Decisive Factors in the Photoisomerization Behavior of Crowned Spirobenzopyrans: Metal Ion Interaction with Crown Ether and Phenolate Anion Moieties

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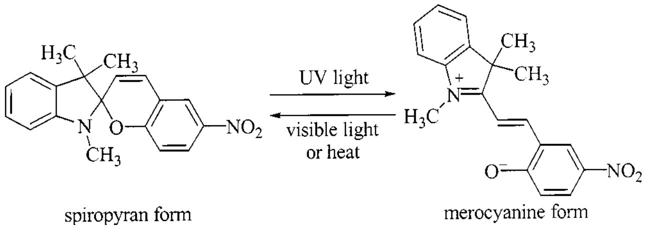
The influence of metal ion interaction with crowned spirobenzopyrans on the photoisomerization behavior was investigated through the use of various solvents, crowned spirobenzopyrans, and metal ions. Studies on the photoisomerization behavior of crowned spirobenzopyrans in various solvents revealed that solvation of the phenolate anion moiety in the merocyanine form induced photoisomerization back to the spiropyran form, giving rise to negative photochromism. Metal ion interaction with the phenolate anion moiety similarly caused photoisomerization back to the spiropyran form, while that with the crown ether moiety just produced a polar environment and its influence on photoisomerization behavior was dependent on the affinity of the metal ion captured by the crown ether moiety for the phenolate anion. Therefore, photochromic switching of crowned spirobenzopyrans between positive and negative to control the metal ion interaction with the phenolate anion moiety through the crown ether moiety is possible. This finding suggests a molecular design method for crowned spirobenzopyrans showing desired ion-responsive photochromism.

Introduction

Since the early studies on the applications of the photochromic reactions for a photochemical erasable memory, a great number of studies based on reversible changes in physical and chemical properties have been suggested and examined for photochromic materials such as azobenzenes, spiropyrans, dithienylethenes, and so on.[1] One of the most important photochromic materials, spirobenzopyrans have received much interest thanks to their high photosensitivity and fast response even in a rigid medium.[2] The photochromism of spirobenzopyrans is recognized as a phenomenon that arises from the photo-induced reversible isomerization process between spiropyran and merocyanine forms, in which spirobenzopyrans change their color upon UV irradiation and revert to their original color when exposed to visible light or heat (Scheme 1).[3]



Scheme 1. Photoisomerization of spirobenzopyran

The photochromism of spirobenzopyrans is highly affected by several factors, such as the substitution on the spirobenzopyran molecules, temperature, and the nature of the solvent.[4] It is noteworthy that a highly polar solvent can convert spirobenzopyrans into the merocyanine form through solvation without UV irradiation.

Recently, incorporation of a crown ether moiety into spirobenzopyrans has been found to afford metal ion responsive photochromic materials.[5,6] The role of the crown ether moiety is considered to be the production of a polar environment to stabilize the merocyanine form through metal ion complex formation, similarly to the action of a polar solvent. In our previous studies[7,8] of spirobenzopyrans bearing crown ether moieties, crowned spirobenzopyrans showed metal ion responsive photochromism and isomerization to the merocyanine form without UV irradiation; that

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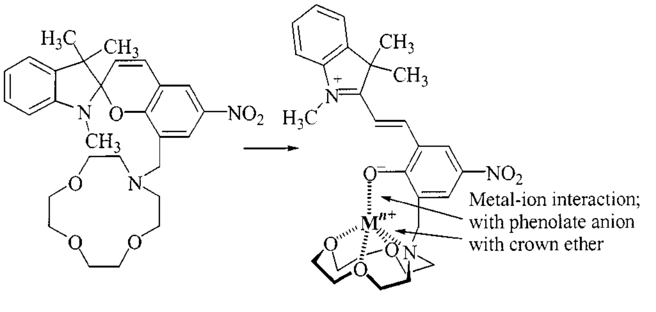
is, thermal isomerization was observed when the metal ion interaction with crowned spirobenzopyrans was strong enough. Furthermore, upon UV irradiation, some crowned spirobenzopyrans showed unexpected negative photochromism.[8] It was obvious that the strong metal ion interaction caused by the crown ether moiety induced this negative photochromism. In the merocyanine form of crowned spirobenzopyrans, however, there are two sites to interact with metal ions, the crown ether and the phenolate anion moieties, as shown in Scheme 2. Metal ion interaction with the phenolate anion moiety could influence photoisomerization behavior, but interaction with the crown ether moiety may not always cause change in photoisomerization behavior. It was of great interest to know how this dual metal ion interaction influenced the photoisomerization behavior to cause negative photochromism, as that could suggest a molecular design method for crowned spirobenzopyrans showing particular desired ion-responsive photochromism. In this paper, we report on the influence of the dual metal ion interaction on photoisomerization behavior in control of positive and negative photochromism of crowned spirobenzopyrans.

