Synthesis and Photochromism of Crowned Spirobenzothiapyran: Facilitated Photoisomerization by Cooperative Complexation of Crown Ether and Thiophenolate Moieties with Metal Ions

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Spirobenzothiapyrans bearing monoaza-12-crown-4, -15-crown-5, -18-crown-6, and oligooxyethylene moieties were synthesized, and their photochromism was examined in the presence of cations in acetonitrile. The cation complexation by their crown ether moieties cannot induce thermal isomerization to their corresponding colored merocyanine form, unlike the corresponding spirobenzopyran derivatives. The UV-light-induced isomerization was, however, facilitated by the cation complexation of the crown ether moieties and the affinity of the merocyanine thiophenolate anion to metal ions, especially in the presence of Li^+ and Ag^+. The presence of Ag^+ brought about the most remarkable effect in the facilitation of photoisomerization of the spirobenzothiapyrans and the thermal stability of the colored merocyanine form mainly due to the powerful interaction of the thiophenolate anion with the soft metal ion.

It is of great interest to apply photochromic compounds for photoresponsive devices. Various photochromic compounds have been synthesized and their photochromism has been examined extensively.[1] Spirobenzopyrans[2] and spirobenzothiapyrans[3,4] are well-known photochromic compounds, which isomerize from the spiropyran forms to their corresponding merocyanine forms by UV light, and vice versa by visible light or heat. However, the application of spirobenzothiapyrans to photochromic devices does not seem to be very easy due to the poor thermal stability of their merocyanine forms as compared with spirobenzopyrans.

It has been recognized, on the other hand, that the incorporation of a crown ether moiety to spirobenzopyrans facilitates photoisomerization to merocyanine forms by the metal-ion complexation of the crown ether moiety in the presence of metal ions.[5−7] This concept prompted us to design spirobenzothiapyrans bearing a crown ether moiety, what we call crowned spirobenzothiapyrans, expecting facilitated photoisomerization similar to the crowned spirobenzopyrans. In our preliminary results, significant facilitated photoisomerization was observed with a crowned spirobenzothiapyran in the presence of alkali metal ions, especially Li^+.[8] Here, we report the syntheses and photochromism of crowned spirobenzothiapyrans carrying different crown ether rings in details.

Results and Discussion

Synthesis. The syntheses of crowned spirobenzothiapyrans **1**−**3** and its noncyclic analogue **4** were carried out according to the synthetic route outlined by Scheme

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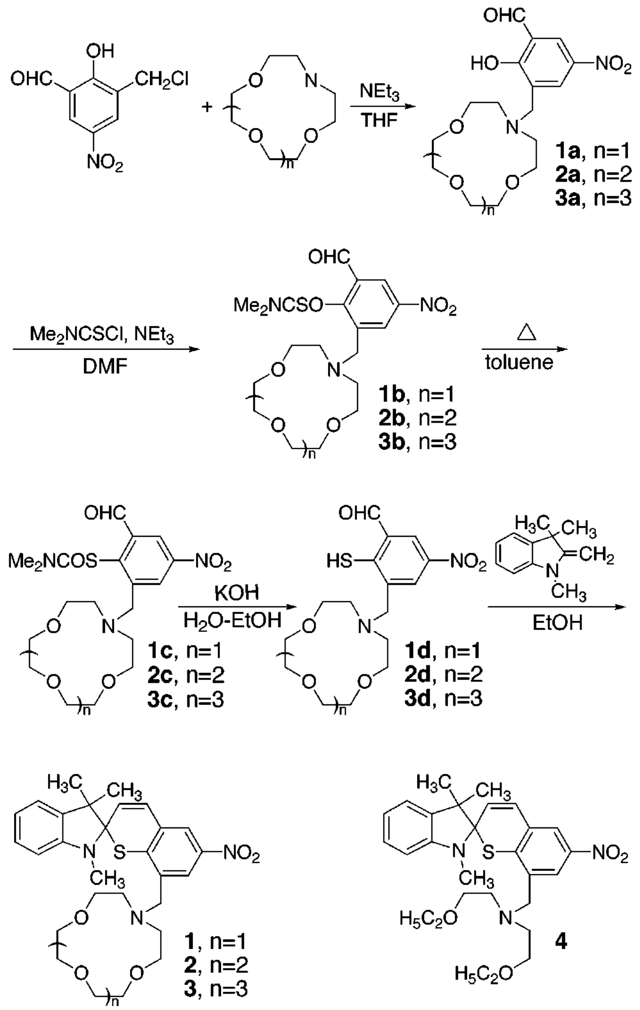
Scheme 1



