine does not show any significant absorption spectral change on the alkali metal ion addition under identical conditions. This indicates that the isomerization of **15** to its open colored form is induced by the metal-ion 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 complex of the open form of **15** appears to contribute considerably to this cation-induced isomerization. This again means that the position into which the crown ether moiety is incorporated is quite crucial for the effective intramolecular interaction.

Photoisomerization of crowned spironaphthoxazine **15** proceeds reversibly even in the presence of Li^+.[53] The metal-ion complexation of **15** affects the thermal stability of crowned spironaphthoxazine open form to a great extent. Lithium-ion complexation remarkably stabilizes the open colored form of 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^+ as compared with that in the absence of any metal ion (3.0×10^{-2} s^{-1}). Addition of Na^+ also decreases the rate constant by about an order of magnitude (6.0×10^{-3} s^{-1}), but K^+ can hardly change the rate constant (2.1×10^{-2} s^{-1}) at all. The Li^+ selectivity for the thermal stability enhancement of the open colored form of **15** is as anticipated from that for the cation-complexation-induced isomerization under dark conditions. The thermal stability enhancement of the open colored form of **15** by Li^+ addition is derived from the intramolecular interaction between the oxo group and Li^+, combined with the selective cation binding of its crown ether moiety. The thermal stability of the open colored form of **15** can also be regulated by the concentration of added Li^+. Thus, the crowned spironaphthoxazine - Li^+ system has advantages over conventional spironaphthoxazines for practical applications as photochromic compounds.[54]

No significant cation-induced enhancement in the isomerization of the spironaphthoxazine moiety to its open form, which is based on the interaction between the oxo group and crown-ether-complexed cation, was found in a spironaphthoxazine derivative carrying a crown ether moiety at the 9′-position, **16**, which is relatively remote from the oxo group.[55] Even a spironaphthoxazine derivative carrying a crown ether moiety at the 5′-position, **17**, cannot augment the thermal stability of its open form by metal-ion complexation of its crown ether moiety so remarkably as **15**, due to the poor alignment of its crown ether ring and oxo group.[56]

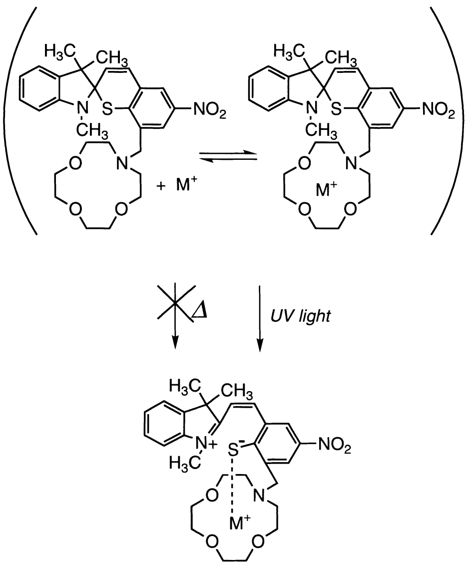
Photoirradiation of crowned spironaphthoxazine in the presence of Li^+ can alter the complexation equilibrium established between **15** and Li^+ under dark conditions. When UV light enhances the isomerization of **15** to the corresponding open form, the participation of its oxo group as an additional binding site augments its metal-ion complexing ability, as also illustrated in Scheme 1 (bottom). The metal-ion complexing ability of **15** can thus be modified by photoirradiation as was the case for crowned spirobenzopyrans **7**–**9**.[53]

Crowned Spirobenzothiopyran. Not only spirobenzopyrans but also spirobenzothiopyrans are well-known photochromic compounds and have been studied extensively in view of photochromic devices. However, the application of spirobenzothiopyrans does not seem to be very easy due to the low thermal stability of their open colored form.[57–59] One might expect that the incorporation of crown ether moiety to the spirobenzothiopyran skeleton would improve the thermal stability of its open form by the cation complexation of its crown ether moiety.[41,60] Also, it is of much interest to determine how crowned spirobenzothiopyran differs in photochromism from the corresponding spirobenzopyrans. Absorption-spectral changes of crowned spirobenzothiopyran **18** in acetonitrile were followed on addition of a metal ion (alkali and alkaline-earth metals and soft metal ions such as Ag^+ and Tl^+) (Chart 4). The spectrum was hardly changed by adding an equimolar amount of Li^+, Na^+, and K^+, unless otherwise irradiated by UV light. This means that the isomerization to their merocyanine form accompanying the benzothiopyran-ring opening cannot proceed by the metal-ion complexation of their crown ether ring under dark conditions (Scheme 2). This isomerization behavior of **18** is, therefore, very different from that of crowned spirobenzopyran **7**, the benzopyran ring of which can be opened readily by metal-ion complexation even without UV irradiation. A drastic change in the absorption spectrum of the **18** solution containing Li^+ occurs on UV irradiation. On the other hand, little spectral change was observed in the **18** solution without any metal ion and with an equimolar amount of K^+. The Na^+ addition also affords only a slight spectral change. Definitely, the metal-ion complexing ability of a crown ether moiety of **18** stabilizes the colored merocyanine isomer that is formed only on UV irradiation, owing to the polarity enhancement. The stabilization of the open form of crowned spirobenzothiopyran is highly selective for Li^+ among alkali metal ions. In addition to the selective Li^+ complexation with the monoaza-12-crown-4 moiety of **18**($n = 1$), some interaction between the thiolate anion and Li^+ complexed by the crown ether moiety probably contributes to the



18 **19** **20**

Chart 4.

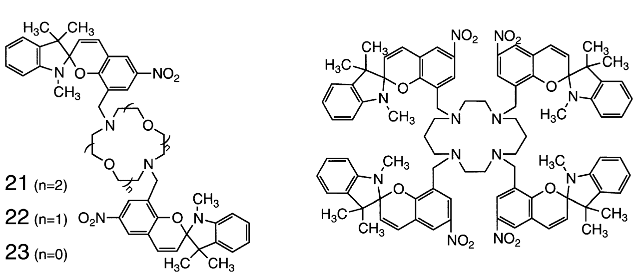


Scheme 2. Isomerization behavior of spirobenzothiopyran **18**(n = 1) in the presence of metal ion.[41]

stabilization of the colored merocyanine isomer of **18**(n = 1), as is the case with the Li^+ complex for merocyanine form of crowned spirobenzopyran (Scheme 1). This Li^+-specific stabilization of photoinduced colored form of **18**(n = 1) is also supported by photochromism for a model compound carrying a linear oligo(oxyethylene) moiety instead of a crown ether moiety, **19**. Since the linear oligo(oxyethylene) moiety of **19** cannot bind a metal ion very powerfully, even Li^+ scarcely induces such UV-light-induced isomerization to the open colored isomer. Soft metal ions such as Ag^+ and Tl^+, especially Ag^+, also promote the UV-induced isomerization of crowned spirobenzothiopyran **18** to its merocyanine form. Taking into consideration that even the photoisomerization of spirobenzothiopyran derivative carrying an acyclic oligo(oxyethylene) moiety **19** is enhanced by Ag^+ addition, one see that the Ag^+-facilitated photoisomerization of the spirobenzothiopyran derivatives is caused mainly by high affinity of the thiophenolate anion to Ag^+ rather than by Ag^+ complexation of the crown ether moiety. On the other hand, Ag^+-induced remarkable stabilization of the merocyanine form in spirobenzothiopyran derivative incorporating an acyclic thiacrown ether moiety **20**(n = 0) is evidently derived from the cooperation of sulfur atoms in 3,9-dithia-6-azaundecane and its thiophenolate anion on the interaction with a metal ion.[50]

Crowned Bis(spirobenzopyran). Crowned spirobenzopyrans **7–9**, which carry only one spirobenzopyran moiety, readily bind monovalent alkali metal ions due to the intramolecular interaction of a crown-complexed monovalent cation and a phenolate anion with 1 : 1 stoichiometry in the merocyanine-metal ion complex. Therefore, it can be expected that the incorporation of two or more spirobenzopyran moieties into a crown ether will result in preferable complexation of multivalent metal cations. Therefore, the crown ethers carrying more than one spirobenzopyran moiety are candidates as a material for photochemical complexation control of multivalent metal ions (Chart 5).

Crowned bis(spirobenzopyran) **21** is expected to show a selectivity for divalent metal ions in the metal-ion complexation and subsequent isomerization, provided that the complex stoichiometry of **21** and metal ion is 1 : 1.[40,61] The cation-complexation-induced isomerization of crowned bis(spirobenzopyran) **21** to its corresponding merocyanine form can be followed spectrophotometrically in acetonitrile solutions containing an equimolar amount of **21** and a metal salt under dark conditions, using various nitrates of mono-, di-, and trivalent cations. Figure 5 summarizes the absorption-spectral data for the merocyanine isomer of **21**, together with the data for the corresponding crowned *mono*(spirobenzopyran) **9**(R = CH_3) for comparison. The solutions of the crowned spirobenzopyrans without any metal salt had no detectable absorption in the visible region that is assignable to their merocyanine form. Also, an acetonitrile solution of a spirobenzopyran derivative without any crown ether moiety exhibits negligible spectral changes on addition of metal salts under identical conditions. This convinces us that the isomerization of crowned bis(spirobenzopyran) to its merocyanine form in the presence of metal salts is derived from the metal-ion complexation by its crown ether



21 (n=2)
22 (n=1)
23 (n=0)

24

Chart 5.

