

Liquid–Liquid Extraction of Alkali Metal Ions with Photochromic Crowned Spirobenzopyrans

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On the liquid–liquid extraction using 1,2-dichloroethane as an organic solvent, the crowned spirobenzopyrans exhibited extractability in the following order: $\text{Li}^+ \gg \text{Na}^+ > \text{K}^+ \geq$ tetramethylammonium ion (TMA^+), $\text{Li}^+ > \text{Na}^+ \gg \text{K}^+ > \text{TMA}^+$, and $\text{Na}^+ > \text{K}^+ \gg \text{Li}^+ > \text{TMA}^+$ for spirobenzopyran derivatives bearing monoaza-12-crown-4, 1; monoaza-15-crown-5, 2; and monoaza-18-crown-6, 3; respectively, under dark conditions. The ion selectivity of 1 depends on the metal-ion complexing ability of monoaza-12-crown-4. Even 2, which carries a 15-crown-5 moiety, showed Li^+ selectivity because of the much stronger interaction of Li^+ with the phenolate ion of the merocyanine form of 2 than that of Na^+ . The Na^+ selectivity of 3 is also attributed to the ionic interaction with the phenolate ion of the merocyanine form, since the ionic interaction prefers Na^+ to K^+ regardless of the higher affinity of the 18-crown-6 ring itself to the latter ion. The Li^+ extraction into the organic phase with 1 was enhanced by UV irradiation (300–400 nm), while some depression in the extraction was found by visible irradiation (>500 nm). The effect of visible irradiation on the Li^+ complexing ability of 1 was also examined with electrospray ionization mass spectrometry.

Some studies on the photocontrol of cation selectivity and extractability have been reported for liquid–liquid extraction using photoresponsive crown ethers.^{1–3} Most of the photoresponsive crown ethers reported so far have an azobenzene moiety in the periphery of their crown ether moieties. The azobenzene moiety is isomerized from the *E* form to the *Z* form by UV irradiation and vice versa by visible irradiation or heating. The difference in size or shape of the crown ether ring results in the change in cation complexing ability. Since the isomerization reaction of azobenzene derivatives is based on a conformation change of the azo group, the electric charge on the compound is not affected by photoirradiation.

Spirobenzopyran derivatives are well-known photochromic compounds and are isomerized to their merocyanine form by UV irradiation, which is reverted to the spiropyran form by subsequent

visible irradiation or heating.^{4–9} The spiropyran form has an electrically neutral form, and the merocyanine one has a zwitter ion. Some physical properties in the periphery are, therefore, modified by photoirradiation. For instance, it is expected that Coulombic interaction can be controlled by the photoisomerization of spirobenzopyran derivatives.

We have been studying the metal-ion recognition properties of spirobenzopyran derivatives bearing a crown ether moiety.^{10–20} We have already observed that, on the complexation of the spirobenzopyran derivative bearing a 12-crown-4 moiety with a lithium ion in acetonitrile solution under dark conditions, the compound was isomerized from the spiropyran form to the merocyanine one and that the resultant complex showed an absorption spectrum between 500 and 600 nm.

Two types of chromogenic crown ethers have been reported as colorimetric reagents for alkali metal ions.^{21–23} One of them is

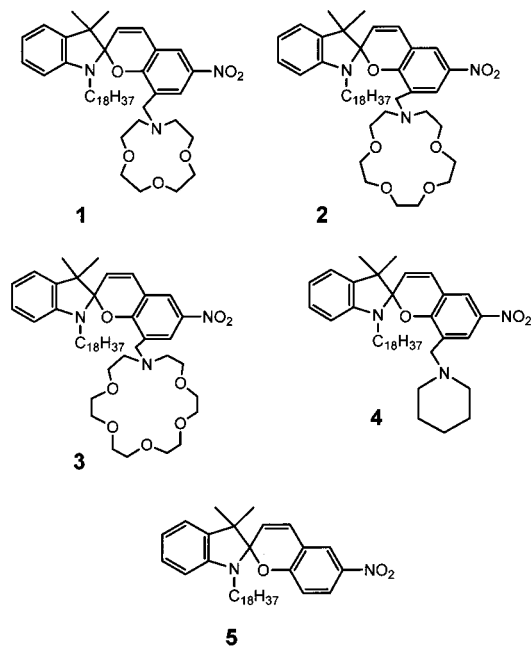
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an electrically neutral compound bearing a donor–acceptor-type chromophore. On the complexation of such compounds with a metal ion, their donor atoms in the chromophore interact directly with the metal ion to change its absorption spectra.^{22,23} The absorption spectra of the organic phase, however, depended on water contents in the organic solvents on liquid–liquid extraction. Another one is a compound having a chromophore with an ionic site that is induced by deprotonation of its chromophore moiety based on metal-ion complexation with its ionophore moiety.^{21,23} The spectral change of the chromophore moiety is caused by the deprotonation and interaction between its ionic site and a metal ion. The deprotonation behavior depends considerably on the pH of the aqueous phase for extraction. The pH value of the aqueous phase should, therefore, be adjusted precisely on liquid–liquid extraction of metal ions. On the other hand, the isomerization of crowned spirobenzopyran derivatives to their corresponding merocyanine form is not affected by the pH value of the aqueous phase in the high pH range; it is affected only by the extent of the interaction between the phenolate ion of the merocyanine form and a metal ion bound to the ionophore moiety. Crowned spirobenzopyran, which does not belong to any of the categories mentioned above for crown ether dyes, is therefore a new type of colorimetric reagent. A most interesting aspect for analytical applications of crowned spirobenzopyran is in photocontrol of separation and analysis. Since the complexing ability of crowned spirobenzopyran for metal ions can be controlled by photoirradiation, its extractability and selectivity for metal ions may be adjusted or changed by photoirradiation. Thus, crowned spirobenzopyran is expected to be an efficient extraction–spectrophotometric reagent.