1. The conversion of the phenol groups of **1a**−**3a** to the corresponding thiophenol groups of **1d**−**3d** was made subsequently by the reaction with $(CH_3)_2NCSCl$ in DMF in the presence of NEt_3, by the treatment in refluxing toluene, and by the hydrolysis with KOH in $H_2O-EtOH$.[4] The crowned thiosalicyl aldehyde was then reacted with 2-methylene-1,3,3-trimethylindoline in refluxing ethanol to yield the spirobenzothiapyran bearing monoaza-12-crown-4 **1**, which was purified by recrystallization from ethanol after preparative gel-permeation chromatography (GPC). Some products were used for the subsequent reaction without further purification because of their lability. Especially in the case of the crowned nitrosalicyl aldehyde synthesis, the product decomposed gradually during the GPC purification. In a similar way to **1**, spirobenzothiapyrans bearing monoaza-15-crown-5 **2**, monoaza-18-crown-6 **3**, and an oligooxyethylene moiety **4** were synthesized and purified by GPC.

Photoisomerization of Crowned Spirobenzothiapyrans. Absorption spectra of **1** were measured in acetonitrile in the presence and absence of a metal ion (alkali and alkaline-earth metal ions, NH_4^+, Ag^+, Tl^+, and Pb^{2+}) at room temperature (Figure 1). The spectra were hardly changed by the equimolar amount addition of any of the metal ions. This means that isomerization to the merocyanine form do not proceed by metal-ion complexation of the crown ether moiety under dark conditions (Scheme 2). This isomerization behavior of **1** is very different from that of corresponding crowned spirobenzopyran, the pyran ring of which is opened readily by metal-ion complexation of the crown ether moiety without UV irradiation (Scheme 3).[6] The same tendencies concerning the cation effect under dark conditions were found with **2**, **3**, and **4**. Exceptionally, the addition of Hg^+, Zn^{2+}, and Cu^{2+} under dark conditions changed the absorption spectrum of the spirobenzothiapyrans remarkably. In the presence of Hg^+, Zn^{2+}, and Cu^{2+}, the present spirobenzothiapyran derivatives hardly exhibited any significant photochromism, probably due to the irreversible complex formation.

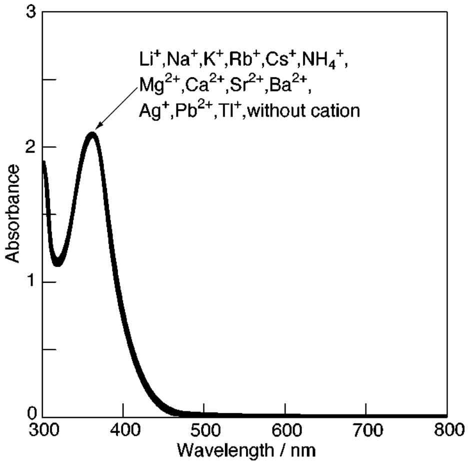
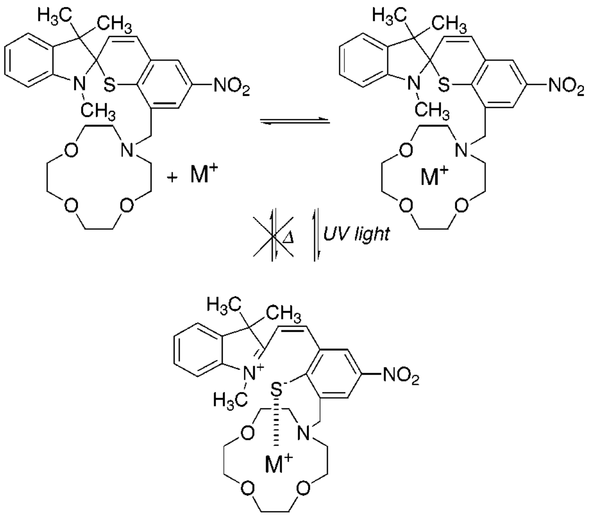


Figure 1. Absorption spectra for acetonitrile solution of spirobenzothiapyran derivative incorporating monoaza-12-crown-4 moiety **1** in the presence of metal ions and NH_4^+ under dark conditions.