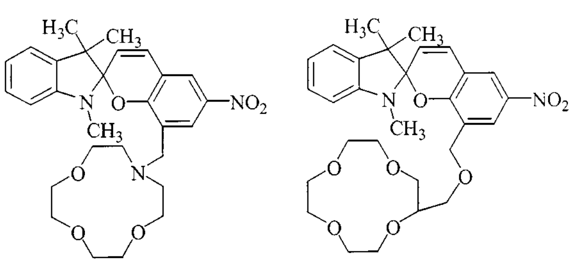


Scheme 2. Metal ion interaction with crowned spirobenzopyran

Results and Discussion

Influence of Solvents on Photochromism

Firstly, the influence of solvents on photochromism was examined with THF, MeCN, MeOH, DMF, and DMSO in the presence of alkali and alkaline-earth metal ions and with two crowned spirobenzopyrans, **1** and **2** (Scheme 3). Solvation has been regarded as proportional to solvent polarity, usually represented by dielectric constants, and an empirical solvation scale for photochromic compounds has been proposed.[9] The dielectric constant order is DMSO > MeCN > DMF > MeOH > THF (48.9, 37.5, 36.7, 33.1, 7.6 at 20−25 °C), while the empirical solvation scale order is MeOH > MeCN > DMSO > DMF > THF (55.4, 45.6, 45.1, 43.2, 37.4 kcal/mol at 25 °C).[9]



1 **2**

Scheme 3. Monoaza- and oxymethyl-crowned spirobenzopyrans

In THF solutions of **1**, Li^+ enhanced the photoisomerization to the merocyanine form, but other alkali metal ions suppressed the photoisomerization to this form, as judged on the basis of the absorption spectrum in the absence of metal ions (Figure 1). With alkali metal ions in THF, however, negative photochromism was not observed and thermal isomerization was not induced. The alkaline-earth metal ions Ca^{2+} and Sr^{2+}, on the other hand, brought about significant thermal isomerization in THF to produce negative photochromism (Figure 2). All MeCN solutions of **1** both with alkali and with alkaline-earth metal ions produced negative photochromism (Figures 3 and 4). In the case of MeOH solution of **1**, while Ca^{2+}, Sr^{2+} and Ba^{2+} showed negative photochromism, positive photochromism appeared with Mg^{2+} (Figure 5). None of the alkali metal ions, however, afforded any discernible change in photochromism, indicating no interaction between alkali metal ions and **1** in MeOH. Similarly, DMF and DMSO solutions of **1** showed no change in photochromism with either alkali or alkaline-earth metal ions. The dielectric constants for DMF, DMSO, and MeOH are quite higher than that for THF. Therefore, solvation of metal ions, especially of alkali metal ions, by those polar solvents could be significant in quenching of the metal ion interaction with **1**. The photochromism solvent dependency for the crowned spirobenzopyran **2** was similar to that for **1**, but instances of negative photochromism for **2** were fewer than those for **1**. Negative photochromism for **2** was observed in THF with Ca^{2+} (Figure 6), in MeCN[8] with Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}, and in MeOH with Ca^{2+} systems. As shown in Figure 6, thermal isomerization for **2** was not as drastic as for **1** (Figure 2), reflecting weaker metal ion interaction with **2** than with **1**. This difference clearly stems from the difference between the crown ether moieties in **1** and **2**. On the other hand, the wavelength of maximal absorption for **2** in the presence of Mg^{2+} after UV irradiation was similar to that for metal ion free conditions in Figure 6, which implies that the interaction between Mg^{2+} and the phenolate anion moiety of the merocyanine form of **2** is weak.

In order to evaluate complex formation abilities with metal ions in various solvents, the coloration and decoloration rate constants were determined for negative and positive photochromism systems, respectively. A smaller value for a positive photochromism system means more stable complex formation, as the merocyanine form is converted into the spiropyran form thermally after UV irradiation. In the case of a negative photochromism system, in contrast, the spiropyran form reverts thermally to the merocyanine form after UV irradiation, and so a larger value indicates more stable complex formation. The results are summarized in Tables 1 and 2 for **1** and **2**, respectively. The wavelengths

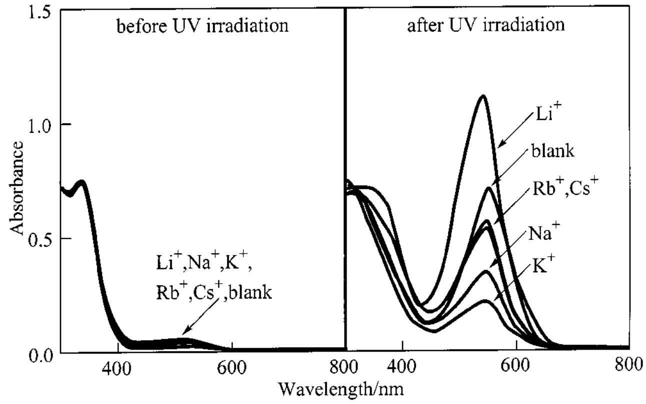


Figure 1. Absorption spectra of **1** in the presence of an alkali metal ion in THF