In this study, we used spirobenzopyran derivatives bearing a monoazacrown ether moiety and a lipophilic alkyl group. The liquid–liquid extraction behavior of several crowned spirobenzopyran derivatives, **1–3**, and analogous spirobenzopyrans, **4** and **5**, for alkali metal ions was examined by spectrophotometry under dark conditions. The extraction of Li^+ with **1** is also described under UV and visible irradiation conditions.



EXPERIMENTAL SECTION

Materials. Crowned spirobenzopyran **1** and spirobenzopyran without crown ether moiety **5** were synthesized as mentioned elsewhere.¹⁷ Chloroform, dichloromethane, 1,2-dichloroethane, methanol, ethanol, and ethyl acetate were purified by distillation. Tetrahydrofuran (THF) was distilled over LiAlH_4 . Methyl isobutyl ketone (MIBK) and 1,1,1-trichloroethane were of analytical reagent grade. Water was deionized. The organic solvents were shaken with deionized water before using for extraction experiments. The buffer reagents, 2-morpholinoethanesulfonic acid monohydrate (MES), 2-[4-(2-hydroxyethyl)-1-piperazinyl]ethanesulfonic acid (HEPES), *N*-cyclohexyl-2-aminoethanesulfonic acid (CHES), and *N*-cyclohexyl-3-aminopropanesulfonic acid (CAPS) were of analytical grade from Dojindo Lab.

Synthesis. *15-Crown-5 Spirobenzopyran 2.* An ethanol solution (100 mL) of 1-octadecyl-3,3-dimethyl-2-methyleneindoline²⁴ (5.6 mmol) and 2-hydroxy-3-formyl-5-nitrobenzyl monoaza-15-crown-5¹² (5.2 mmol) was refluxed for 20 h. After the reaction, the ethanol was evaporated off to yield a crude product of 15-crown-5 spirobenzopyran **2**, which was then purified by silica gel column chromatography using chloroform–ethyl acetate (3/2) as an eluent to yield a dark-brown viscous liquid (yield: 29%) (R_f = 0.45 in silica gel thin-layer chromatography). ^1H NMR (CDCl_3) δ 0.88 (t, J = 6.9 Hz, 3H, $\text{N}(\text{CH}_2)_{17}\text{CH}_3$), 1.17–1.33 (m, 38H, $\text{NCH}_2(\text{CH}_2)_{16}\text{CH}_3$ and $\text{C}(\text{CH}_3)_2$), 2.63 (t, J = 3.6, 4H, $\text{ph-CH}_2\text{NCH}_2\text{CH}_2\text{O}$), 3.08 (t, J = 7.4, 2H, $\text{NCH}_2(\text{CH}_2)_{16}\text{CH}_3$), 3.44–3.70 (m, 18H, OCH_2 and $\text{ph-CH}_2\text{N}$), 5.82 (d, J = 10.5, 1H, $\text{CCH}=\text{CH-ph}$), 6.53 (d, J = 7.8, 1H, 7'-H of indoline), 6.82 (d, J = 7.2, 1H, 6'-H of indoline), 6.88 (d, J = 10.5, 1H, $\text{CCH}=\text{CH-ph}$), 7.06 (d, J = 6.6, 1H, 5'-H of indoline), 7.15 (t, J = 7.5, 1H, 4'-H of indoline), 7.88 (d, J = 2.7, 1H, 5-H of benzopyran), 8.27 (d, J = 2.7, 1H, 7'-H of indoline); m/z (relative intensity) = 792 ($\text{M} + \text{H}^+$; 100).

18-Crown-6 Spirobenzopyran 3. The compound was synthesized by the coupling reaction of monoaza-18-crown-6²⁵ and 1-octadecyl-3,3-dimethylindolino-6'-nitro-8'-chloromethylspirobenzopyran, which was in turn prepared in a similar way to that reported in the literature.^{26,27} The mixture of 1-octadecyl-3,3-dimethyl-2-methyleneindoline (4.8 mmol) and 2-chloromethyl-5-nitrosalicylaldehyde (4.5 mmol) in dry THF (50 mL) was stirred while refluxing for 90 min. After the reaction, the solvent was evaporated in vacuo to yield 1-octadecyl-3,3-dimethylindolino-6'-nitro-8'-chloromethylspirobenzopyran, which was then subjected to the subsequent reaction without purification. The mixture of 1-octadecyl-3,3-dimethylindolino-6'-nitro-8'-chloromethylspirobenzopyran (4.3 mmol), 1,4,7,10,13-pentaoxa-16-aza-cyclooctadecane (monoaza-18-crown-6) (3.6 mmol) and triethylamine (10.8 mmol) in dry THF (70 mL) was refluxed while stirring for 36 h and then was allowed to stand for cooling. The THF was evaporated off in vacuo to yield 18-crown-6 spirobenzopyran **3**, which was purified by silica gel column chromatography using ethyl acetate–methanol (9/1) as an eluent to yield a dark brown viscous liquid (yield: 23%) (R_f = 0.55 in silica gel thin-layer chromatography). ^1H NMR (CDCl_3) δ 0.88 (t, J = 6.8 Hz, 3H, $\text{N}(\text{CH}_2)_{17}\text{CH}_3$), 1.25–1.63 (m,