Scheme 2



Upon irradiation of 365-nm UV light on the **1** solution containing Li^+, a drastic change in the absorption spectrum was seen as shown in Figure 2. On the other hand, any significant spectral change was hardly observed without any metal ion and with an equimolar amount of K^+, Rb^+, and Cs^+. The addition of Na^+ and NH_4^+ allowed some photoinduced spectral change of **1**. The cation-facilitated photoisomerization was promoted in the order $Li^+ > NH_4^+ > Na^+ > K^+, Rb^+, Cs^+$, which is almost consistent with the order in the cation-complexing ability of 12-crown-4 ring. This means that the cation complexation of the 12-crown-4 moiety of **1** clearly stabilizes the

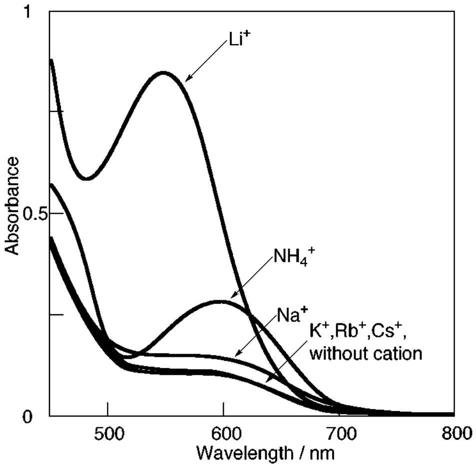
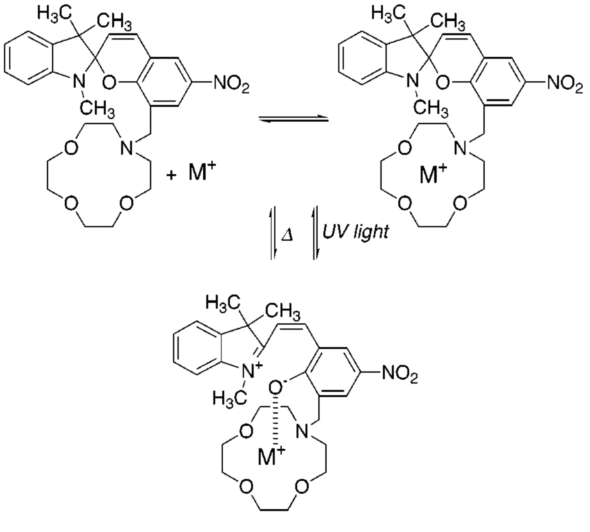


Figure 2. Absorption spectra for acetonitrile solution of spirobenzothiapyran derivative incorporating monoaza-12-crown-4 moiety **1** in the presence of alkali metal ions and NH_4^+ on UV-light irradiation.

Scheme 3



merocyanine form induced by the photoisomerization. Similarly, the facilitated photoisomerization of **2** and **3** reflected the cation-complexing ability of their crown ether moieties remarkably, being the most notable with Li^+ and Na^+, respectively (Figures 3 and 4). In addition, some interaction of thiophenolate anion of the merocyanine form with a metal ion, especially high-charge-density cations such as Li^+, as well as the cation complexation by the crown ether moieties probably contributes to the stabilization of the merocyanine form. The additional interaction may be suggested by the absorption spectra of **3** in the presence of Li^+, Na^+, and K^+ (Figure 4). A peak shift of the merocyanine absorption spectrum appeared corresponding to the cation radii, the Li^+ addition causing the most significant blue shifts.[7] To the contrary, the solution of **4** did not show any significant photoinduced spectral change with Na^+, K^+, Rb^+, or Cs^+ (Figure 5). This indicates that the metal-ion complexation of crown ether moieties of crowned spirobenzothiapyrans is a crucial factor to facilitate photoisomerization. Figure 5 may suggest that the diethoxyamino group of **4** interacts with NH_4^+ to some extent.