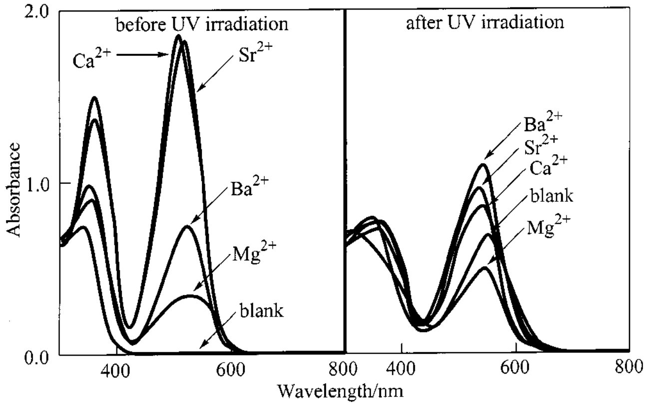


Figure 2. Absorption spectra of **1** in the presence of an alkaline-earth metal ion in THF

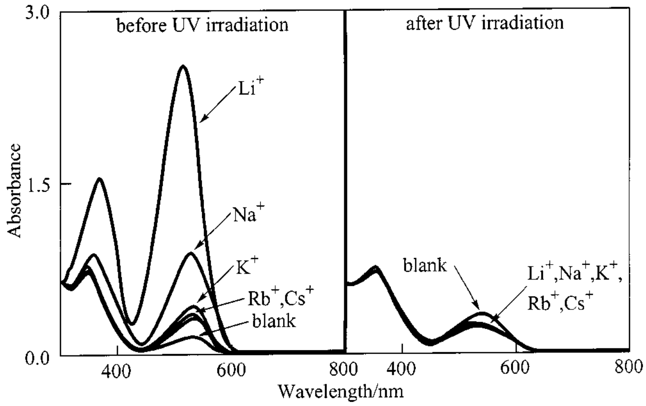


Figure 3. Absorption spectra of **1** in the presence of an alkali metal ion in MeCN

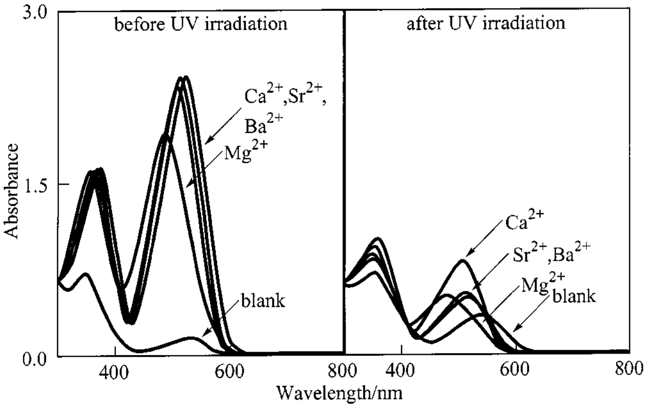


Figure 4. Absorption spectra of **1** in the presence of an alkaline-earth metal ion in MeCN

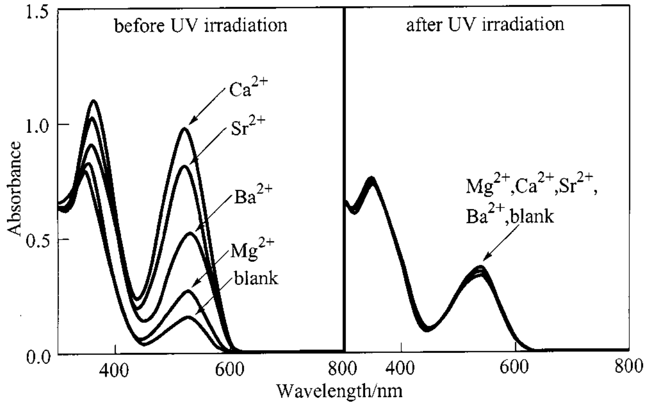


Figure 5. Absorption spectra of **1** in the presence of an alkaline-earth metal ion in MeOH

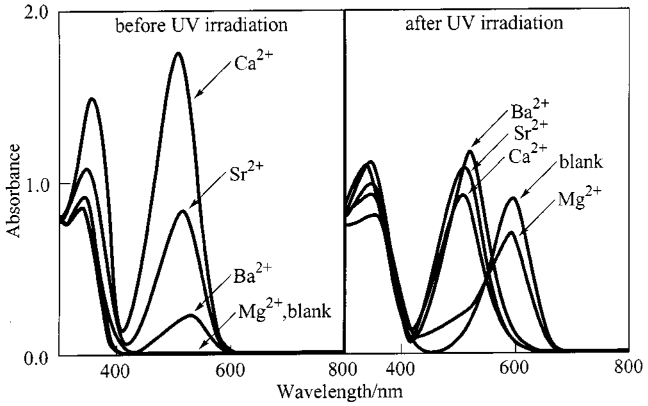


Figure 6. Absorption spectra of **2** in the presence of an alkaline-earth metal ion in THF

of maximal absorption (λ_{max}) are discussed in the next section.