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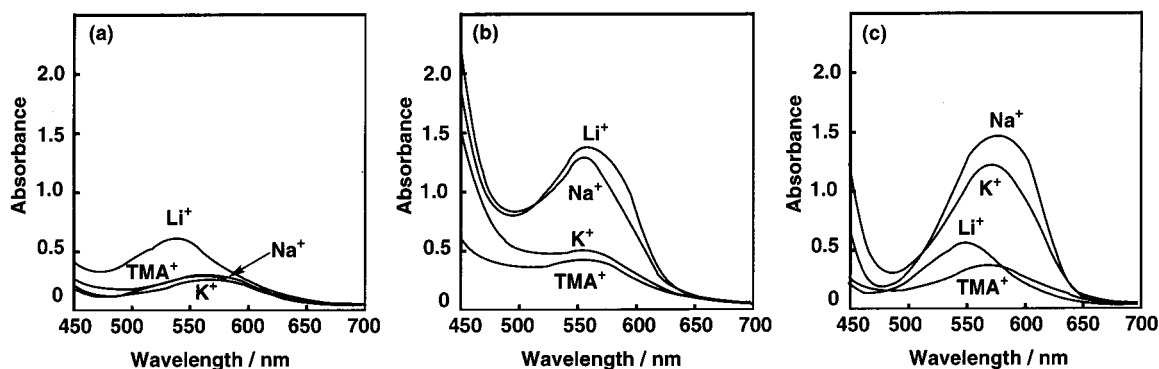


Figure 1. Absorption spectra of the organic phase on extraction of alkali metal ions with (a) **1**, (b) **2**, and (c) **3** under dark conditions. Organic phase: [crowned spirobenzopyran] = 1.0×10^{-3} M in 1,2-dichloroethane. Aqueous phase: [MOH] = 1.0×10^{-2} M, [picric acid] = 5.0×10^{-5} M.

38H, $(\text{CH}_2)_{16}\text{CH}_3$ and $\text{C}(\text{CH}_3)_2$, 2.60–2.72 (m, 4H, $\text{ph-CH}_2\text{NCH}_2\text{-CH}_2\text{O}$), 3.05–3.16 (m, 2H, $\text{NCH}_2(\text{CH}_2)_{16}\text{CH}_3$), 3.44–3.67 (m, 22H, OCH_2 and $\text{ph-CH}_2\text{N}$), 5.84 (d, $J = 10.3$, 1H, $\text{CCH}=\text{CH-ph}$), 6.54 (d, $J = 7.8$, 1H, 7'-H of indoline), 6.83 (1H, t, $J = 7.0$, 6'-H of indoline), 6.89 (1H, d, $J = 10.2$, $\text{CCH}=\text{CH-ph}$), 7.06 (1H, d, $J = 5.9$, 5'-H of indoline), 7.15 (m, 4H, 4'-H of indoline), 7.89 (d, $J = 2.9$, 1H, 5-H of benzopyran), 8.26 (d, $J = 2.8$, 1H, 7'-H of indoline); m/z (relative intensity) = 836 ($\text{M} + \text{H}^+$; 100).

Piperidine Spirobenzopyran 4. The compound was synthesized with 1-octadecyl-3,3-dimethyl-2-methyleneindoline (1.5 mmol) and 2-hydroxy-3-formyl-5-nitrobenzyl piperidine (1.5 mmol)²⁸ in a manner similar to that described for 15-crown-5 spirobenzopyran **2**. The purification of piperidine spirobenzopyran **4** was performed using silica gel column chromatography with chloroform–methanol (97/3) to yield a dark brown viscous liquid (yield, 61%) ($R_f = 0.7$ in silica gel thin-layer chromatography using chloroform–ethyl acetate (1/1) as an eluent). ^1H NMR (CDCl_3) δ 0.87 (t, $J = 7.0$ Hz, 3H, $\text{N}(\text{CH}_2)_{17}\text{CH}_3$), 1.18–1.64 (m, 44H, $(\text{CH}_2)_{16}\text{CH}_3$, piperidine $\text{NCH}_2(\text{CH}_2)_3\text{CH}_2$ and $\text{C}(\text{CH}_3)_2$), 2.60–2.63 (m, 4H, $\text{ph-CH}_2\text{NCH}_2\text{CH}_2$), 3.06–3.14 (m, 2H, $\text{NCH}_2(\text{CH}_2)_{16}\text{CH}_3$), 5.83 (d, $J = 10.3$, 1H, $\text{CCH}=\text{CH-ph}$), 6.55 (d, $J = 7.7$, 1H, 7'-H of indoline), 6.82 (t, $J = 7.0$, 1H, 6'-H of indoline), 6.89 (d, $J = 10.2$, 1H, $\text{CCH}=\text{CH-ph}$), 7.06 (d, $J = 5.9$, 1H, 5'-H of indoline), 7.15 (t, $J = 7.0$, 1H, 4'-H of indoline), 7.85 (d, $J = 2.8$, 1H, 5-H of benzopyran), 8.24 (d, $J = 2.8$, 1H, 7'-H of indoline); m/z (relative intensity) = 658 ($\text{M} + \text{H}^+$, 100). Anal. Calcd. for $\text{C}_{42}\text{H}_{63}\text{N}_3\text{O}_3$: C, 76.67; H, 9.65; N, 6.39. Found: C, 76.71; H, 9.70; N, 5.91.