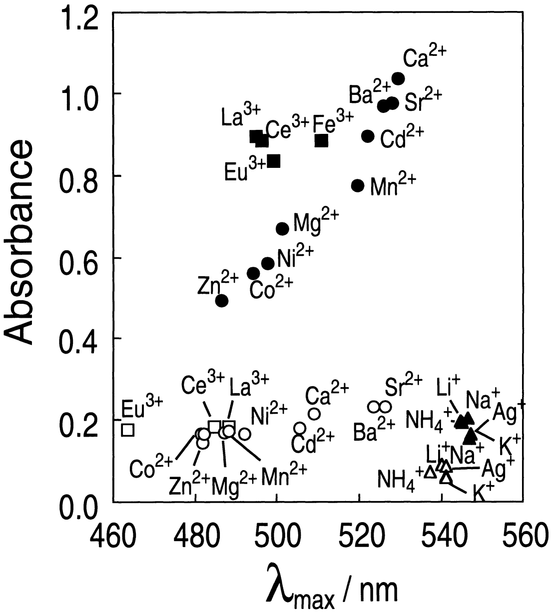


Fig. 5. Absorption-spectral data in visible region for crowned spirobenzopyran **21**(n = 2) (full marks) and **9**(R = CH_3) (empty marks) in the presence of metal ions [monovalent (triangle); divalent (circle); trivalent (square)] under dark conditions.[61] [**21**(n = 2)], [**9**(R = CH_3)], and [metal nitrate]: 2×10^{-5} mol dm^{-3} in acetonitrile.

moiety. In the system of crowned bis(spirobenzopyran), multivalent metal ions can induce isomerization of its spirobenzopyran moiety to the corresponding merocyanine form more efficiently than monovalent ones can. Multivalent metal ions also give absorption peaks of merocyanine form at lower wavelengths than monovalent ones do in both of the crowned mono- and bis(spirobenzopyran). ^{1}H-NMR spectroscopy indicates that, on the Li^+ complexation by crowned bis(spirobenzopyran) **21**, one of the two spirobenzopyran moieties isomerizes to its merocyanine form, while the other remained unchanged. On the contrary, the Ca^{2+} complexation by **21** can bring about concurrent isomerization of the plural spirobenzopyran moieties. This is the case with the systems of **21** with trivalent metal ions such as La^{3+}. This is probably because a monovalent metal ion captured by the crown ether moiety of **21** interacts intramolecularly with only a phenolate anion of its merocyanine moiety so as to compensate for the single positive charge. The complexation of divalent and trivalent metal ions by **21**, on the other hand, forces two of the spirobenzopyran moieties to isomerize for the intramolecular interaction between a multivalent metal ion and two phenolate anions.

In bis(spirobenzopyran) of diaza-12-crown-4 **22**, similar absorption-spectral changes are observed by complexation with multivalent metal ions such as Ca^{2+} and La^{3+}.[62] In bis(spirobenzopyran) of piperazine **23**, however, little absorption-spectral change is observed even in the presence of alkaline-earth metal ions, although trivalent metal ions such as La^{3+} afford some spectral changes probably due to the strong interaction between the phenolate anion of spirobenzopyran moiety and a high-charge-density cation. Stability constants for metal ion complexes of **21**–**23** with 1:1 stoichiometry can be determined by using electrospray-ionization mass spectrometry (ESI-MS), together with the constants for their corresponding parent crown ethers, diaza-12-crown-4 and diaza-18-crown-6, for comparison. Table 1 summarizes the stability constants of metal ion complexes of **21**–**23**, together with those of the parent crown ethers, diaza-12-crown-4 and diaza-18-crown-6 for comparison. The stability constants of metal ion complexes of **21** and **22** generally increase with increasing valence of a given metal ion, reflecting the powerful ionic interaction between the phenolate anion of the merocyanine form and a metal ion in the crown ether moiety. Thus, both **21** and **22** have the greatest stability-constant values for their La^{3+} complexes. Noticeably, crowned bis(spirobenzopyran)s form much more stable complexes with metal ions than the corresponding parent crown ethers do. In particular, the stability constant for the **21**/La^{3+} complex is about 6 orders greater than its corresponding metal ion complex of the parent crown ether, diaza-18-crown-6. The stability constant for **21**/La^{2+} complex (log K = 11.4 in methanol) is extraordinarily high, being still greater than those for metal ion complexes for powerful macrobicyclic ligands such as cryptand.

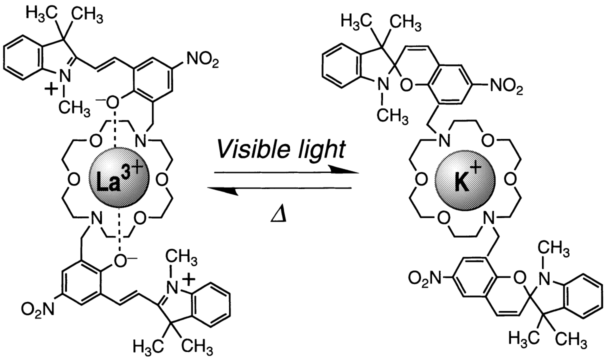
Photoisomerization of crowned bis(spirobenzopyran) **21** proceeds reversibly even in the presence of metal ion.[61] Although isomerization of the spirobenzopyran moiety occurs on addition of metal salts, as mentioned above, UV irradiation on an acetonitrile solution of a 1:1 mixture of **21** and a metal salt enhances the isomerization to merocyanine form. Visible irradiation, on the other hand, causes the isomerization back to the corresponding spirobenzopyran form to a great extent. When visible light is turned off in the crowned bis(spirobenzopyran)–Ca^{2+} system, the isomerization to merocyanine form occurs together with coloration of the solution, the isomerization percentage returning to the initial values under dark conditions. This means that crowned bis(spirobenzopyran)s **21** and **22** are promising for photochemical control in the complexation of multivalent metal ions such as Ca^{2+} and La^{3+}.

Since the La^{3+} affinity of **21** is very different from its parent crown ether, diaza-18-crown-6, which does not undergo such ion-ion interaction, one can expect that photoisomerization of the merocyanine moiety of **21** back to the electrically neutral spiropyran form restores its ion selectivity from multivalent metal ions to monovalent ones as illustrated in Scheme 3.[38] The photoinduced ion-selectivity switching of crowned

Table 1. Stability Constants (log K) for Metal Ion Complexes of Crowned Bis(spirobenzopyran)s and Their Parent Crown Ether Complexes

	Li^+	Ca^{2+}	Sr^{2+}	La^{3+}
21	6.85 [c)]	8.38 [b)]	9.00 [c)]	11.4 [c)]
Diaza-18-crown-6	3.50 [d)]	4.05 [d)]	5.93 [e)]	5.70 [d)]
22	6.62 [a)]	7.80 [b)]	6.66 [a)]	9.17 [a)]
Diaza-12-crown-4	— [f)]	4.65 [e)]	4.47 [d)]	— [f)]
23	— [f)]	— [f)]	— [f)]	— [f)]

The log K values were determined in methanol by using a) **22**/Ca^{2+} complex, b) cryptand[2.2.2]/Ca^{2+} complex, c) **21**/Ca^{2+} complex, d) diaza-18-crown-6/Sr^{2+} complex, and e) 18-crown-6/Ca^{2+} complex as the reference complex. f) Stability constants are too small to obtain reliable values.

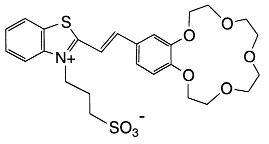


Scheme 3. Photochemical switching of metal ion selectivity between multivalent and monovalent metal ions by crowned bis(spirobenzopyran).

bis(spirobenzopyran) can be detected by using an ESI-MS apparatus equipped with an on-line photoirradiation device. Under dark conditions, crowned bis(spirobenzopyran) **21** possesses much higher affinity to the multivalent metal ions than the monovalent ones due to the ionic interaction between the two phenolate anions and a metal ion in the crown ether moiety. The isomerization of the merocyanine to spiropyran forms induced by visible irradiation can switch the ion selectivity of **21** from La^{3+} to K$^+$. If one turns off the visible light, the high La^{3+} selectivity of **21** is restored. Thus, crowned bis(spirobenzopyran) **21** realizes extremely high affinity to La^{3+} by the powerful interaction with two phenolate anions of its merocyanine moiety and visible-light-induced selectivity switching from La^{3+} to K$^+$.

It is interesting to determine what happens with crown ether derivatives carrying more than two spirobenzopyran moieties, which we call crowned oligo(spirobenzopyran). For instance, crowned tetrakis(spirobenzopyran) **24** showed an affinity to transition metal ions such as Cu^{2+} and Ni^{2+} in a preliminary experiment.[63]

Crowned Styryl Dye. Crown ether derivatives carrying styryl dyes such as **25** and **26**,[64] which are already zwitterionic without photoirradiation, have potentiality to control metal-ion complexation of their crown ether moiety by cis–trans isomerization of their styryl dye moiety (Chart 6). The crown ether styryl dyes resemble the above-mentioned crowned spirobenzopyrans in that the photoisomerization of their photochromic moiety induces stable-complex formation of their crown ether moiety by intramolecular ionic interaction between the anionic site and a metal ion, although the present photochromic crown compounds are not photoionizable. For instance, the styryl C=C bond of crown ether styryl dye **25** is isomerized from its trans to cis forms by UV irradiation. In the cis form of **25**, the sulfonate anion has easy access to a high-charge-density metal ion complexed by its crown ether moiety and makes a stable intramolecular ion pair. As a result, the cis isomer forms more stable complexes with Mg^{2+} by two orders of magnitude than the corresponding trans isomer. On the other hand, the trans isomer of **25** tends to form an intermolecular aggregate in the presence of Mg^{2+} by forming a dimeric complex (2:2 complex of **25** and a metal ion). A similar styryl dye incorporating a benzothiacrown ether moiety shows a high affinity to Hg^{2+} and Ag$^+$ and the photoisomerization of styryl C=C bond from trans to cis forms augments the complex stability constant for Hg^{2+} by an order of magnitude.[65] Azacrown ether styryl dye **26** behaves as a usual chromoionophore for Ba^{2+} and Na$^+$ at high concentrations.[66] In other words, the addition of high-concentration metal ions facilitates the trans-to-cis isomerization of the styryl dye moiety even without photoirradiation, thus leading to the intramolecular ionic interaction between the sulfonate anion and a metal ion in the crown ether moiety. Such photoinduced enhancement of metal-ion complexing ability of **26** as seen in **25** can be attained even at the low metal-ion concentrations. The mechanism for the crown ether styryl dyes in the photochemical control of metal-ion complexation is quite similar to that for "anionic" crowned azobenzene derivatives that also undergo the photoisomerization of their azobenzene moiety between trans and cis forms.[67,68]



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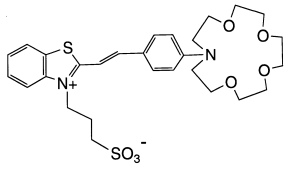

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Chart 6.