In the presence of alkaline-earth metal ions, the absorption spectra of **1** on UV-light irradiation also showed remarkable facilitated photoisomerization (Figure 6), but there was hardly any noteworthy ion selectivity among Ca^{2+}, Sr^{2+}, and Ba^{2+}. The addition of Mg^{2+} did not enhance the photoisomerization of crowned spirobenzothiapyran so much as the other alkaline-earth metal ions. The facilitation for the photoisomerization of crowned spirobenzothiapyran **1** in the presence of alkaline-earth metal ions is also considered to be derived from the cooperative interaction of the crown ether moiety and the thiophenolate anion with metal ions. In the case of alkaline-earth metal ions, the ionic interaction derived from thiophenolate anion seems to contribute to the facilitated photoisomerization more effectively than the complexation only by the crown ether moiety, as compared with in the presence of alkali metal ions. Similar tendencies for the addition effect of alkaline-earth metal ions on the facilitated photoisomerization were observed with crowned spirobenzothiapyrans **2** and **3**, and even with the noncyclic analogue **4**.

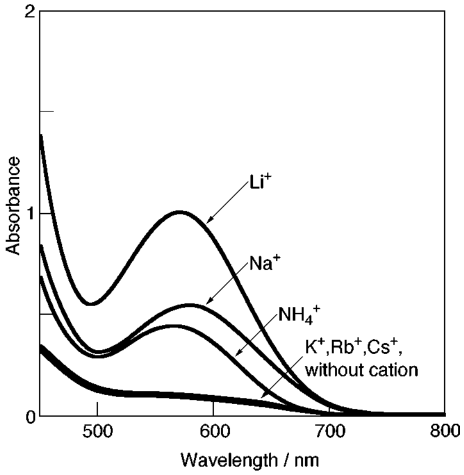


Figure 3. Absorption spectra for acetonitrile solution of spirobenzothiapyran derivative incorporating monoaza-15-crown-5 moiety **2** in the presence of alkali metal ions and NH_4^+ on UV-light irradiation.

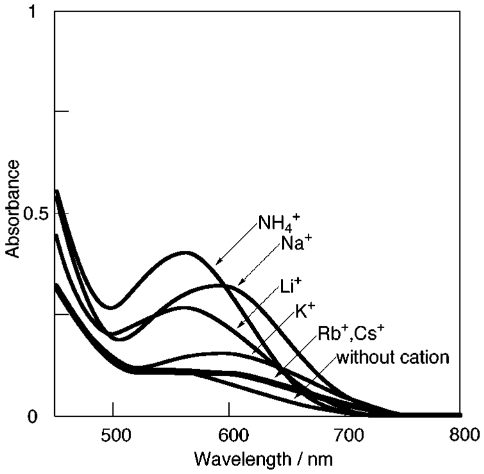


Figure 4. Absorption spectra for acetonitrile solution of spirobenzothiapyran derivative incorporating monoaza-18-crown-6 moiety **3** in the presence of alkali metal ions and NH_4^+ on UV-light irradiation.

The facilitated photoisomerization of crowned spirobenzothiapyrans in the presence of heavy metal ions were also followed, expecting a powerful interaction between

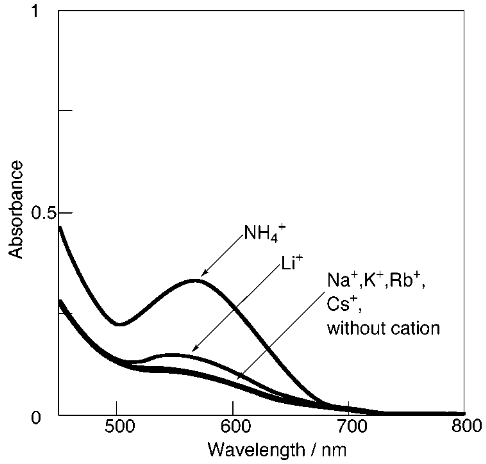


Figure 5. Absorption spectra for acetonitrile solution of spirobenzothiapyran derivative incorporating noncyclic moiety **4** in the presence of alkali metal ions and NH_4^+ on UV-light irradiation.