Cation Extraction. The cation extraction was carried out under dark,¹⁴ UV, and visible irradiation conditions. Under dark conditions, into a 50-mL centrifuge tube were placed an organic solution (4 mL) of 1.0×10^{-3} M spirobenzopyran derivative and an aqueous solution (4 mL) containing 5.0×10^{-5} M picric acid and 1.0×10^{-2} M alkali metal hydroxide or 1.0×10^{-2} M tetramethylammonium hydroxide (TMAOH). Unless otherwise stated, 1,2-dichloroethane was used as the organic solvent. The Good's buffer solutions (1.0×10^{-2} M), such as MES (for pH 6.0 and 6.5), HEPES (for pH 7.0, 7.5, and 8.0), CHES (for pH 8.5, 9.0, 9.5, and 10.0), and CAPS (pH 10.5 and 11.0), and TMAOH (for pH higher than 11.5) were employed for adjusting the pH. The alkali metal perchlorates were used as metal salts when the pH effect of the aqueous phase on cation extraction was investigated. A mixture of the aqueous and organic solutions was shaken by a

reciprocating shaker under dark conditions for 20 min. After phase separation, the organic phase was subjected to the subsequent absorption-spectral measurement. For the calibration graph, the concentrations of LiClO_4 in the aqueous phase were altered between 2.0×10^{-3} and 1.0×10^{-2} M, and the pH value was adjusted using 1.0×10^{-2} M TMAOH. Under UV and visible irradiation conditions, a 1,2-dichloroethane solution (3 mL) of 1.0×10^{-3} M spirobenzopyran derivative and an aqueous solution (4 mL) containing 5.0×10^{-5} M picric acid and 1.0×10^{-2} M alkali metal hydroxide or 1.0×10^{-2} M tetramethylammonium hydroxide (TMAOH) were introduced into a 10-mL quartz cell for photoirradiation. The mixed solution was allowed to stand for 10 min with photoirradiation through a quartz cell at a distance of 8 cm from a light source and was then shaken for 30 s with photoirradiation. UV light (300–400 nm) and visible light (>500 nm) were obtained by passing a light from a Xe lamp equipped with a quartz waveguide through a Toshiba UV-D36B and a Toshiba Y-50 color filter, respectively. After the shaking, the mixed solution was allowed to stand for 3 min for phase separation under photoirradiation conditions. The organic phase was separated for absorption-spectral measurement.

Mass Spectral Measurements. Electrospray ionization mass spectrometry (ESI-MS) was used for the elucidation of species extracted with the spirobenzopyran derivatives into the organic phase for extraction. Cation competitive extraction was carried out under dark conditions in the same way as mentioned above. The 1,2-dichloroethane solution (4 mL) of **1** and the aqueous solution containing LiOH , NaOH , KOH , and TMAOH at 1.0×10^{-2} M each and 5.0×10^{-5} M picric acid were used for the extraction. After the competitive extraction, the organic phase was supplied for ESI-MS measurement using a Finnigan LCQ-Deca mass spectrometer. ESI-MS was performed at 250 °C under dark conditions with a sample flow rate of $10 \mu\text{L min}^{-1}$. The sheath gas rate was set at 20 units under a condition of N_2 pressure at 0.73 MPa. The measurements for the competitive Li^+ complexation between **1** and 15-crown-5 in acetonitrile were carried out under dark and visible irradiation conditions. The acetonitrile solution contained **1**, 15-crown-5, and LiNO_3 at a concentration of 5.0×10^{-5} M each.

RESULTS AND DISCUSSION

Cation Extraction with Crowned Spirobenzopyran under Dark Conditions. For the liquid–liquid extraction, we used an aqueous phase containing an alkali metal or tetramethylammonium (TMA^+) hydroxide and picric acid and an organic phase of

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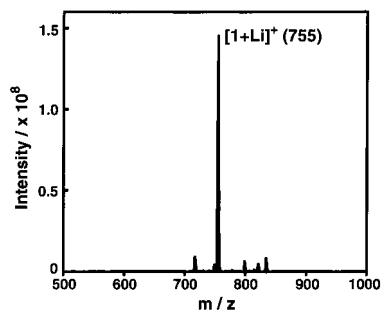


Figure 2. ESI-MS for organic phase on competitive extraction of alkali metal ion mixture with **1** under dark conditions. Organic phase: **[1]** = 1.0×10^{-3} M in 1,2-dichloroethane. Aqueous phase: **[MOH]** = 1.0×10^{-2} M each (M = Li, Na, K, TMA), **[picric acid]** = 5.0×10^{-5} M.