2. Photochromic Crown Compounds Photoionizing Intermolecularly

Crowned Malachite Green. Well-known photochromic compounds undergoing intermolecular photoionization are Malachite Green dyes, which dissociate to a triphenylmethyl cation and an anion on UV irradiation.[1] This photochromism of Malachite Green dyes has been receiving attention as an attractive tool for photocontrol of ionic environments.[27–31,69] A unique type of photochemical control system of metal-ion complexation can be designed by providing Malachite Green dyes with a crown ether moiety (Chart 7). In a Malachite Green leuconitrile carrying a crown ether moiety, crowned Malachite Green **27**, the metal-ion complexation of its crown ether moiety can be controlled photochemically, based on electrostatic repulsion between its triphenylmethyl cation and a metal ion complexed by its crown ether moiety, as shown in Scheme 4 (top).[36,37] Crowned Malachite Green **27** can complex Na$^+$ easily, provided that the photochromic moiety is not ionized. When UV light forces the cation-complexed **27** to ionize to its triphenylmethyl or quinoid cation and a cyanide anion, the Na$^+$ in the crown moiety is presumably repelled by the intramolecular electrostatic repulsion between the Na$^+$ and the resulting organic cation. In an experiment to detect the photoinduced changes of metal-ion complexing ability of **27** in aqueous methanol potentiometrically by using a Na$^+$-selective glass electrode, UV irradiation raised the activity of free Na$^+$, while the following dark reaction restored the ion activity to the initial value. This potentiometry clearly indicates that releasing and binding of Na$^+$ by the crown ether moiety of crowned Malachite Green occur on the photoionization and recombination of its Malachite Green moiety, respectively. However, the photoionized crowned Malachite Green does not

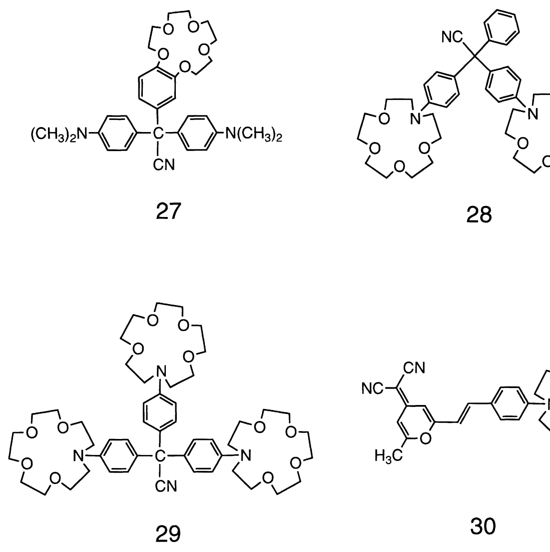
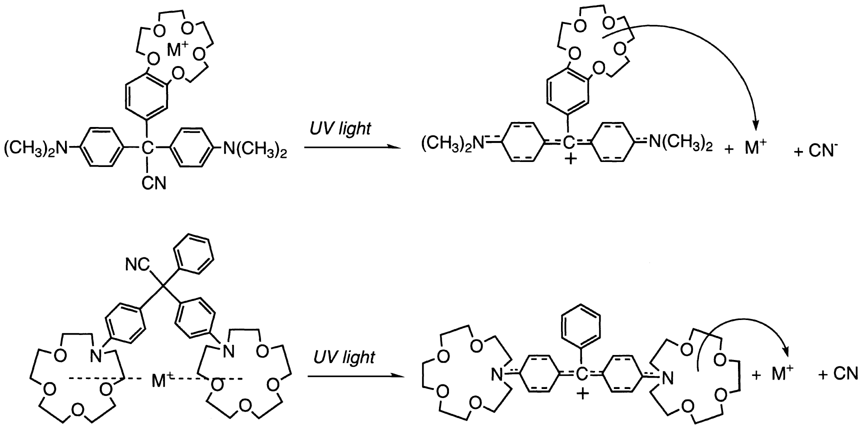


Chart 7.

necessarily reject a metal ion. Mass spectrometry (ESI-MS) proved that even the cationic form of **27** still can bind a metal ion with its crown ether moiety in spite of the intramolecular electrostatic repulsion between the crown-ether-complexed metal ion and the triphenylmethyl cation. This is because the electrostatic repulsion for the **27** system is not very effective due to the difficult delocalization of the photoinduced cationic charge on the crown ether moiety. In addition, the benzocrown ether itself does not have very high cation-binding ability even in the non-ionized state of **27** under dark conditions. Unlike crowned Malachite Green **27**, Malachite Green derivative incorporating a bis(monoazacrown ether) structure **28** realizes not only high metal-ion complexing ability of the bis(crown ether) moiety[10,11] under dark conditions but also efficient metal-ion release by electrostatic repulsion with positively charged nitrogen atoms in the crown ether ring under photoirradiated conditions.[38,39] A typical spectrum for ESI-MS of an acetonitrile solution of **28** and $KClO_4$ shows a strong peak for its K^+ complexes at *m/z* 742 under dark conditions (Fig. 6, top). UV irradiation afforded a single, significant peak at *m/z* 677, which is assigned to the corresponding cationic form of **28** (Fig. 6, bottom). Such a peak assigned to the metal ion complexes of **28** as observed under dark conditions cannot be seen at all on UV irradiation. This means that almost all metal ions complexed by the crown ether moiety of **28** are released on the photoionization of the Malachite Green moiety. Thus, biscrowned Malachite Green leuconitrile **28** can undergo clear-cut switching from the powerful metal-ion complexation to the perfect metal-ion release, so-called all-or-none type switching in the metal-ion complexation on its photoionization, as illustrated in Scheme 4 (bottom). The photoionization behavior of biscrowned Malachite Green leuconitrile depends considerably on the kind of solvents.[70]

Crowned Crystal Violet. A triphenylmethane dye derivative incorporating three monoaza-15-crown-5 rings, **29**, what we call triscrowned Crystal Violet, has been designed.[39] An all-or-none type photochemical switching behavior of metal-ion complexation similar to that by biscrowned Malachite Green **28** is attained with the triscrowned Crystal Violet. Triscrowned Crystal Violet **29** is not a useful chromoionophore for ion sensing at the visible region (by color change),[71,72] but it exhibits an interesting metal-ion complexing property.[73] Triscrowned Crystal Violet **29** binds Cs^+ more than other alkali metal ions on liquid–liquid extraction. If one considers that the highest extractability of biscrowned Malachite Green **28**[39] was observed for K^+ and that the sandwich-type complexation is an important factor to raise complexing ability for K^+, one may conclude that the Cs^+ complexation with the triscrowned Crystal Violet is probably performed by the intramolecular cooperation of the three crown ether rings of **29**. Since Na^+ fits into the ring of monoaza-15-crown-5 ether,[74] the ion tends to form multinuclear metal complexes with the triscrowned Crystal Violet. This in turn suppresses the metal-ion extraction due to the significantly increased hydrophilicity of the highly charged complexes. A very striking thing about the metal-ion complexation by **29** is a conformational change forced by Cs^+ complexation. Absorbance in the absorption spectrum at the UV region (around 270 nm) of **29** depends on Cs^+ concentration and is reduced with increasing Cs^+ concentration at its low concentration range. After the ion concentration is equal to that of triscrowned Crystal Violet, further Cs^+ addition again augments its absorbance. The absorbance dependence is



Scheme 4. Photocontrol of metal ion complexation by crowned Malachite Green derivatives **27** and **28**.