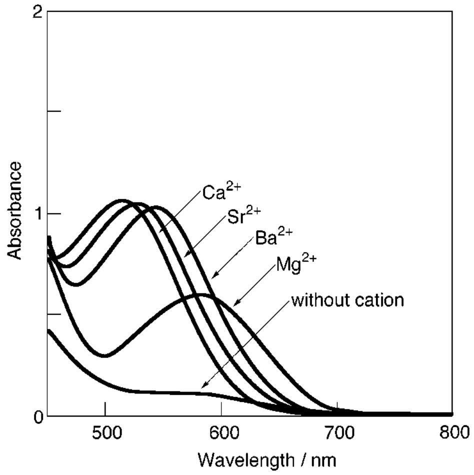


Figure 6. Absorption spectra for acetonitrile solution of crowned spirobenzothiapyran **1** in the presence of alkaline-earth metal ions on UV-light irradiation.

the merocyanie thiophenolate anion and a heavy metal ion, which may enhance their photoisomerization efficiently. UV-light irradiation on a solution of **1** in the presence of Ag^+ and Tl^+ caused drastic spectral change as shown in Figure 7. The Pb^{2+} addition exhibited some enhancement effect on the photoisomerization of **1**. Similar results were obtained with the other crowned spirobenzothiapyrans **2** and **3,** and even with the noncyclic analogue **4**, as illustrated by the photoinduced absorption-spectral changes for **4** in Figure 8. We previously reported that spirobenzopyran bearing monoaza-12-crown-4, which corresponds to **1**, shows remarkable facilitated photoisomerization in the presence of Li^+ in THF solution.[6] In control experiments, the presence of Ag^+ allowed only a slight spectral change although Li^+ caused a dramatic absorption-spectral change in acetonitrile solution of the crowned spirobenzopyran under dark conditions. These results clearly show that the Ag^+-facilitated photoisomerization of the spirobenzothiapyran derivatives is caused mainly by high affinity of the thiophenolate anion to Ag^+ but not by Ag^+ complexation of the crown ether moiety. This is also supported by the fact that Ag^+ still promotes the photoisomerization of noncyclic analogue **4** strikingly.

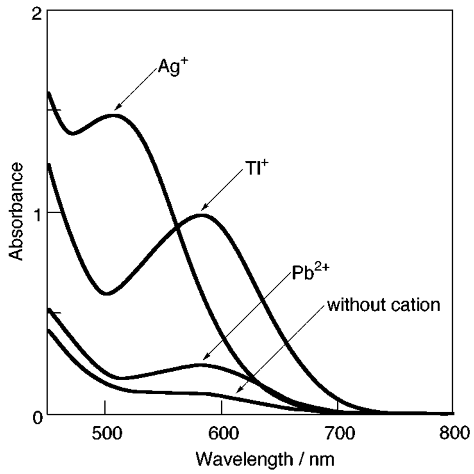


Figure 7. Absorption spectra for acetonitrile solution of crowned spirobenzothiapyran **1** in the presence of heavy metal ions on UV-light irradiation.

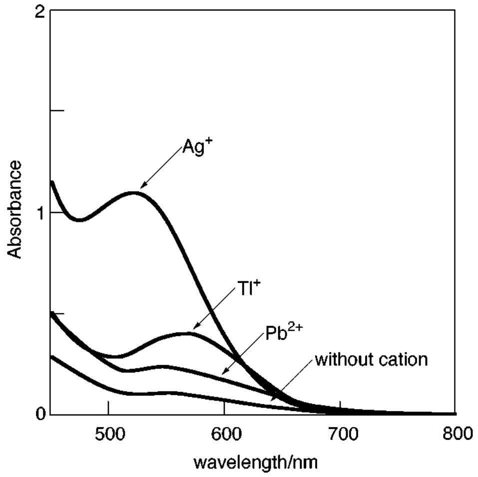


Figure 8. Absorption spectra for acetonitrile solution of spirobenzothiapyran derivative incorporating noncyclic moiety **4** in the presence of heavy metal ions on UV-light irradiation.