a crowned spirobenzopyran 1,2-dichloroethane solution. Extraction was carried out at first under dark conditions. The absorption spectra of the organic phases after the liquid–liquid extraction are summarized in Figure 1. For 12-crown-4 derivative **1**, the absorbance at 540 nm on the extraction of Li^+ is much greater than those in the case of the other metal ions. The absorption-spectral change was caused by isomerization of the spirobenzopyran derivative from its spiropyran form to the merocyanine one, because Li^+ complexed by its crown ether moiety interacts with a phenolate ion of the merocyanine form.^{10–18} The stoichiometry of the Li^+ complexes extracted into the organic phase was determined by ESI-MS (Figure 2). The mass spectrum for the organic phase on the competitive extraction of Li^+ , Na^+ , and K^+ shows a single strong peak for the Li^+ complex of **1**, and no significant peak was observed for the other metal ion complexes. This result suggests the high Li^+ complexing ability of compound **1** and demonstrates that the remarkable spectral changes of the organic phase on liquid–liquid extraction are caused by the efficient complexation with Li^+ . The monoaza-12-crown-4 moiety interacts weakly with the larger cations, and therefore, the isomerization of **1** is not very remarkable. The 15-crown-5 spirobenzopyran, **2**, also exhibited the greatest change in the absorption spectrum on Li^+ extraction of the three crowned spirobenzopyrans. Although it is well known that 15-crown-5 derivatives form the most stable complex with Na^+ of all alkali metal ions, the extractability of 15-crown-5 spirobenzopyran, **2**, is different from the metal ion complexing ability of the parent crown ether. The 15-crown-5 ring also has an ability to form complexes with Li^+ , although the complex stability for Li^+ is lower than that for Na^+ . On the other hand, Li^+ interacts with the phenolate ion more strongly than Na^+ does, thus forming a more stable complex with **2**. The less spectral change was, therefore, observed on Na^+ extraction with **2**. For 18-crown-6 spirobenzopyran, **3**, the largest change in the absorption spectrum of the organic phase was observed for Na^+ extraction. The sodium ion interacts with the phenolate ion much more strongly than K^+ , whereas, of all alkali metal ions, K^+ generally forms the most stable complex with 18-crown-6 ring. Thus, the stronger interaction of Na^+ with a phenolate ion of the **3** merocyanine form is reflected in the enhanced isomerization and, thereby, extraction. The organic phases containing piperidine spirobenzopyran **4** and the spirobenzopyran derivative without crown ether moiety **5** exhibited no absorption-spectral change on extraction of any alkali metal ions. These results again suggest that, on metal ion

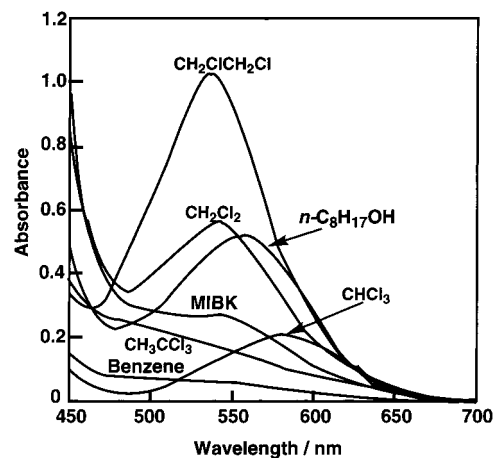


Figure 3. Solvent effect on the absorption spectra of the organic phase on Li^+ extraction with **1** under dark conditions. Organic phase: **[1]** = 1.0×10^{-3} M. Aqueous phase: **[LiOH]** = 5.0×10^{-2} M, **[picric acid]** = 5.0×10^{-5} M.

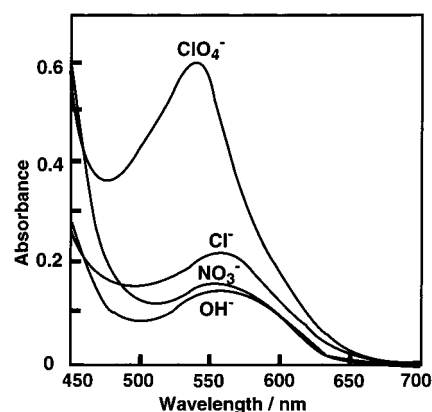


Figure 4. Counterion effect on absorption spectra of the organic phase on Li^+ extraction with **1** under dark conditions. Organic phase: **[1]** = 1.0×10^{-3} M in 1,2-dichloroethane. Aqueous phase: **[LiX]** = 1.0×10^{-2} M (X = ClO_4 , Cl, NO_3) or **[LiOH]** = 1.0×10^{-2} M; **[TMAOH]** = 1.0×10^{-2} M.

extraction with crowned spirobenzopyrans, the absorption-spectral change of the organic phase is attributable to the ionic interaction of the resultant merocyanine form with a metal ion bound to their crown ether moieties.

Solvent Effect on Li^+ Extraction with 12-Crown-4 Spirobenzopyran, 1. The liquid–liquid extraction of Li^+ with **1** was also carried out using other organic solvents under similar dark conditions. Figure 3 shows that the absorption-spectral changes of the organic phase in the visible region, based on the merocyanine isomer of **1**, decreased in the following order: 1,2-dichloroethane (dielectric constant, $\epsilon = 10.5$) \gg dichloromethane (9.1) \geq 1-octanol (10.3) $>$ MIBK (13.1) \geq chloroform (4.9) $>$ 1,1,1-trichloroethane (7.5) $>$ benzene (2.3). The largest absorption change was observed with 1,2-dichloroethane. This means the Li^+ extractability of crowned spirobenzopyran is not necessarily dependent on the dielectric constant of organic solvent employed.