THF solutions with alkaline-earth metal ions, especially with Mg^{2+}, were seriously sensitive to moisture; addition of water (1 vol %) to the Mg^{2+} solution resulted in disappearance of thermal isomerization before UV irradiation. This tendency hampered the determination of some constants. In Tables 1 and 2, stabilization of the merocyanine form, reflecting the selective metal ion binding ability of the crown ether moieties, was observed as reported previously,[5−8] but the stabilization was not evident in DMF and DMSO solutions or in MeOH solution with alkali metal ions. Furthermore, stabilization of the merocyanine form by alkali metal ions was indeterminate in THF solution compared with MeCN solution, although − in view of the much smaller dielectric constant for THF than

Table 1. Decoloration and coloration rate constants with wavelength of maximal absorption before UV irradiation for **1** in various solvents

[a]	blank	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
THF	1.7	1.4	1.8	2.2	1.8	2.4	−	(−)	(−)	1.1
	545	541	545	545	544	544	540	(507)	(518)	524
MeCN	1.2	(0.26)	(0.26)	(−)	(−)	(−)	(0.17)	(5.9)	(3.0)	(2.3)
	537	(517)	(534)	(533)	(534)	(534)	(482)	(508)	(513)	(521)
MeOH	0.57	0.54	0.61	0.58	0.74	0.70	0.72	(0.09)	(0.04)	(−)
	538	539	538	538	537	538	524	(516)	(520)	(526)
DMF	2.3	2.1	2.2	2.2	1.9	2.4	3.0	2.6	2.6	2.7
	553	553	553	552	552	553	553	553	552	553
DMSO	0.83	0.74	0.88	0.66	0.73	0.63	0.77	0.86	0.76	−
	551	551	551	552	552	551	551	552	551	550

[a] Upper and lower values represent the rate constants (10^{-3} s^{-1}) and the wavelength (nm), respectively. Values for negative photochromism systems are given in parentheses. "−" indicates that the rate constant was not determined because of small change in spectra or high sensitivity to moisture.

Table 2. Decoloration and coloration rate constants with wavelength of maximum absorption before UV irradiation for **2** in various solvents

[a]	blank	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
THF	34	26	26	29	25	24	20	(−)	−	27
	542	543	542	542	543	541	521	(508)	516	523
MeCN	6.9	1.2	4.5	5.9	5.4	4.9	(0.03)	(0.47)	(0.34)	(0.22)
	554	524	546	552	552	554	(483)	(494)	(511)	(521)
MeOH	1.3	0.95	0.98	1.1	1.1	1.2	1.1	(−)	0.81	0.70
	540	540	541	539	539	540	538	(508)	530	533
DMF	3.0	3.1	3.3	3.3	3.4	3.5	3.4	3.9	3.6	3.6
	564	565	563	565	565	564	565	565	563	565
DMSO	1.0	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1
	561	561	560	560	560	561	561	560	560	561

[a] Upper and lower values represent the rate constants (10^{-3} s^{-1}) and the wavelength (nm), respectively. Values for negative photochromism systems are given in parentheses. "−" indicates that the rate constant was not determined because of small change in spectra or high sensitivity to moisture.

that for MeCN − a metal ion in THF may be less solvated and so should interact more distinctively than that in MeCN. These tendencies imply that it is not only the interaction of metal ions with crowned spirobenzopyrans that is essential for the appearance of metal ion influence on photochromism, but also the solvation of the merocyanine form, although solvation of metal ions can disrupt the interaction of metal ions with crowned spirobenzopyrans. The most significant metal ion influence on photochromism was observed with MeCN, with MeCN solvation seeming to stabilize the merocyanine form enough, but not to abolish the interaction of metal ions with crowned spirobenzopyrans.