The cation-dependent photoisomerization of spirobenzothiapyran derivatives **1** − **4** suggests that the dual-mode facilitation of photoisomerization by the cation complexation of their crown ether moiety and by the cation affinity to their merocyanine thiophenolate anions.

Thermal Stability of Colored Form. To evaluate thermal stability of colored merocyanine forms of the crowned spirobenzothiapyrans, we studied their thermal decoloration. For instance, time-course absorption-spectral changes for acetonitrile solutions of **1** in the presence and absence of Li^+ were followed at room temperature after turning off UV light. In the absence of Li^+, the thermal isomerization from the merocyanine form of **1** back to its spirothiapyran form was almost complete within 5 s. On the contrary, the thermal back isomerization in the presence of Li^+ was very sluggish, the half-time of the UV-induced merocyanine form being about 2 min. Visible-light irradiation did not promote the thermal back isomerization at all. The slow back isomerization in the presence of Li^+ again proves the Li^+-complexation-induced high stability of the merocyanine form in crowned spirobenzothiapyran **1**.

As the thermal decoloration is a typical first-order reaction for the isomerization to spiropyran form (S) from

Table 1. Thermal Decoloration Rate Constants (10^{-2} s^{-1})

	no cation	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+
1	1.6	0.46	1.6	1.7	1.8	1.9	1.4
2	1.9	0.38	0.95	1.7	1.9	1.7	1.0
3	1.8	1.7	1.6	1.7	1.7	1.8	1.6
4	1.8	1.8	1.8	1.8	1.8	1.8	1.2

	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Ag^+	Pb^{2+}	Tl^+
1	1.0	0.29	0.43	0.46	0.21	1.5	0.38
2	1.7	0.48	0.47	0.50	0.18	1.7	0.34
3	1.7	0.47	0.49	0.51	0.29	1.7	0.45
4	1.4	1.1	1.5	1.4	0.43	1.6	1.0

merocyanine form (M), the thermal decoloration rate constant (k) is defined with eq 1, using the time elapsed (t), initial concentration of M at $t = 0$ ($[M]_0$), and concentration of S at a given time ($[S]_t$). $[M]_0$ and $[S]_t$ are expressed by the initial absorbance of a spirobenzothiapyran solution (A_0), final absorbance at $t = \infty$ (A_∞), absorbance at a given time (A_t), and the molar absorption coefficient for M (ϵ) at 550 nm, eq 1 can be then converted to eq 2. According to eq 2, the thermal decoloration rate constants of spirobenzothiapyran derivatives **1**−**4** in the absence and presence of an equimolar amount of a cation were determined spectrophotometrically, being summarized in Table 1. Significant stabilization for merocyanine forms was attained in the presence of Li^+ with **1** and **2**, showing the contribution of the metal-ion complexation by the crown ether moiety to the merocyanine stabilization. Another remarkable thing is drastic merocyanine stabilization observed in the presence of Ag^+ with **1**, **2**, and **3**. Even with the noncyclic analogue **4**, the presence of Ag^+ allowed considerable effect on the merocyanine stability, although the stability enhancement by **4** is not so dramatic as that by the crowned spirobenzothiapyrans. The results for the thermal decoloration rate constants are clearly reflected in those for the facilitated photoisomerization.

$$\frac{d[S]_t}{dt} = k([M]_o - [S]_t), \qquad kt = \ln \frac{[M]_o}{[M]_o - [S]_t} \qquad (1)$$

$$[M]_o = \frac{A_o - A_\infty}{\varepsilon} \qquad [S]_t = \frac{A_o - A_t}{\varepsilon}$$

$$kt = \ln \frac{A_o - A_\infty}{A_t - A_\infty} \qquad (2)$$

In conclusion, the present crowned spirobenzothiapyrans exhibit an intriguing type of photochromism different from their corresponding spirobenzopyran derivatives reported previously. Their isomerization to the corresponding merocyanine form does not proceed even in the presence of any crown-ether-complexing cation without UV-light irradiation. The cation effect on their photoisomerization suggests that the dual-mode facilitation of photoisomerization by the cation complexation of their crown ether moiety and by the cation affinity to their merocyanine thiophenolate anion. The thermal stability of colored merocyanine form in the present spirobenzothiapyran derivatives was enhanced markedly in the presence of metal ions such as Li^+ and Ag^+.