Counteranion Effect on Li^+ Extraction with 12-Crown-4 Spirobenzopyran, 1. Various lithium salts, LiClO_4 , LiNO_3 , LiCl , and LiOH , were used for comparison of counteranions on the Li^+ extractability of **1**. The extraction was carried out under dark conditions, using equal volumes of a 1,2-dichloroethane solution

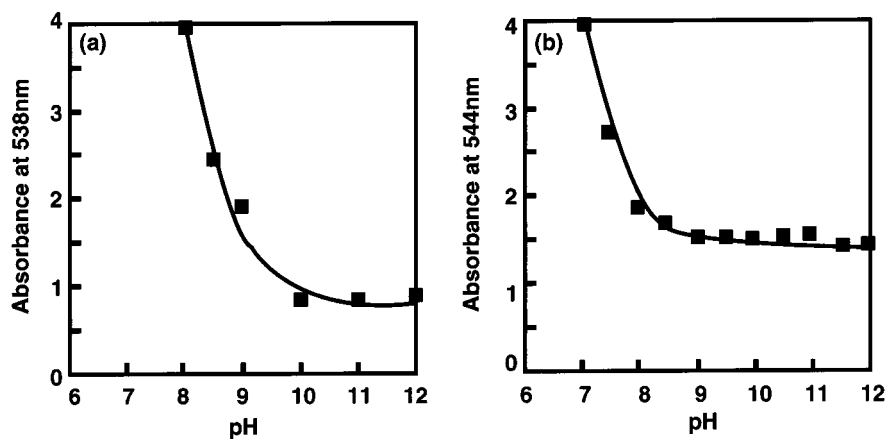


Figure 5. pH dependence on absorbance change of organic phase on extraction of (a) Li^+ with 1, and (b) Na^+ with 2.

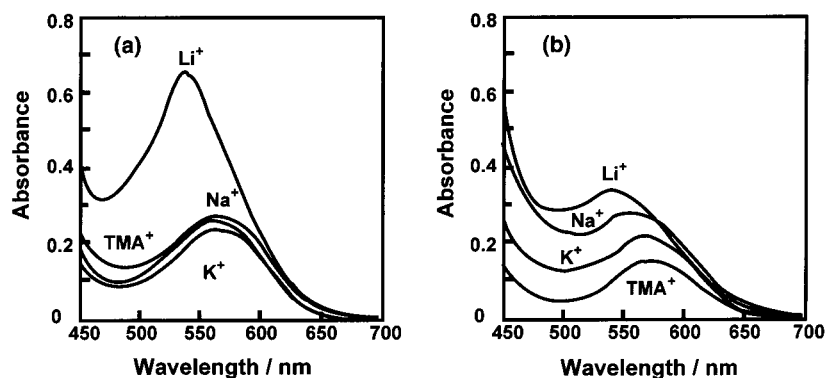


Figure 6. Absorption spectra of the organic phase on metal ion extraction with 1 under (a) UV irradiation and (b) visible irradiation conditions.

of 1.0×10^{-3} M **1** and an aqueous solution containing 1.0×10^{-2} M LiClO_4 , LiNO_3 , or LiCl and 1.0×10^{-2} M TMAOH for adjusting pH or 1.0×10^{-2} M LiOH . The absorption spectra of the organic phase after the extraction were summarized in Figure 4, showing the largest change for the perchlorate extraction. The absorbance change decreased in the following order: $\text{ClO}_4^- \gg \text{Cl}^- > \text{NO}_3^- \geq \text{OH}^-$, which seems dependent on the polarizability, except for Cl^- .^{29,30} This result indicates that the Li^+ extraction is based on the distribution of the ion pair complex in the organic phase. When an aqueous solution containing 1.0×10^{-2} M LiOH and 5.0×10^{-5} M picric acid was used as the aqueous phase, the absorbance at the maximum absorption wavelength (548 nm) was ~ 0.6 , being nearly equal to that on using 1.0×10^{-2} M LiClO_4 . Thus, lithium picrate (LiPic) may be the most favorable Li^+ salt for the extraction.

pH Effects on Cation Extraction with 12-Crown-4 Spirobenzopyran, 1, and 15-Crown-5 Spirobenzopyran, 2. The Li^+ and Na^+ extractions were carried out using **1** and **2**, respectively, under various pH conditions of the aqueous phase (Figure 5). The pH values were adjusted using Good's buffer and TMAOH, and the perchlorates were employed as the salts. Good's buffer exhibited no effect on the absorption-spectral change of the organic phase in the control experiments. For the Li^+ extraction

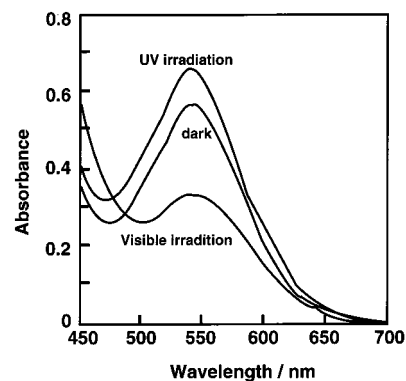


Figure 7. Absorption spectra of the organic phase on Li^+ extraction with **1** under dark, UV, and visible irradiation conditions. Organic phase: $[\mathbf{1}] = 1.0 \times 10^{-3}$ M in 1,2-dichloroethane. Aqueous phase: $[\text{MOH}] = 1.0 \times 10^{-2}$ M ($M = \text{Li, Na, K, TMA}$), $[\text{picric acid}] = 5.0 \times 10^{-5}$ M.