Influence of Solvation of the Phenolate Anion Moiety on the Photoisomerization Behavior

It was recently reported that the blue shift of an absorption spectrum reflects the extent of solvation of the phenolate anion moiety in the merocyanine form of spirobenzopyrans.[10] Therefore, wavelengths of maximal absorption (λ_{max}) are given in Tables 1 and 2, to explore the extent of solvation of phenolate anion moieties. In both Tables 1 and 2, significant blue shifts of absorption spectra can be observed in the negative photochromism systems. When the λ_{max} values for **1** (Table 1) were smaller than 534 nm, negative photochromism appeared regardless of solvents. In the case of MeOH solutions of **1** with Mg^{2+}, negative photochromism was induced when the concentration of Mg^{2+} was ten times that of **1**. Similarly, negative photochromism for **2** can be observed when the λ_{max} values are smaller than 533 nm in Table 2, and negative photochromism was produced in MeCN with Li^+ and in MeOH with Sr^{2+} and Ba^{2+} at higher metal ion concentrations. Attempts to bring about negative photochromism with THF solution for **1** with Ba^{2+} and for **2** with Mg^{2+}, Sr^{2+}, and Ba^{2+} were not successful because of the low solubilities of the metal salts in THF. As blue shifting of absorption spectra was caused by solvation of the phenolate anion moiety in the merocyanine form,[10] the solvation seems to induce photoisomerization back to the spiropyran form, appearing as negative photochromism. However, the solvation for the systems in Tables 1 and 2 could consist of two interactions deriving from solvent and metal ion.[6]

In order to evaluate the influence of net solvation of the phenolate anion moiety on the photoisomerization behavior, water was added to metal ion-free MeCN solutions of **1** and **2** to increase the extent of solvation. The change in the absorption spectrum of **1** depending on the amount of added water is shown in Figure 7, and the λ_{max} values for **1** and **2** are summarized in Table 3. On increasing the amount of added water, thermal isomerization of **1** was promoted, and photoisomerization back to the spiropyran form was induced, resulting in the appearance of negative photochromism as shown in Figure 7. Similar behavior was observed with **2**. The λ_{max} values for **1** and **2** decreased with the amount of added water, reflecting the increase in the extent of solvation of the phenolate anion moieties. Negative photochromism appeared when the λ_{max} values were less than about 534 nm for both **1** and **2**, which was consistent with the tendencies in Tables 1 and 2. It was clearly suggested that net solvation of the phenolate anion moiety in the merocyanine form induces photoisomerization back to the spiropyran form.

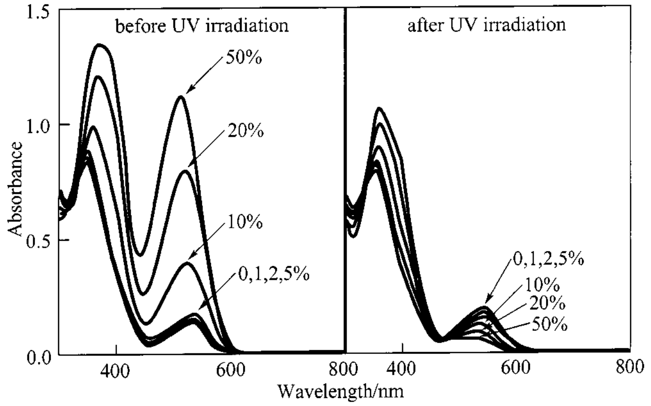


Figure 7. Absorption spectra of **1** in the presence of water

Table 3. Water concentration dependency of the wavelength of maximal absorption before UV irradiation for **1** and **2** in MeCN

H_2O [vol %][a]	0	1	2	5	10	20	50
1	537	535	534	(532)	(524)	(517)	(510)
2	554	552	549	543	539	534	(524)

[a] Wavelength (nm) for negative photochromism systems are given in parentheses.

Influence of Metal Ion Interactions on the Photoisomerization Behavior

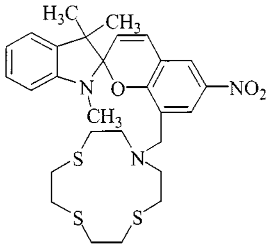
To assess the influence of metal ion interaction with the crown ether moiety on the photoisomerization behavior, the association constants of **1** and **2** with metal ions in MeCN and MeOH in the absence of light were determined. The determination of these association constants is described in detail in the Exp. Sect. The results are summarized in Table 4. The results indicate that photoisomerization back to the spiropyran form to show negative photochromism appears with large association constants, strong metal ion interaction with the crown ether moiety. However, the metal ion interaction with the phenolate anion moiety (Scheme 2) is clearly induced simultaneously, as the phenolate anion moiety is well known to prefer hard metal ions such as alkali and alkaline-earth metal ions.[8,11]

Table 4. Association constants with metal ions for **1** and **2** in MeCN and MeOH

Compound	**1**		**2**	
Solvent[a]	MeCN	MeOH	MeCN	MeOH
Li^+	($> 10^8$)	< 50	(740)	< 50
Na^+	(5.0×10^3)	< 50	< 50	< 50
K^+	(900)	< 50	< 50	< 50
Rb^+	(470)	< 50	< 50	< 50
Cs^+	(380)	< 50	< 50	< 50
Mg^{2+}	(9.7×10^4)	(1.0×10^3)	(9.3×10^4)	< 50
Ca^{2+}	(6.4×10^5)	(5.8×10^4)	(1.4×10^7)	(2.4×10^3)
Sr^{2+}	(1.2×10^6)	(2.5×10^4)	(2.6×10^7)	(840)
Ba^{2+}	(1.0×10^6)	(6.3×10^3)	($> 10^8$)	(720)

[a] Association constants (mol^{-1} dm^3) for negative photochromism systems are given in parentheses.