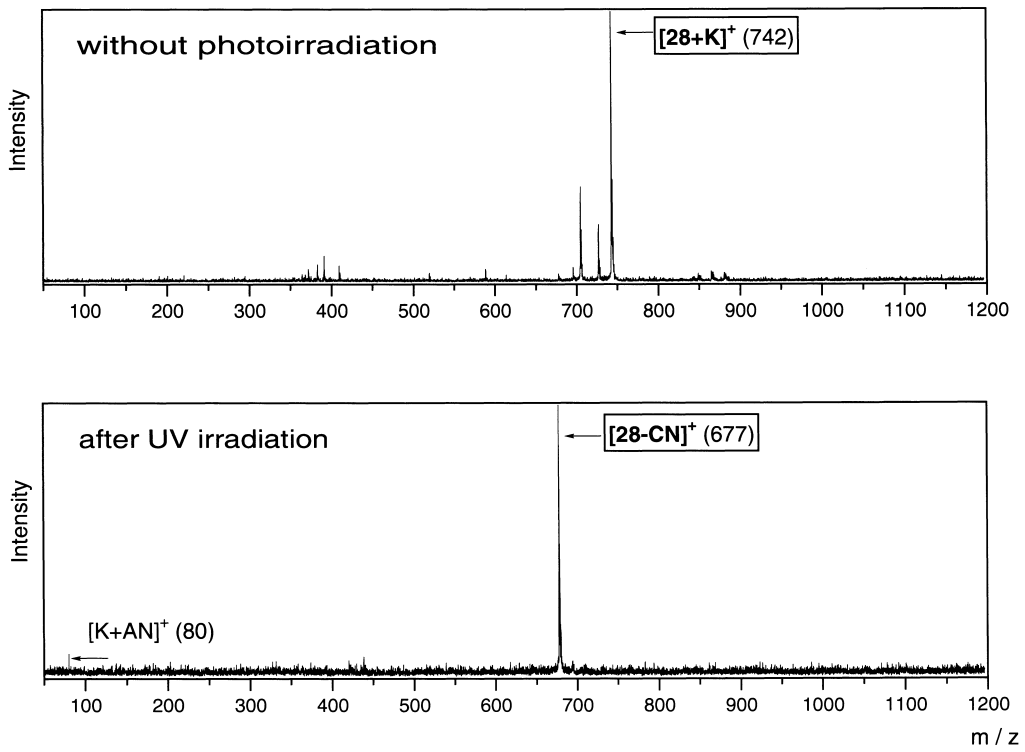


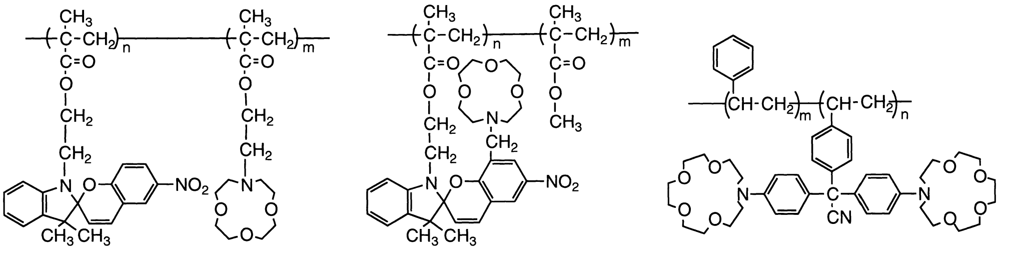
Fig. 6. Mass spectra for acetonitrile solution of biscrowned Malachite Green leuconitrile **28** and $KClO_4$ under dark (top) and UV-irradiated (bottom) conditions.[38] [**28**] and [$KClO_4$]: 2×10^{-4} mol dm^{-3}, UV light: 240–400 nm for 30 s.

anomalous because Cs^+ itself has no absorption at the UV region and the triscrowned Crystal Violet does not ionize without UV irradiation. It is, therefore, anticipated that this unique phenomenon of the triscrowned Crystal Violet is derived from its conformational change on complexing Cs^+. If one compares among the Cs^+, Na^+, and K^+ complexes of **29**, the complex conformation should be different from one another. Since Na^+ forms 1 : 1 complexes with the monoaza-15-crown-5 ring, its complex formation will not affect the conformation of the Crystal Violet skeleton. A K^+ ion may be trapped intramolecularly with two of the crown ether rings of **29**, in which case the resulting conformation change is not very hard to assume for the Crystal Violet skeleton. The intramolecular cooperation of the three crown ether rings is, however, necessary for complexing a Cs^+ and must be accompanied by a serious distortion of the Crystal Violet skeleton, which can be verified by molecular-orbital calculations. The distortion of the Crystal Violet skeleton leads to the absorbance change at the UV region. This phenomenon of the triscrowned Crystal Violet might be applied to spectrophotometry that is highly selective for Cs^+.

Crowned Merocyanine. A monoazacrown ether carrying a laser dye, crowned merocyanine **30**, can bind metal ions such as Ca^{2+} and Li^+ with its crown ether moiety. The excitation of the merocyanine moiety by a laser pulse induces charge transfer in the moiety, the nitrogen atom in the crown ether ring being charged positively. As a result, the positive charge on the nitrogen atom in the excited state of **30** ejects a metal ion complexed by its crown ether moiety due to the electrostatic repulsion between the metal ion and positive charge.[75–77] The photoejection process takes place very fast, within 5 and 20 ns in the Li^+ and Ca^{2+} complexes, respectively. In the ground state without laser irradiation, the crowned merocyanine binds metal ions again. The stability constants of the metal ion complexes are two orders of magnitude lower in the excited state than in the ground state. Although the photocontrol of metal ion complexation by crowned merocyanine **30** is quite reversible, the excited state is thermally unstable with a very short lifetime. Therefore, it will be difficult to observe the photoinduced increase of free metal-ion activity in solution and to apply the photoejection system of **30** practically.

3. Polymers Carrying Photochromic Crown Ether Moiety

Crowned Spirobenzopyran Polymers. An easy way to combine a spirobenzopyran moiety with a crown ether moiety is copolymerization of vinyl monomers carrying their corresponding functional moieties.[42] Copolymerization of vinyl monomers of monoaza-12-crown-4 and spirobenzopyran[78] in an equimolar amount affords crown ether–spirobenzopyran copolymer **31** ($m = n = 0.5$) (Chart 8). The complexing ability of **31** toward alkali metal ions, which can be estimated by a conventional solvent extraction technique, is in the order of $Na^+ > K^+ > Li^+$. The polymeric crowned spirobenzopyran is quite different in the metal-ion complexing property from those for its corresponding monomeric analog, crowned spirobenzopyran **7**.[35] The efficient intramolecular interaction between a phenolate anion and a metal ion complexed by the crown ether moiety in the metal-ion complex of the merocyanine form of **7** reflects the selectivity order of $Li^+ > Na^+ > K^+$, as already discussed. On the contrary, crown ether–spirobenzopyran copolymer **31** does not exhibit such a high Li^+ selectivity in spite of the fact that the polymer also carries crown ether and spirobenzopyran moieties in the vicinity. This

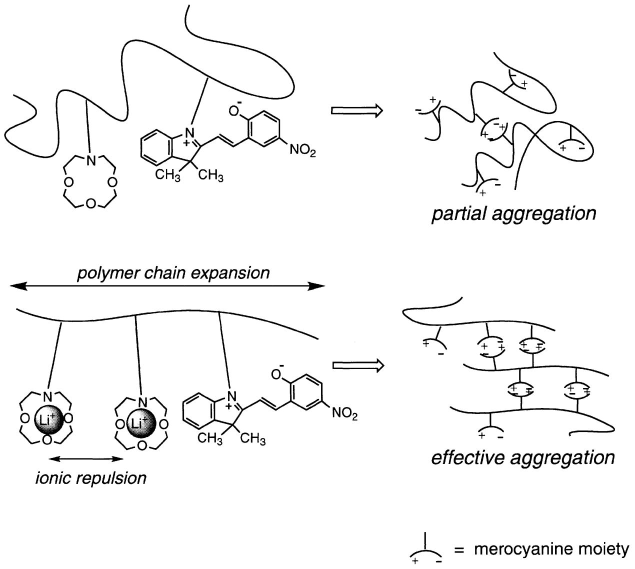


31 **32** **33**

Chart 8.

suggests that such intramolecular interaction as seen in crowned spirobenzopyran **7** is quite difficult in the polymer, **31**, probably due to the comparatively long distance between its crown ether and spirobenzopyran moieties. The higher complexing ability of **31** toward Na^+ and K^+ than Li^+ is probably due to the easy formation of intrapolymer 2:1(crown ether ring/metal ion) complexes with Na^+ and K^+ by cooperative action of two adjacent crown ether rings,[10] as is the case with poly(12-crown-4) derivatives.[79] The intrapolymer sandwich-type complex formation enhances the metal ion complexation and thereby the metal-ion extraction by cooperative action of two adjacent crown ether rings.

An intriguing phenomenon was, however, observed during the course of investigations of metal ion complexation and photochromism of the crown ether–spirobenzopyran copolymer **31** ($m = n = 0.5$).[42] Spirobenzopyran derivatives, when isomerized to their corresponding merocyanine forms, are known to aggregate.[80] Specifically, the aggregation between the merocyanine isomers is remarkable with polymers carrying a spirobenzopyran moiety at the side chain.[81] UV irradiation causes isomerization of the spirobenzopyran moiety of **31** to its corresponding merocyanine form, which in turn brings about polymer-chain aggregation by forming pairs of the zwitterionic merocyanine. This phenomenon is supported by absorption-spectral changes of a tetrahydrofuran (THF) solution of crown ether–spirobenzopyran copolymer **31**. Without any metal ion, the photoirradiation increases an absorption peak around 600 nm assigned to the non-aggregated merocyanine moiety, which is shifted gradually to shorter wavelengths (560 nm) by prolonged photoirradiation. This blue shift of the merocyanine absorption peak can be attributed to the formation of H-type aggregates.[81] The merocyanine absorption disappears almost completely by the following visible irradiation (> 400 nm). In the solution containing Li^+, on the other hand, the absorption around 560 nm, based on the H-type aggregation, appears very quickly by UV irradiation. Further UV irradiation decreased the absorption with a slight red shift. Finally, a purple-colored polymer starts to precipitate with some turbidity in the solution. Since polymer chains of **31** should be contracted without any metal ion in a modestly soluble solvent such as THF, the photoisomerized merocyanine moieties are likely to form H-type aggregates intramolecularly in a polymer chain. In the presence of a crown-ether complexable metal ion, however, the polymer chains carry positive electric charges by the metal ion complexation with its crown ether moiety and thereby the polymer chain expands due to the intramolecular electrostatic repulsion among the cationic charges, as demonstrated in Scheme 5. The expansion of polymer chains can raise the probability for interpolymer formation of the merocyanine aggregate while suppressing the intramolecular (intrapolymer) one. Thus, the interpolymer merocyanine aggregation brings about polymer-chain crosslinking of **31**, finally leading to the polymer precipitation. The polymer precipitate which resulted by UV irradiation in the presence of a metal ion can be again dissolved in the solution by subsequent visible irradiation and then the **31** solution becomes almost transparent. This means that UV-light induced precipitation of polymer **31** and visible-light induced dissolution in the presence of Li^+ is quite reversible. This is the case in the presence of Na^+ instead of Li^+, although the UV-light induced merocyanine aggregation and precipitation in the former metal-ion system is not as easy as in the latter one. Some difficulty for the photoinduced merocyanine aggregation in the Na^+ system is probably because polymers carrying a 12-crown-4 moiety at the side chain tend to form intramolecular 2:1 (crown ether ring/metal ion) complexes with Na^+. This intramolecular formation of the sandwich-type complexes depresses the polymer chain expansion induced by electrostatic repulsion, in turn preventing



Scheme 5. Photoinduced merocyanine aggregation in crown ether–spirobenzopyran copolymer **31** in the absence and presence of metal ion.

the interpolymer aggregation of merocyanine. This is reversible photocontrol in the precipitate formation of crown ether–spirobenzopyran copolymer **31** in THF in the presence of a metal ion.