with **1**, the absorbance at 538 nm was constant between pH 10 and 12, but it increased remarkably below pH 10 with decreasing pH. Such an increase in the absorbance may be attributable to the protonation of a nitrogen atom on the crown ether ring, which in turn leads to the extraction of an ion pair of the protonated **1** with perchlorate anion into the organic phase. The nitrogen atom protonation on the crown ether ring of **1** strongly induces the isomerization of its spirobenzopyran moiety to the corresponding merocyanine form and the absorption-spectral change in the visible region. The Li^+ complexation by crown ether moiety of **1** occurs over pH 10 effectively, on the basis of the ion exchange

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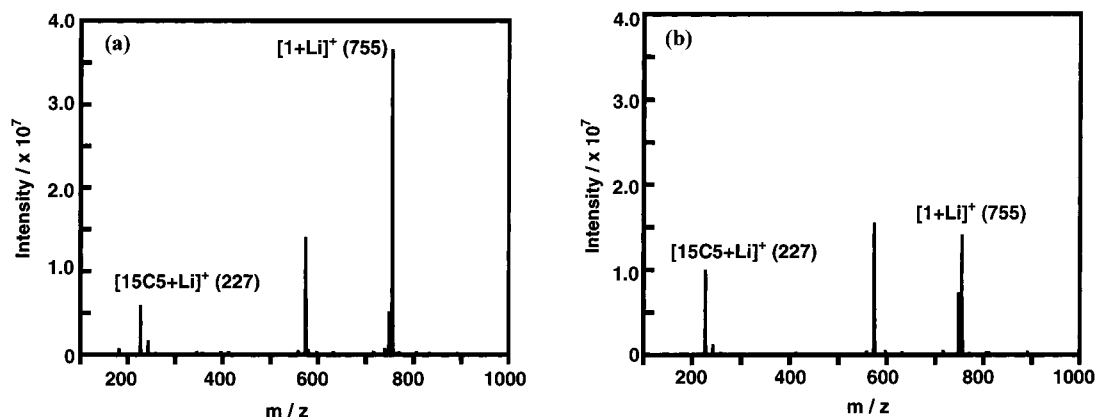


Figure 8. ESI-MS on competitive Li^+ complexation between **1** and 15-crown-5 under (a) dark and (b) visible irradiation conditions. $[\mathbf{1}] = 5.0 \times 10^{-5} \text{ M}$; $[\text{15-crown-5}] = 5.0 \times 10^{-5} \text{ M}$; $[\text{LiNO}_3] = 5.0 \times 10^{-5} \text{ M}$ in acetonitrile.

from proton to Li^+ , thus resulting in the change in the degree of isomerization to the merocyanine form, namely, the absorbance of the organic phase. A similar spectral change was observed for NaClO_4 extraction with **2**. The absorbance of the organic phase was kept constant between pH 9 and 12, and the increase of the absorbance was observed below pH 9. The difference in the pH region for increasing the absorbance, that is, in the ability of ion exchange from proton to metal ion, between **1** and **2** depends on that in the metal ion complexing abilities of their crown ether moieties. Actually, the Na^+ complex of monoaza-15-crown-5 has a much larger stability constant than does the Li^+ complex with monoaza-12-crown-4.³¹ Thus, the extraction experiments in this study were generally carried out at pH 12, unless otherwise specified.

Photoirradiation Effect on Cation Extraction with 12-Crown-4 Spirobenzopyran **1.** The metal ion extraction with **1** was also carried out under UV and visible irradiation conditions. The absorption spectra of the organic phases after extraction are summarized in Figure 6. The absorption spectra on the extraction under photoirradiation conditions are different from those under dark conditions. A comparison in the Li^+ extraction with **1** among under dark, UV, and visible irradiation conditions shows that the absorbance between 540 and 550 nm for the organic phase decreases in the order of UV irradiation > dark > visible irradiation conditions (Figure 7). For the examination of photoirradiation effect on Li^+ complexing behavior of **1**, competitive Li^+ complexation between **1** and 15-crown-5 was investigated in acetonitrile under dark and visible irradiation conditions by using ESI-MS (Figure 8). Under dark conditions, the peak intensity for the Li^+ complex of **1** was much stronger than that for the complex of 15-crown-5. Under visible irradiation conditions, on the other hand, the peak intensity for the Li^+ complex of **1** was decreased, whereas that for the Li^+ complex of 15-crown-5 was increased. These phenomena clearly indicate a marked decrease in the Li^+ complexing ability of **1** under visible irradiation conditions.