Monoazathiacrown ethers have been reported to interact with heavy metal ions such as Ag^+ and Hg^{2+}, but not with alkali and alkaline-earth metal ions.[12] Therefore, a crowned spirobenzopyran **3** bearing monoazatrithia-12-crown-4 was expected to allow us to evaluate the metal ion interaction with the crown ether and the phenolate anion moieties individually (Scheme 4). The photochromism of **3** was examined in the presence of various concentrations of Ag^+ and Sr^{2+} in MeCN, in which the crown ether and the phenolate anion moieties of **3** display preferences for Ag^+ and Sr^{2+}, respectively.[8,11,12] The Ag^+ concentration dependency of absorption spectra of **3** before and after UV irradiation is depicted in Figure 8. The maximum absorbance both before and after UV irradiation increased with the concentration of Ag^+ until the Ag^+ concentration reached the same concentration as **3**, after which the excess Ag^+ showed no further influence on absorption spectra. This behavior reflects a large association constant between **3** and Ag^+ ($K_a = 7.1 \times 10^6$ mol^{-1} dm^3), as strong Ag^+ interaction with the crown ether moiety. However, no negative photochromism was observed in this system. Similarly, the Sr^{2+} concentration dependency of absorption spectra of **3** before and after UV irradiation is shown in Figure 9. The maximum absorbance for UV irradiation increased with excess concentration of Sr^{2+}, showing a smaller association constant between **3** and Sr^{2+} ($K_a = 4.5 \times 10^3$ mol^{-1} dm^3) than between **3** and Ag^+ ($K_a = 7.1 \times 10^6$ mol^{-1} dm^3). On the other hand, the blue shift in the absorption spectra with Sr^{2+} ($\lambda_{max} = 513$ nm) before UV irradiation was more significant than with Ag^+ ($\lambda_{max} = 537$ nm), indicating stronger interaction between the phenolate anion moiety and Sr^{2+} than between the phenolate anion moiety and Ag^+. Although both Ag^+ and Sr^{2+} interactions caused significant thermal isomerization of **3**, negative photochromism – namely, photoisomerization back to the spiropyran form – was induced only by the Sr^{2+} interaction at higher concentrations. This result evidently shows that the Sr^{2+} interaction between the metal ion and the phenolate anion moiety induces photoisomerization back to the spiropyran form, while the Ag^+ interaction, between the metal ion and the crown ether moiety, enhances photoisomerization to the merocyanine form through the formation of a polar environment.



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Scheme 4. Monoazathiacrowned spirobenzopyran