The original property of photoresponsive metal-ion complexing ability for the monomeric crowned spirobenzopyran is, however, lost with the crown ether–spirobenzopyran copolymers **31**. Vinyl polymers carrying a crowned spirobenzopyran moiety itself at the side chain **32**, can also be synthesized instead.[82] The metal ion complexation by the crown ether moiety of **32** affected photochromism of their spirobenzopyran moiety remarkably. The crowned spirobenzopyran polymers have considerable similarity to the corresponding monomeric analog in the metal-ion complexing property and photochromism, with some differences induced by polymer effects. To the contrary, little significant aggregation of photoinduced merocyanine moiety is found in the crowned spirobenzopyran polymers, unlike the polymers carrying spirobenzopyran and crown ether moiety independently.

Crowned Malachite Green Polymers. Polymers carrying a biscrowned Malachite Green moiety at the side chain were synthesized expecting significant polymer effects. Copolymerization of vinyl monomers bearing a biscrowned Malachite Green moiety with several widely-used vinyl monomers such as styrene yielded crowned Malachite Green polymers **33**.[83] Homopolymerization of vinyl monomers of biscrowned Malachite Green does not appear to proceed due to the steric hindrance of a bulky pendant group (biscrowned Malachite Green moiety). The metal-ion complexing ability for Malachite Green polymer **33** ($m = 0.4$, $n = 0.6$), which is evaluated by metal ion extraction with a 1,2-dichloroethane solution from an alkali-metal picrate aqueous solution, is different from its corresponding monomeric model of biscrowned Malachite Green **28** (Fig. 7). The metal-ion complexing ability for polymer **33** ($m = 0.4$, $n = 0.6$) is in the order $Cs^+ > K^+ > Na^+ > Li^+$ and that for the monomeric model **28** is in the order $K^+ > Na^+ > Cs^+, Li^+$. The polymer is generally higher than the monomeric model **28** in the metal-ion complexing ability, especially towards Cs^+. In general, 15-crown-5 derivatives tend to form 2:1(crown ether ring/metal ion) sandwich-type complexes with metal ions that are slightly greater in size than the crown ether cavity. So, the bis(15-crown-5) derivative, biscrowned Malachite Green **28**, can form sandwich -type K^+ complexes very easily by cooperative action of two adjacent crown ether rings, that is, by a bis(crown ether) effect. This is the reason for the high affinity of **28** on the K^+ extraction. The higher affinity of biscrowned Malachite Green polymers towards Cs^+ than towards K^+ may be attributed to a kind of polymer effect, that is, a more sophisticated cooperative action of two or more crown ether rings at the polymer side chain on the metal-ion complexation. In addition to the bis- and poly(crown ether) effects on the metal ion complexation, the higher lipophilicity of biscrowned Malachite Green polymers than that of the monomeric model **28** may augment the metal-ion complexing ability of the polymers, which is evaluated by cation extraction from aqueous to organic phases. Another remarkable thing is a great difference between the biscrowned Malachite Green polymer and its monomeric model **28** in the thermal decoloration after UV irradiation. In any metal-ion addition system, the biscrowned Malachite Green systems are always greater in the thermal decoloration rate than the monomeric model system. The high rates in the thermal reversion reaction from the ionic form to electrically neutral one in the biscrowned Malachite Green moiety must be related to the polymer rheology changes induced by intrapolymer electrostatic interaction among the cationic species of Malachite Green.[30] The polymers of biscrowned Malachite Green **33** are modestly soluble in THF/acetonitrile (50/50 vol%), and therefore the polymer chains are probably contracted in solution. The photoinduced ionization in the biscrowned Malachite Green moiety of the polymers results in the cationic-site formation in the polymer side chain. The resulting contracted polymer chain is apt to expand due to the intrapolymer electrostatic repulsion among the cationic sites, thus resulting in some strain in the polymer chain. The photoinduced expansion of the polymer chain is evidenced by the measurements of reduced viscosity of the polymer solutions. This polymer chain strain accelerates the thermal reversion reaction due to its alleviation, enhancing the thermal decoloration reaction as compared with the corresponding monomeric analog.

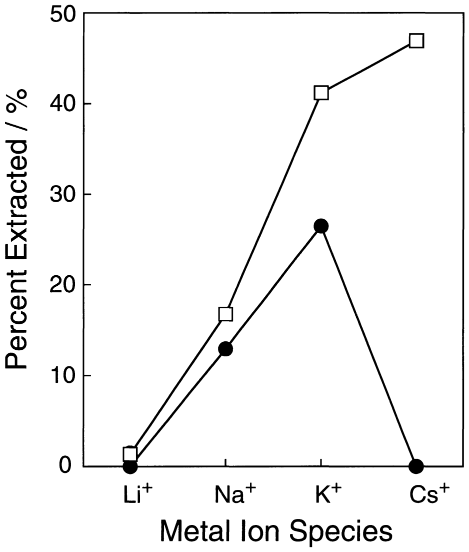


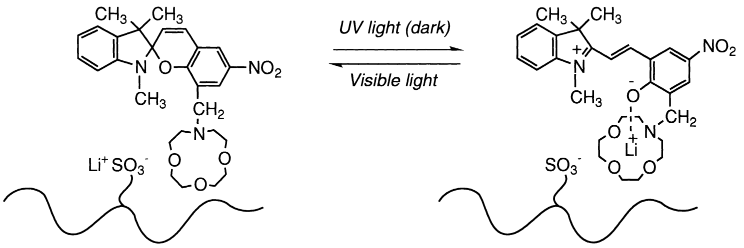
Fig. 7. Alkali-metal ion extraction by crowned Malachite Green polymer **33**($m = 0.4$, $n = 0.6$) (□) and comparison with monomeric model **28** (●).[83]

4. Applications to Photoresponsive Ion-Conducting Materials

Photoresponsive Ion-Conducting Materials. Organic ion conductors or polymer electrolytes are attractive materials for ionics.[84,85] Many organic ion-conductors have been designed aiming at making their electrical conductivity comparable to the high values for conventional inorganic ion conductors. There are, however, very few organic ion conductors whose ionic conductivities can be switched by external stimuli such as light. For instance, polymer composite films containing a lithium salt and an azobenzene liquid crystal were investigated as photoresponsive ionic conductors.[86] The azobenzene liquid crystal isomerizes reversibly from its *trans* to *cis* forms by photoirradiation and thereby experiences drastic phase transitions. UV irradiation on the composite film causes distinct phase transitions from the crystal or liquid crystal to the isotropic liquid states, drastically enhancing ion mobility and therefore ionic conductivity in the film. Subsequent visible irradiation again diminished the ionic conductivity. Thus, ionic-conductivity switching is photochemically feasible with the composite films containing photoresponsive azobenzene liquid crystal.

The photoinduced change in the metal-ion complexing ability of crowned spirobenzopyrans in solution opens up the possibility for photochemically controllable ionic conductivity of films containing a crowned spirobenzopyran as the key material. Crowned spirobenzopyran **7**(R = CH_3) was first applied to a bi-ionic conducting system, in which both the cation and anion are able to participate in the ionic conduction.[43] The bi-ionic conducting system is plasticized poly(vinyl chloride) (PVC) film incorporating $LiClO_4$ as the ion-conducting species. In the ion-conducting composite containing crowned spirobenzopyran **7**(R = CH_3), the photoisomerization of crowned spirobenzopyran is quite reversible in the composite film. Visible and UV irradiation increases and decreases, respectively, the free Li^+ activity that contributes mainly to the ionic conductivity and thereby to the ionic conductivity in the composite film. The photoinduced ionic-conductivity changes are synchronized by the photoirradiation.