Experimental Section

Chemicals. Any chemicals for the synthesis were of available purity and used without further purification. For measurements, spectroscopic-grade acetonitrile was used as a solvent, while all salts were of the highest available purity and used without further purification.

Synthesis of Monoaza-12-crown-4 Derivative 1. 1a. Under N_2 atmosphere, monoaza-12-crown-4 (1.75 g, 10 mmol), NEt_3 (2.02 g, 20 mmol), and dry THF (20 mL) were placed in a three-necked flask (100 mL), and the mixture was cooled at 0 °C. A dry THF (10 mL) solution of 3-chloromethyl-5-nitrosalycylaldehyde (2.16 g, 10 mmol) was added dropwise to the mixture. The reaction mixture was stirred for 3 h at 0 °C and then stirred for additional 12 h at room temperature. The reaction mixture was poured into water and extracted twice with $CHCl_3$. The crude product obtained by solvent evaporation was used for the subsequent reaction without further purification.

1b. Under N_2 atmosphere, crude **1a** (2.83 g, 8 mmol), NEt_3 (2.42 g, 24 mmol), and dry DMF (60 mL) were placed in a three-necked flask (100 mL), and the mixture was cooled at 0 °C. A dry DMF (30 mL) solution of $(CH_3)_2NCSCl$ (2.96 g, 24 mmol) was added dropwise to the mixture. The reaction mixture was stirred for 3 h at 0 °C and then stirred for additional 12 h at room temperature. The reaction mixture was poured to water and extracted twice with $CHCl_3$. The crude product obtained by solvent evaporation was used for the subsequent reaction without further purification.

1c. Crude **1b** (2.65 g, 6 mmol) and dry toluene (100 mL) were introduced to a three-necked flask (300 mL) under N_2 atmosphere, and then the mixture was refluxed for 6 h. After evaporation of toluene, the product was purified by GPC. The isolated yield from **1a** was 46%.

1d. 1c (1.76 g, 4 mmol) and EtOH (100 mL) were introduced into a three-necked flask (300 mL) under N_2 atmosphere. An aqueous solution (100 mL) of KOH (2.24 g, 40 mmol) was added, and then the reaction mixture was stirred for 2 h at room temperature. After addition of CH_3COOH (2.40 g, 40 mmol), the reaction mixture was poured into water and extracted twice with $CHCl_3$. The crude product obtained by solvent evaporation was used for the subsequent reaction without further purification.

1. Crude **1d** (1.30 g, 3.5 mmol), 1,3,3-trimethyl-2-methyleneindolin (606 mg, 3.5 mmol), and dry EtOH (100 mL) were placed in a three-necked flask (300 mL) under N_2 atmosphere, and the reaction mixture was refluxed for 6 h. The EtOH evaporation afforded a crude product, which was purified by GPC. The isolated yield from **1d** was 49%, and, therefore, the overall isolated yield of **1** from monoaza-12-crown-4 was 23%.

Synthesis of Monoaza-15-crown-5 Derivative 2. Compound **2** was prepared according to the same procedures as for **1**, and the overall isolated yield was 21%.

Synthesis of Monoaza-18-crown-6 Derivative 3. Compound **3** was prepared according to the same procedures as for **1**, and the overall isolated yield was 16%.

Synthesis of Noncyclic Analogue 4. 2-Chloroethyl Ethyl Ether. 2-Ethoxyethanol (90 g, 1 mol), pyridine (94.8 g, 1.2 mol), and benzene (500 mL) were placed into a three-necked flask (1 L). Thionyl chloride (142.8 g, 1.2 mol) was added dropwise to the mixture at room temperature, and then the reaction mixture was refluxed for 16 h. After the reaction mixture was allowed to cool at room temperature, aqueous HCl (18 wt %, 100 mL) was added dropwise, and the organic layer was rinsed twice with water. The benzene solution of 2-chloroethyl ethyl ether (ca. 500 mL) was used for the subsequent reaction after drying over P_2O_5.