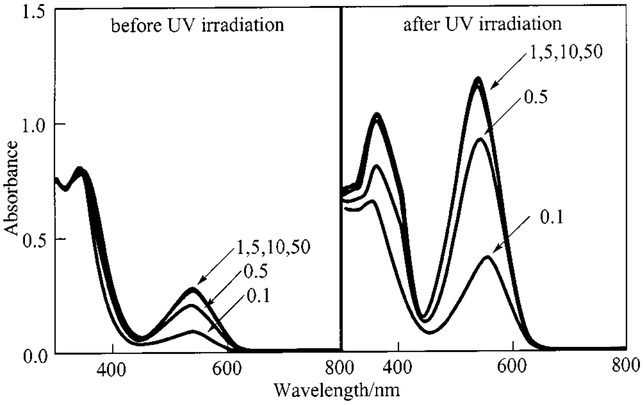


Figure 8. Ag^+ concentration dependency of absorption spectra for **3**

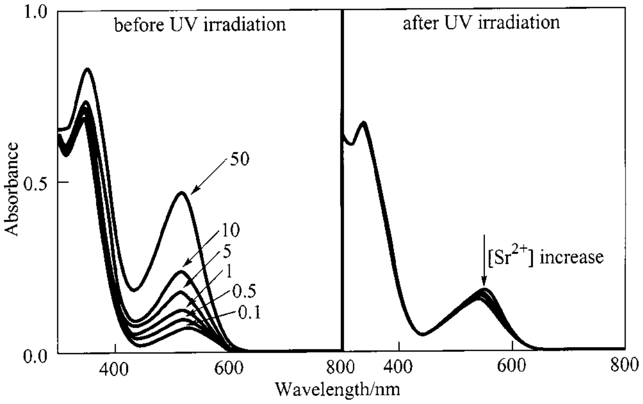


Figure 9. Sr^{2+} concentration dependency of absorption spectra for **3**

Conclusion

Studies on the photoisomerization behavior of crowned spirobenzopyrans in various solvents found that solvation of the phenolate anion moiety in the merocyanine form induced photoisomerization back to the spiropyran form, giving rise to negative photochromism. Metal ion interaction with the phenolate anion moiety similarly caused photoisomerization back to the spiropyran form, while that with the crown ether moiety just produced a polar environment and its influence on photoisomerization behavior was dependent on the affinity of the metal ion captured by the crown ether moiety for the phenolate anion. Therefore, photochromic switching of crowned spirobenzopyrans between positive and negative states should make it possible to control the metal ion interaction with the phenolate anion moiety through the crown ether moiety. This finding suggests a molecular design method for crowned spirobenzopyrans to produce particular desired ion-responsive photochromism.

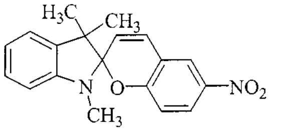
Experimental Section

General Remarks: All metal salts (perchlorate for alkali and alkaline-earth metal salts and nitrate for Ag^+) were the purest grade available and were employed as received. Acetonitrile (MeCN), methanol (MeOH), tetrahydrofuran (THF), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) were all of spectroscopic grade. The crowned spirobenzopyrans used – **1**,[7b] **2**,[8] and **3**[12c,12d] – were synthesized according to literature procedures. A UV/Vis spectrophotometer (JASCO, V-560) and a UV spot light source (HAMAMATSU, PHOTOCURE 200) were used for absorption spectra measurements.

Absorption Spectra Measurements: A solution of the appropriate solvent containing similar concentrations (1×10^{-4} mol dm^{-3}) of crowned spirobenzopyran and metal ion was prepared and allowed to stand in the darkness overnight at room temperature. The absorption spectrum before UV irradiation were then measured. Measurements were then carried out after UV irradiation (3 min), while irradiating the solution in the measurement cell in the direction perpendicular to that of the measuring incident light. The UV light (552 mW/cm^2), obtained by passing light from a 250-W Xe-Hg lamp through a light filter ($\lambda_0 = 365$ nm, $\lambda/2 = 9.5$ nm, transmittance 0.53), was introduced into the cell compartment of a spectrophotometer by a glass fiber guide and used to irradiate a quartz cell containing the solution.

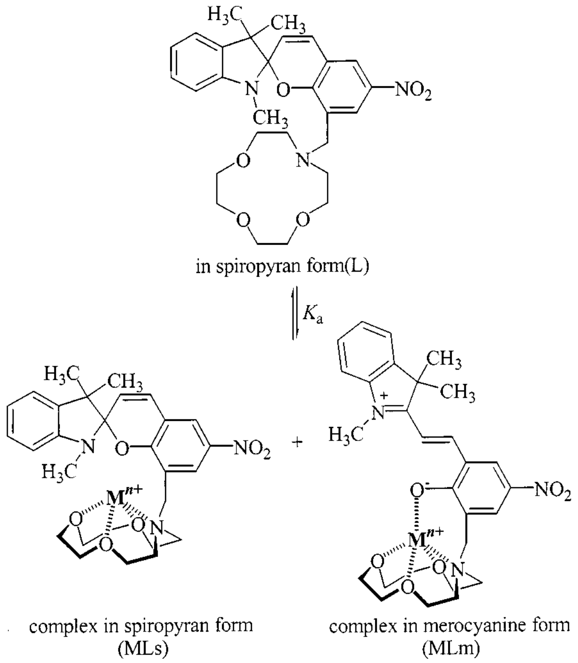
Determination of Thermal Decoloration and Coloration Rate Constants: The thermal decoloration and coloration rate constants for the studied compounds were determined according to the procedures in ref.[8]