The photochemical ionic-conductivity control driven by the isomerization of crowned spirobenzopyran can be extended to a single-ionic conducting system, where only a cation participates in ionic conduction, to attain effective ionic-conductivity switching induced by photoirradiation. An example of the single-ionic conducting film is a composite films consisting of lithium poly(perfluorosulfonate) (Li-PPFS) whose ion-conducting carrier is essentially Li^+. Since the cation transference number is nearly 1 in the single-ionic conducting system, drastic photoinduced changes in the ionic conductivity can be expected, based on the mechanism in Scheme 6. In this single-ionic conducting composite film, the photoiomerization of crowned spirobenzopyran also occurs rather efficiently, which in turn leads to such a marked photoresponse of ionic conductivity as shown in Fig. 8, when turning on and off visible light while heating under dark conditions. Isothermal transient ionic-current measurements explain the significant photoinduced change in ionic conductivity of the Li-PPFS/**7**(R = CH_3) composite film (Fig. 9). After an appropriate direct-current voltage is applied across the composite film, the quick polarity switching produces transient ionic current. Each ionic current peak in the plots of ionic current (I) vs time is derived from Li^+ conduction in the single-ionic conducting composite film. The current peak appeared under visible-irradiated conditions earlier than under dark conditions. This indicates a higher Li^+ mobility under visible-irradiated conditions, i.e. the spiropyran-rich (nearly 100 %) conditions than under dark conditions, i.e. the merocyanine-rich (> 70 %) conditions. The drift mobility 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 to 3.0×10^{-11} $cm^2\,s^{-1}\,V^{-1}$ for visible irradiation. Turning off the visible light restores the ion mobility to 2.7×10^{-11} $cm^2\,s^{-1}\,V^{-1}$. In general, ionic conductivity can be expressed as $s = q\,n\,\mu$, where q, n, and μ stand for ionic charge, carrier density, and ion mobility, respectively. Taking into consideration that the ionic conductivity is about 20-fold greater under visible-irradiated conditions than under dark conditions, while the ion mobility is about 10-fold greater under the former conditions than under the latter ones, one can conclude that the photoinduced ionic-conductivity change for the single-ionic conducting composite film containing crowned spirobenzopyran **7**(R = CH_3) is governed by a change in the Li^+ mobility rather than in the carrier density. Spironaphthoxazine derivatives, which generally show excellent light-fatigue resistance,[87,88] are expected to be more reliable and durable photochromic materials than their corresponding spirobenzopyran derivatives. Marked photochemical switching of ionic conductivity can also be realized with both of the PVC- and Li-PPFS-based composite films containing crowned spironaphthoxazine **15**.[53] By visible irradiation, Li^+, the ionic carrier in films tends to be released from the crowned spironaphthoxazine–metal complexes. The ionic conductivity of the composite film is thus increased as anticipated from Scheme 1 (bottom). Following UV irradiation allows the open colored form of crowned spironaphthoxazine to bind Li^+ strongly, therefore decreasing the ionic conductivity. The photochemical ionic-conductivity switching in the composite films containing crowned spironaphthoxazine **15** is excellently reversible and reproducible, as demonstrated in Fig. 10. Even after 30-cycle irradiation of UV and visible lights, the magnitude in the ionic-conductivity change is almost constant in the Li-PPFS-based composite films. In similar composite films containing a crowned spirobenzopyran instead of the crowned spironaphthoxazine,[43] some light fatigue or deterioration is observed after several photoirradiation cycles; the magnitude in the photochemical ionic-conductivity change decreases with photoirradiation cycle. Definitely, the high durability of the photochemical ionic-conductivity switching system containing **15** as the key compound is ascribable to the excellent light-fa-



Scheme 6. Photocontrol of ionic conduction in single-ionic systems consisting of lithium poly(perfluorosulfonate) and crowned spirobenzopyran **7**(R = CH_3).

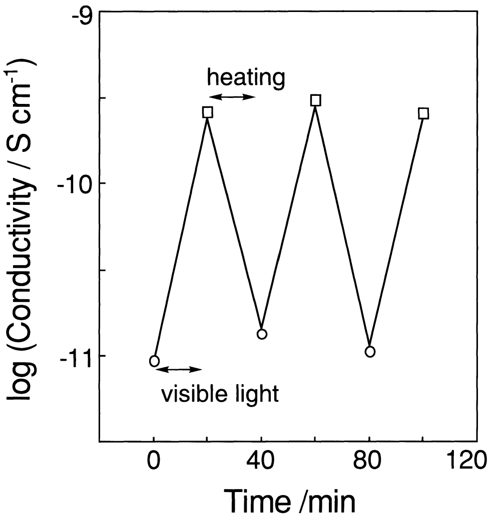


Fig. 8. Photoinduced ionic-conductivity changes in single-ionic conducting composite film of Li-PPFS/**7**(R = CH_3) on turning on and off visible light while heating at 70 °C under dark conditions.[43] Photoirradiation started at each point of ○ and then finished at the point of □ for visible light, and vice versa for heating at dark.

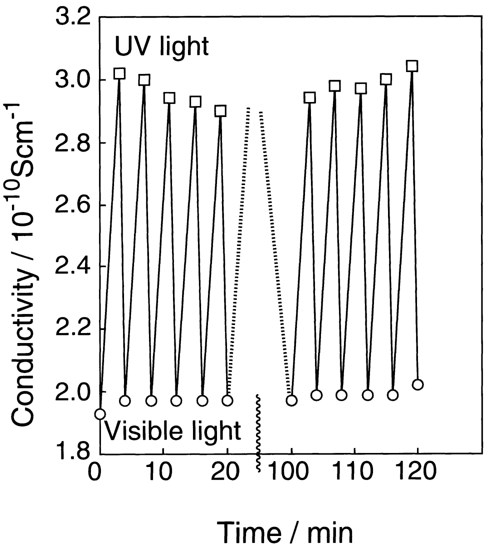


Fig. 10. Photoinduced ionic-conductivity changes for single-ionic conducting composite film of Li-PPFS/crowned spironaphthoxazine **15**.[53] Photoirradiation started at each point of ○ and then finished at the point of □ for visible light, and vice versa for UV light.

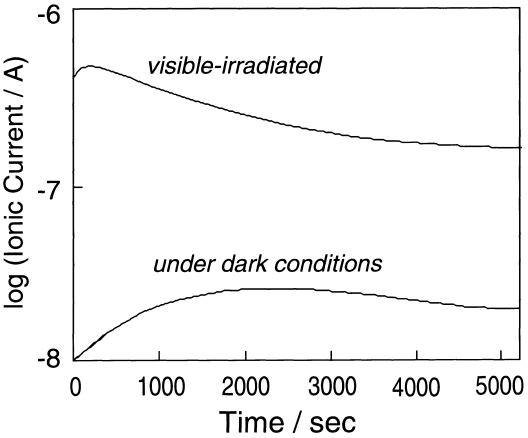


Fig. 9. Isothermal transient ionic-currents for single-ionic conducting composite film of Li-PPFS/**7**(R = CH_3).[43]

tigue resistance of the spironaphthoxazine derivative itself.

Since the photoisomerization of crowned bis(spirobenzopyran)s such as **21**–**23** proceeds even in the presence of a multivalent metal ion like Ca^{2+}, the intramolecular interaction of a crown-ether-complexed multivalent metal ion with two phenolate anions of its merocyanine moiety can be controlled photochemically. The photochemical metal-ion complexation control system of the crowned bis(spirobenzopyran) can therefore be applied to ionic-conductivity photocontrol in systems using multivalent cations as the ion-conducting carrier, which are promising for high-energy ion-conducting devices.[61] Visible irradiation on a composite film of plasticized PVC, **21**(n = 2), and $Ca(ClO_4)_2$ increases the ionic conductivity and the following UV irradiation decreases it. Similar ionic-conductivity changes can be also found by alternation of visible irradiation and heating in the dark. However, since not only Ca^{2+} but also its counteranion takes part in ionic conduction in the ion-conducting composite films containing $Ca(ClO_4)_2$, the contribution of the photoinduced changes of metal-ion complexing ability to the ionic-conductivity changes might be lowered by that of the counteranion. If a Ca^{2+} salt with large anions is employed, the contribution of anion conduction may be alleviated, leading to more remarkable photoinduced ionic-conductivity changes. The photoinduced switching for composite films containing calcium bis{bis[p-(1,1,3,3-tetrametylbutyl)phenyl]phosphate} (Ca-HDOPP) instead of $Ca(ClO_4)_2$ enhanced the switching magnitude in the ionic-conductivity changes by alternation of visible irradiation and heating in the dark, as expected. In both of the ion-conducting systems containing $Ca(ClO_4)_2$ and Ca-HDOPP, the photoinduced ionic-conductivity switching is almost reversible.

Malachite Green leuconitrile itself photoionizes intermolecularly, and ionic conductivities can be therefore regulated photochemically, by using Malachite Green dyes in solution and polymer.[27–29] Photoinduced switching of ionic conductivity was also attempted in PVC- and Na-PPFS-based composite films containing crowned Malachite Green **27**. The photoionization of the Malachite Green leuconitrile moiety of **27** generates two ion-conducting carriers, i.e. a cyanide anion and a triphenylmethyl 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-ether complexable metal ion, Na^+, as shown in Scheme 4 (top), the photoionization brings about release of Na^+ complexed by the crown ether moiety of **27**. The resulting free Na^+ is also able to participate in ionic conduction. In other words, the photoionization of Na^+-complexed crowned Malachite Green **27** 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 irradiation and vice versa by heating without photoirradiation.

The above-mentioned photoresponsive ion-conducting systems containing photochromic crown ethers may be useful for device applications. The ion-conducting materials are applicable to electrostatic imaging,[89] although electron (or hole)-conducting materials are generally employed in recent electrostatic imaging systems.[90] The ionic-conductivity difference between photoirradiated and unirradiated regions of composite films containing a photochromic crown ether can afford image storage, which can be read easily by corona charging. The surface charges induced by corona charging are easily canceled out on the highly ion-conducting photoirradiated region by its internal polarization, while the low ion-conducting unirradiated region still possesses stable surface charges. The latent image can be readily duplicated by a conventional xerographic method. The latent image can last for a while, being memorized after turning off the light. This indicates a possibility for one-time exposure and multi-time printing by the electrostatic imaging systems using the photoresponsive ion-conducting composite films. The latent image can be erased immediately by visible irradiation. Also, the write-in and erasing of the electrostatic image are quite reversible. One other possibility for the device applications of the photoresponsive ion-conducting systems of photochromic crown ethers may be in photowritable electrochromic displays.