2-Iodoethyl Ethyl Ether. The benzene solution of 2-chloroethyl ethyl ether (ca. 500 mL), NaI (180 g, 1.2 mol), and acetone (500 mL) was placed in a three-necked flask (2 L), and the reaction mixture was refluxed for 4 days. After the reaction mixture was cooled, the precipitated solid (NaCl) was filtrated off. The filtrate was poured into water, and the benzene layer was separated and washed twice with an aqueous solution of $Na_2S_2O_3$ (5 wt %, 50 mL). The benzene solution of 2-iodoethyl

ethyl ether (ca. 500 mL) was dried over P_2O_5 and used for the following preparation.

Benzylbis(ethoxyethyl)amine. Benzylamine (21.4 g, 0.2 mol), Na_2CO_3 (84.8 g, 0.8 mol), and acetonitrile (500 mL) were introduced into a three-necked flask (2 L), and the mixture was then refluxed under N_2 atmosphere. The benzene solution of 2-iodoethyl ethyl ether (ca. 500 mL) was added dropwise to the mixture and then stirred for 48 h under refluxing conditions. After the solvent evaporation, $CHCl_3$ and a KOH (5 wt %, 400 mL) aqueous solution were added, and the organic layer was separated. The product was isolated by vacuum distillation (bp 87 °C/0.2 mmHg) with an overall yield of 17% from 2-ethoxyethanol.

Bis(ethoxyethyl)amine. Benzylbis(ethoxyethyl)amine (43.3 g, 0.17 mol), 5 wt % Pd/C (1.5 g), *p*-toluenesulfonic acid (0.5 g), and EtOH (150 mL) were placed in a stainles-steel autoclave (300 mL). The mixture was stirred at 120 °C for 6 h under 7.5 atm H_2 pressure. The Pd/C was filtrated off from the reaction mixture. Vacuum distillation (bp 78 °C/12 mmHg) of the crude product afforded pure bis(ethoxyethyl)amine with an isolated yield of 71%.

4. Compound **4** was prepared according to the same procedures as for **1**, and the overall isolated yield from bis(ethoxyethyl)amine was 25%.

Absorption-Spectral Measurements. The absorption spectra were measured at room temperature using acetonitrile as the solvent. The concentrations of metal ions and spirobenzothiapyrans were 2×10^{-4} M. Perchlorate salts of alkali and alkaline-earth metal ions and NH_4^+ and nitrate salts of heavy metal ions were used as the metal salts. As Pb^{2+} and Tl^+ nitrates were poorly soluble in acetonitrile, the concentration of spirobenzothiapyrans and metal ions was 5×10^{-5} M. In Figure 5, the concentrations of metal ions and **3** were 2×10^{-3} and 2×10^{-4} M, respectively. The absorbance values of the Pb^{2+} and Tl^+ systems were normalized to compare with other metal ion systems in Figures 7 and 8. The absorption spectra under dark conditions were taken after allowing a measuring solution to stand under dark conditions overnight. The absorption-spectral measurements under photoirradiated conditions were carried out after UV-light irradiation for 30s. The light was irradiated on a measurement cell in perpendicular direction to a measuring incident light. The UV light (675 mW/cm^2), obtained by passing light of a 250-W Hg lamp through a light filter (λ_o; 365 nm, $\lambda/2$; 9.5 nm, transmittance 0.53), was introduced to the cell compartment for a spectrophotometer by using a glass fiber guide and was irradiated on the quartz cell containing a solution.

Determination of Thermal Decoloration Rate Constants. The thermal decoloration of spirobenzothiapyran derivatives was followed in acetonitrile in the absence and presence of an equimolar amount of a cation, by measuring the absorbance at 550 nm after UV irradiation for 1.5 min. The UV irradiation conditions were the same as for the absorption-spectral measurements.

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Supporting Information Available: Data about properties and identification (^{1}H NMR, IR, and mass spectra and elemental analysis) for newly synthesized compounds **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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