Determination of Association Constants: In a control experiment, an MeCN solution (1×10^{-4} mol dm^{-3}) of a spirobenzopyran **4** (Scheme 5) that did not possess a crown ether moiety showed no spectra change in the presence of Ca^{2+} (1×10^{-4} mol dm^{-3}) at room temperature, implying that the affinity of the phenolate anion moiety for Ca^{2+} is not strong enough to convert the spirobenzopyran from the spiropyran form to the merocyanine form. Therefore, the concentration of crowned spirobenzopyran in the merocyanine form could be viewed as small enough to be negligible and so there were three species to consider with crowned spirobenzopyrans in the presence of metal ions (Scheme 6), conditions under which the merocyanine form is essential for metal ion interaction with the crown ether moiety. On the other hand, a metal ion complex of a crowned spirobenzopyran (ML) is in an equilibrium between the spiropyran (MLs) and the merocyanine forms (MLm), depending on the affinity of the phenolate anion moiety for the metal ion captured by the crown ether moiety. When the complex composition is 1:1, the association constant K_a can be expressed in terms of [ML]/[M][L] (Scheme 6); where [ML], [M], and [L] are the concentrations of crowned spirobenzopyran complexes, metal ion, and crowned spirobenzopyran in the spiropyran form, respectively. [L] and [M] are represented by $[M]_o$ (original concentration of [M]), $[L]_o$ (original concentration of [L]), A_L (absorbance derived from L), ε_L (molar extinction coefficient for L), and [ML], which is the sum of [MLs] and [MLm]. The observed absorbance A_{obs} consists of absorbances from crowned spirobenzopyran in the spiropyran form (L) and crowned spirobenzopyran complexes in the spiropyran (MLs) and the merocyanine forms (MLm). Thus, A_{obs} can be expressed as A_L, ε_S (molar extinction coefficient for MLs), [MLs], ε_M (molar extinction coefficient for MLm), and [MLm]. As the ratio of [MLs] to [MLm] is dependent on the affinity of the phenolate anion moiety for the metal ion captured by the crown ether moiety, the ratio of [MLs] to [MLm] and the apparent molar extinction coefficient ε_{S+M} for [ML] are constant regardless of [M]. Therefore, A_{obs} can be represented by A_L, ε_{S+M}, and [ML]. When $[M]_o$ is equal to $[L]_o$, the K_a is expressed as Equation (1) (Scheme 6).



4

Scheme 5. Spirobenzopyran



$$[M] + [L] \rightleftharpoons [ML] = [MLs] + [MLm]$$

$$K_a = \frac{[ML]}{[M][L]}$$

$$[M] = [M]_o - [ML]$$

$$[L] = [L]_o - [ML] = \frac{A_L}{\varepsilon_L}$$

$$[ML] = [MLs] + [MLm]$$

$$A_{obs} = A_L + \varepsilon_S[MLs] + \varepsilon_M[MLm] = A_L + \varepsilon_{S+M}[ML]$$

Scheme 6. Complex formation by crowned spirobenzopyrans

$$K_a = \frac{(\varepsilon_{S+M} - \varepsilon_L)(A_{obs} - \varepsilon_L[M]_o)}{(\varepsilon_{S+M}[M]_o - A_{obs})^2} \quad (1)$$

The spectral change of a MeCN solution (1×10^{-4} mol dm^{-3}) of **1** as a function of metal ion concentration was examined with Li^+ and Ca^{2+}. The maximum absorbance measured for the crowned spirobenzopyran complexes at 517 nm with Li^+ and 508 nm with Ca^{2+} increased with the metal ion concentration until the concentrations of both Li^+ and Ca^{2+} reached that of **1**. Excess Li^+ and Ca^{2+} did not cause discernible change in the spectra. This shows that the complexes of **1** with Li^+ and Ca^{2+} each have 1:1 composition regardless of metal ion valence. The obtained maximum absorbances for **1** with Li^+ and Ca^{2+} were similar. This implies that alkali and alkaline-earth metal ions captured by the crown ether moiety force the crowned spirobenzopyran complex (ML) to adopt the merocyanine form (MLm). In order to determine ε_{S+M}, the concentration of metal ion was increased to convert all L to ML. While Li^+ and Ca^{2+} produced the most significant spectral change among alkaline and alkaline-earth metal ions, to give reliable ε_{S+M} values, there was difficulty in determining ε_{S+M} with some metal ions owing to lack of complex formation ability with the crown ether moiety. Therefore, the approximation that all ε_{S+M} values were the same as that with Ca^{2+} was adopted to determine K_a with all metal ions. K_a values were determined with a solution containing the same concentration (1×10^{-4} mol dm^{-3}) of crowned spirobenzopyran and metal ion. In a similar fashion, K_a values for **1** in MeOH and for **2** in MeCN and MeOH were determined with the ε_{S+M} value for Ca^{2+} for **1** in MeOH, and for **2** in MeCN and MeOH, respectively. In the case of THF, K_a could not be determined by this method because of the low solubility of Ca^{2+}. For **3**, the ε_{S+M} value with Ag^+ was determined similarly, but determination of the ε_{S+M} value with Sr^{2+} was not successful because of lack of complex formation ability with the crown ether moiety. Therefore, the molar extinction coefficient ε when the Sr^{2+} concentration was 5×10^{-3} mol dm^{-3} was applied to determine K_a instead of ε_{S+M}. The obtained K_a with Sr^{2+} (4.5×10^3 mol^{-1} dm^3) by this approximation is greater than the accurate K_a, as the ε value is smaller than the ε_{S+M} value.

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