Photorefractive Materials. The photorefractive effect can be applied to various types of optical information processing, such as real-time image processing, optical switching, and holographic memory. Design of organic photorefractive materials is being promoted recently.[91,92] In order to attain photorefractivity, the organic materials must possess both photoconductivity and electro-optic effect. Photorefractive materials should, therefore, contain a photoinduced carrier (electric charge) generator, a carrier-transporting medium, a carrier-trapping site, and a nonlinear optical moiety whose refractive index is changed by a space-charge field. In most cases, photoinduced redistribution of electrons or holes (charge generation followed by electric-field induced drift) is responsible for the space-charge field formation, which in turn brings about ordered orientation of the nonlinear optical moiety. Ionic carriers, i.e., cation and anion, should also produce such space-charge fields by ion migration. Ionic conduction is also expected to provide photorefractive systems with memory effect, since ions migrate slowly in the composite films due to their masses. As mentioned above, the photochemical control of metal-ion complexing ability by **7**(R = CH_3) can afford photoinduced ionic-conductivity changes, if the photochromic crown compound is contained in ion-conducting composite polymers. The ionic-conductivity switching system of crowned spirobenzopyran **7**(R = CH_3) in turn leads to a photorefractive effect by redistribution of ionic species.[93]

In composite films consisting of *N*-(4-dimethylaminobenzylidene)-2-methyl-4-nitroaniline (DBMNA) as the nonlinear optical compound, crowned spirobenzopyran **7**(R = CH_3) as the photocontrol agent of ionic conductivity, a lithium salt as the ion-conducting species, and poly(methyl methacrylate) (PMMA) as the binder polymer, diffraction efficiency measured by a four-wave mixing system is increased, when an electric field is applied while irradiating writing and reading beams. Turning off the electric voltage immediately restores most of the initial signal. This suggests that the photoinduced diffraction is ascribable to a photorefractive effect based on space-charge formation caused by the photoinduced metal-ion complexing ability change of crowned spirobenzopyran **7**(R = CH_3). A two-beam coupling experiment proves that the photorefractivity in the present system is based on photoinduced ionic-conductivity switching by crowned spirobenzopyran (Fig. 11). When one applies an electric field to a composite film containing crowned spirobenzopyran **7**(R = CH_3) and Li^+ while irradiating two writing beams of an equal light intensity, one of the writing beams (probe light) is enhanced in the intensity and the other writing beam (pump light) is weakened. This self-diffraction is a decisive proof for the photorefractivity of the present photoinduced ionic-conductivity switching systems of crowned spirobenzopyran. The "straightforward" space-charge formation by the ion migration may be expected to realize higher diffraction efficiencies than that available by the conventional electron (or hole) migration, although the photorefractive system containing crowned spirobenzopyran **7**(R = CH_3) does not show very high diffraction efficiency at the moment.

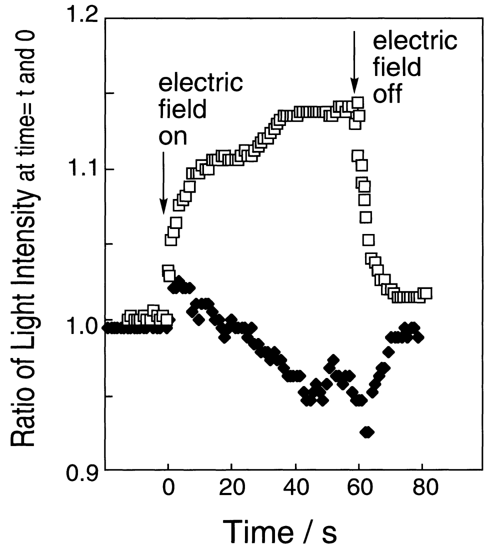


Fig. 11. Two-beam coupling measurement for photorefractive composite film of Li-PMMA/DBMNA/**7**(R = CH_3).[93] Electric field: 75 Vmm^{-1}. (□) probe light; (■) pump light.

5. Applications to Ion Sensing and Separation (Photo-Enhanced Sensing and Separation)

Photo-Enhanced Metal-Ion Extraction. Chromogenic crown ethers have been reported as colorimetric reagents for alkali metal ions. One type is in compounds bearing a chromophore that cannot ionize potentially. On complexation of such compounds with a metal ion, the donor atom in the chromophore interacts directly with the metal ion to change its absorption spectra.[72] For instance, triscrowned Crystal Violet **29** exhibits an anomalous absorbance change at the UV region of absorption spectrum, based on its distorted structural change by Cs^+ complexation.[73] Triscrowned Crystal Violet **29** is a candidate for Cs^+ spectrophotometric reagent by virtue of its perfect selectivity for Cs^+ in the spectral change. The absorption spectra of the chromogenic crown ethers bearing a nonionizable chromophore may, however, not change remarkably on the metal ion complexation with their crown ether moiety, because the perturbation of their chromophore by the metal ion complexation is generally not very significant. In crown ethers having an ionizable chromophore, which is deprotonated on the metal ion complexation with their crown ether moiety, on the other hand, the spectral change of their chromophore moiety is generally drastic due to the marked perturbation by their ionization of the chromophore moiety themselves.[94] Taking into consideration that the ionizable chromogenic crown ethers can extract metal ions from aqueous to organic phases without accompanying independent counteranions, one can conclude that they are promising reagents for extraction spectrophotometry of metal ions.

The crowned spirobenzopyrans and spironaphthoxazines as described above are a kind of chromogenic crown ethers incorporating an ionizable chromophore. The spirobenzopyran and spironaphthoxazine moieties are isomerized to their corresponding merocyanine form (open form) on their metal ion complexation with the crown ether moiety, which in turn brings about significant color changes. For instance, crowned spirobenzopyran **7**(R = CH_3) undergoes metal-ion induced coloration, based on the isomerization from the spiropyran to merocyanine forms, which are selective for Li^+ in alkali metal ions. In crowned spironaphthoxazine **15**, the Li^+ selectivity in the metal-ion induced coloration may be more drastic than the corresponding spirobenzopyran, as already shown in Fig. 4. The authors have attempted to use crowned spirobenzopyran **7**(R = CH_3, $C_{18}H_{37}$) as an extraction-spectrophotometric reagent for alkali metal ions.[44,95] On extraction of alkali metal picrates, crowned spirobenzopyran **7**(R = CH_3) is quite selective for Li^+. As expected, the absorption spectra for the organic phase after extraction of alkali metal ions with crowned spirobenzopyran show strong absorption peaks which have been assigned to its merocyanine form, indicating clearly that the metal ion extraction causes the isomerization of **7**(R = CH_3) to its merocyanine form in a similar way to the metal ion complexation in the one-phase system. A lipophilic counter anion is required for the effective metal-ion extraction with crowned spirobenzopyran (Fig. 12). Even at a high pH value, Li^+ extraction does not occur without a lipophilic anion such as picrate anion. A comparison in the extraction behavior of crowned spirobenzopyran **7**(R = CH_3) shows that the Li^+ selectivity against Na^+, which is an important factor for practical applications, is quite good on the extraction spectrophotometry.

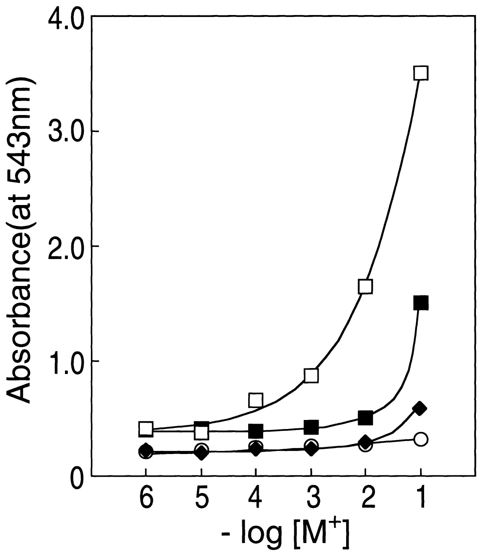
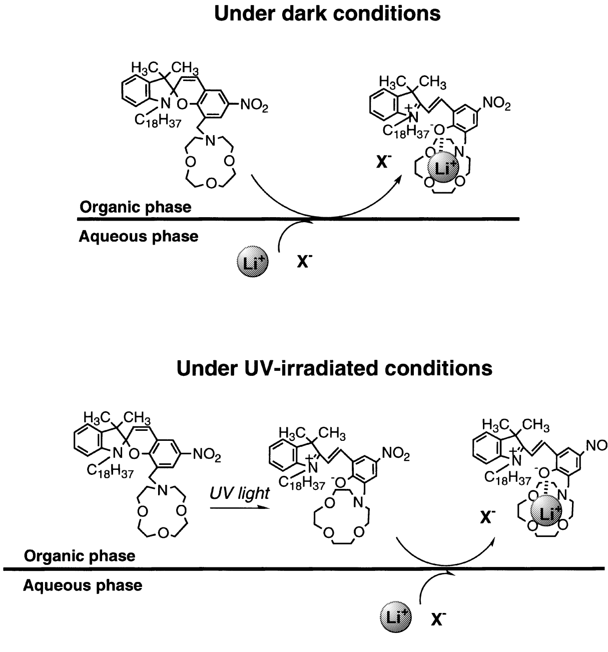


Fig. 12. Metal ion extraction with crowned spirobenzopyran **7**(R = CH_3). (□) Li^+, with picric acid ; (◆) Li^+, with perchloric acid; (○) Li^+, without acid ; (■) Na^+, with picric acid. Organic phase: 2×10^{-3} mol dm^{-3} **7**(R = CH_3) in 1,2-dichloroethane.[44] Aqueous phase: different concentrations of MCl and 1×10^{-1} mol dm^{-3} (pH 12.7) KOH, with and without 1×10^{-3} mol dm^{-3} acid (picric or perchloric acid). Extracted for 20 min under dark conditions.