These results suggest such extraction mechanisms by crowned spirobenzopyran as shown in Figure 9. Even under dark conditions, the spirobenzopyran moiety of crowned spirobenzopyran is isomerized to its corresponding merocyanine form when its crown ether moiety binds a Li^+ at the boundary phase between

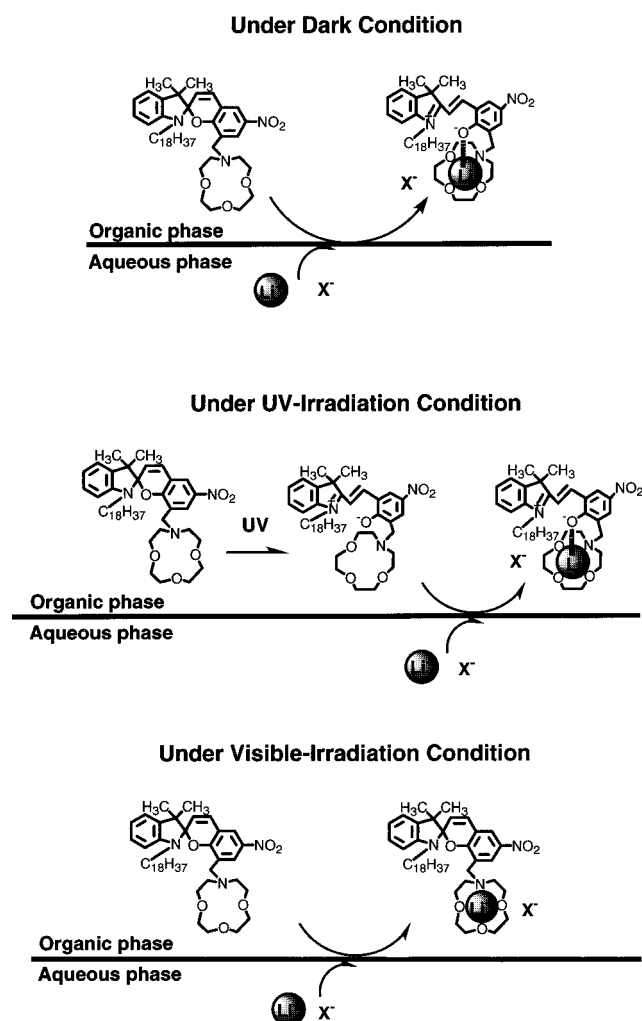


Figure 9. Plausible mechanisms for liquid-liquid extraction of metal ion with crowned spirobenzopyran.

the organic and aqueous phases. A phenolate ion induced by the isomerization to merocyanine form strongly interacts with the Li^+ to form a stable complex, which is then extracted into the organic phase with a counteranion. The **1**- Li^+ complex in the organic phase affords an absorption spectrum at 540 nm. Under UV irradiation conditions, the Li^+ extraction into the organic phase

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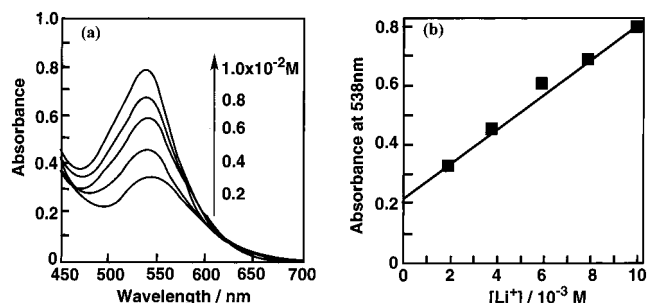


Figure 10. Absorption spectra of organic phase containing crowned spirobenzopyran **1** (a) and Li^+ concentration dependence of absorbance (b) on extraction under dark conditions. Organic phase: $[\mathbf{1}] = 1.0 \times 10^{-3}$ M in 1,2-dichloroethane. Aqueous phase: $[\text{LiClO}_4] = 2.0 \times 10^{-3}$ to 1.0×10^{-2} M; $[\text{TMAOH}] = 1.0 \times 10^{-2}$ M.

is promoted due to the interaction between a crown ether-bound Li^+ and a phenolate ion in the merocyanine form, because most of the spirobenzopyran molecules are isomerized to their merocyanine form by UV irradiation. To the contrary, the spiropyran form of **1** is stabilized by the reverse isomerization on Li^+ extraction under visible irradiation conditions. Thus, the Li^+ extraction is suppressed and, thereby, the absorbance based on the merocyanine form in the organic phase is decreased under visible irradiation conditions.

Calibration Graph of Li^+ for Extraction with **1.** The absorption spectra of the organic phase were measured with various Li^+ concentrations on extraction under dark conditions. The absorption spectra and the absorbance change at 538 nm are shown in Figure 10. The absorbance is increased with an absorption shift to shorter wavelength with an increase in the Li^+ concentration. The plots of absorbance at 538 nm vs Li^+ concen-

tration afford a straight line, implying a possibility of quantitative analysis for Li^+ .

CONCLUSION

On metal ion extraction with spirobenzopyran derivative bearing a monoaza-12-crown-4 moiety, the organic phases exhibit remarkable absorption-spectral changes, especially on Li^+ extraction. Spirobenzopyran derivatives bearing a monoaza-15-crown-5 and 18-crown-6 moiety prefer Li^+ and Na^+ , respectively, on the alkali metal ion extraction. These absorption-spectral changes are originated from the isomerization of their spiropyran moieties to the corresponding merocyanine form, which was in turn caused by the metal ion complexation of its crown ether moiety, followed by the ionic interaction between the phenolate ion and metal ion. The Li^+ extractability of **1** can be modified by photoirradiation that affects the isomerization of **1**, that is, UV irradiation enhances the extractability, whereas visible irradiation suppresses it. The 12-crown-4 spirobenzopyran, **1**, which exhibits a significant absorbance change with Li^+ concentration, is a promising candidate for an efficient extraction-spectrophotometric reagent for Li^+ .

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