Scheme 7. Plausible mechanism in photo-enhanced metal-ion extraction by crowned spirobenzopyran **7**(R = $C_{18}H_{37}$).

Marked promotion in the Li^+ extraction is expected in the present Li^+ extraction–spectrophotometric system by the photoisomerization of crowned spirobenzopyran **7**(R = $C_{18}H_{37}$), as illustrated in Scheme 7. Extraction of Li^+ by crowned spirobenzopyran **7**(R = $C_{18}H_{37}$) was carried out under UV-irradiated conditions. The absorbance for the merocyanine isomer in the organic phase, that is, the sensitivity on the Li^+ extraction spectrophotometry is higher under UV-irradiated conditions than under dark conditions, especially at relatively short extraction times. Thus, crowned spirobenzopyran is useful for extraction spectrophotometry whose sensitivity can be attenuated by photoirradiation. Similarly, the other crowned spirobenzopyrans, spironaphthoxazines, and spirobenzothiopyrans also have potentiality for use as photo-enhanced extraction-spectrophotometric reagents.

Liquid–liquid extraction using water and a water-immiscible organic solvent is a conventional system for metal ion separation with ion-selective ligands, but the two-liquid-phase system is not necessarily efficient for the extraction. Metal-ion extraction through micelle, which is called coalescence extraction, may be a better extraction system, due to the efficient extraction based on the wide area of micellar interface and the easy phase separation. Metal-ion complexing property of crowned spirobenzopyran **7**(R = $C_{18}H_{37}$) in aqueous micellar solutions containing dodecyl sulfate ion as an anionic surface-active agent was investigated by the authors who expected effective extraction of metal ion and thereby efficient coloration of spirobenzopyran derivative in micellar solution.[96] The aqueous alkaline solution containing **7**(R = $C_{18}H_{37}$) without any metal ion shows an absorption spectrum with a maximum absorption wavelength at 549 nm. On addition of a metal ion, the maximum absorption wavelength was shifted to a shorter wavelength with increasing Li^+ concentration selectively (Fig. 13). Addition of Na^+ gives rise to a slight shift of the maximum absorption wavelength, while addition of K^+ and Cs^+ hardly changes the original wavelength. To the contrary, no significant shift in the maximum absorption wavelength of the solution containing a spirobenzopyran carrying a piperidine moiety was observed after addition of any alkali metal chloride. The monoaza-12-crown-4 moiety of crowned spirobenzopyran **7**(R = $C_{18}H_{37}$), therefore, forms complexes with Li^+ selectively in the micellar surface, as shown schematically in Scheme 8. Thus, the Li^+ selectivity in the absorption-spectral change and the concentration dependence of the maximum absorption wavelength may be useful for Li^+ analysis. Sensitivity and selectivity in the Li^+ analysis using the micellar system might be enhanced by photoirradiation that induces the isomerization of the photochromic moiety of crowned spirobenzopyran.

Although some photoinduced enhancement is expected in the metal-ion extraction spectrophotometry using photochromic crown ethers, the extraction spectrophotometry under photoirradiated conditions may not be very easy during a batch process. Flow injection analysis (FIA) systems may allow the extraction spectrophotometry under photoirradiated conditions to be more effective and reproducible.[97]

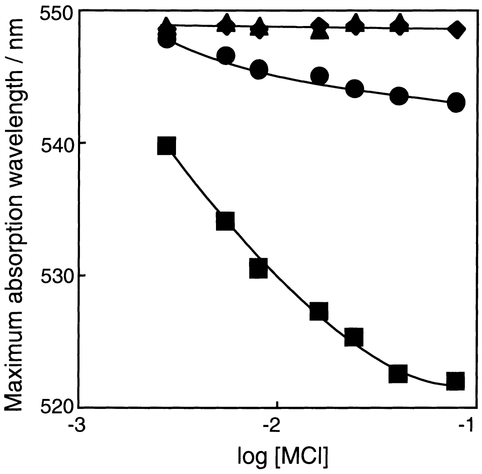
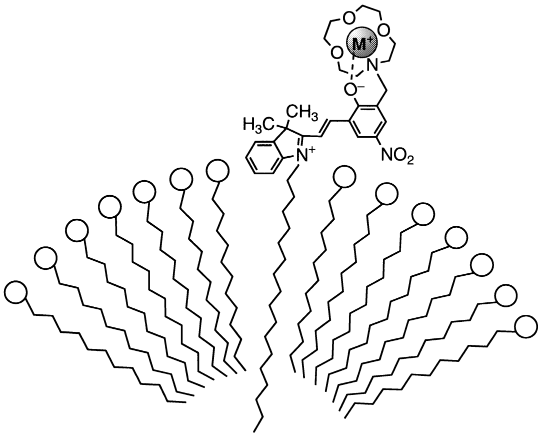


Fig. 13. Dependence of maximum absorption wavelength of aqueous micellar alkaline solution on concentration of **7**(R = $C_{18}H_{37}$). (■) Li^+; (●) Na^+; (▲) K^+; (◆) Cs^+. [**7**(R = $C_{18}H_{37}$)]: 1.4 × 10^{-5} mol dm^{-3}; [tetramethylammonium dodecyl sulfate]: 8.6 × 10^{-3} mol dm^{-3}; [tetramethylammonium hydroxide]: 0.1 mol dm^{-3}.[96]



Scheme 8. Plausible structure for formation of complexes of **7**(R = $C_{18}H_{37}$) and metal ion in aqueous micellar alkaline solution.[96]

Photocontrolled Ion Selectivity in Membrane Potential. An application of photochromic crown ethers to photo-enhanced sensing and separation is expected in potentiometric ion sensors such as ion-selective electrodes. Since crowned spirobenzopyran is electrically neutral in its spiropyran form, its crown ether moiety may exchange cations by ion-dipole interaction. 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 interaction. It is, therefore, of much interest to investigate how the membrane potential occurs at the interface between electrolyte solutions and membranes containing a crowned spirobenzopyran and how the potential responds to its photoisomerization. This is also the case with crowned Malachite Green (or Crystal Violet), i.e., its electrically neutral form is cation-selective and its photoinduced cationic form is anion-selective. The photochromic crown ethers might, therefore, realize sophisticated ion-sensing systems such as ion sensors whose ion selectivity can be photochemically switched between cations and anions.

In membranes containing a spirobenzopyran without crown ether moiety, the membrane potential is changed photochemically at the interface with an aqueous phase.[22,24,98–100] At the interface with an aqueous phase, the UV-light induced merocyanine isomer of the spirobenzopyran, zwitterionic species, is protonated, affording positively charged species in the membrane, which in turn leads to a membrane potential change. Even in membranes containing a crowned spirobenzopyran, similar membrane-potential photoresponse can be seen to some extent at the interface with an electrolyte aqueous solution, but some metal ion dependence is reflected in the photoresponse of membrane potential owing to the competitive binding of its merocyanine isomer carrying a crown ether moiety between H^+ and a metal ion.[33,45] Anyway, at the membrane interface with an aqueous phase, no dramatic photoresponse in membrane potential, such as photoinduced selectivity switching between cation and anion, have yet been attained with membrane systems containing a crowned spirobenzopyran mainly due to the easy protonation of the merocyanine isomer by water-dissociated protons. At the membrane interphase with an aprotic organic solution, photoinduced selectivity switching between cation and anion might be realized as expected.

6. Conclusion

This account has proved that photochromic crown compounds undergoing photoionization are promising key materials for efficient photochemical control of metal ion complexation based on molecular control of ionic interaction of their photoinduced ionic sites with a metal ion in their crown ether rings. Several applications of the photochromic crown compounds have been made in materials and analytical chemistry.

Drastic photoinduced switching in the ionic conductivity is feasible by designing ion-conducting systems of photochromic crown ethers. Ion-conducting composite films containing photochromic crown compounds are useful for device applications for memory, display, and printing such as electrostatic image storage and photorefractivity. Another application of photoresponsive ion-conducting materials might be in photowritable electrochromic display. The photoinduced control between the precipitation and solubilization of the vinyl copolymers of spirobenzopyran and crown ether monomers might be utilized in photo-mechanochemistry such as photochemical valves.

The analytical application of photochromic crown compounds, that is, photo-enhanced sensing and separation such as photo-enhanced cation extraction and photocontrolled membrane ion sensing, is now being made by the authors' group. One other possibility for application of photochromic crown compounds to photo-enhanced separation systems may be in light-driven membrane transport and photoregulative chromatography. Taking into consideration that the metal-ion complexing property of the photochromic crown ethers mentioned above can be controlled photochemically, one can see that uphill transport of metal ions would be possible with membranes containing a photochromic crown ether, by photoirradiation at either or both membrane interface(s) with source and receiving aqueous phases. A selective separation and concentration system of valuable metal ions from aqueous solutions by using solar energy might appear in the near future. It is also expected that chromatographic systems using photochromic crown compounds as the stationary and mobile phases will afford a variety of separation behaviors induced by photoirradiation of the separation system.

Finally, since the applications of photochromic crown compounds undergoing photoionization to materials and analytical chemistry are limited at the moment, the authors really hope that the applications are extended to wider areas of science very soon.

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