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Synthesis and Photochromism of Spirobenzopyran Derivatives Bearing an Oxymethylcrown Ether Moiety: Metal Ion-Induced Switching between Positive and Negative Photochromisms

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Spirobenzopyran derivatives carrying an oxymethylcrown ether moiety were synthesized, and their photochromism was studied in the presence of various metal ions in acetonitrile. The metal ion complexing ability of the crown ether moiety in crowned spirobenzopyrans affects both thermal isomerization and photoisomerization of their spirobenzopyran moiety to a great extent. When the interaction of the crown ether moiety with a metal ion was strong enough to cause thermal isomerization of the spirobenzopyran moiety to its 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 photochromisms.

The application of photochromic compounds in optical devices is of great interest. Various photochromic compounds have so far been prepared and examined for this purpose.[1] Spirobenzopyran derivatives are well-known photochromic compounds that isomerize to their corresponding merocyanine forms upon UV irradiation and vice versa upon visible-light irradiation or heating.[2]

Recently, spirobenzopyrans bearing a crown ether moiety, namely, crowned spirobenzopyrans were found to show new photochromic behavior reflecting the metal ion binding ability of their crown ether moiety.[3] In our previous studies of monoazacrowned spirobenzopyrans[4] and spirobenzothiapyrans,[5] the complex formation of their crown ether moiety with a metal ion facilitates the photoisomerization of their spiropyran moiety to the merocyanine form. Thermal isomerization of their spiropyran moiety to the corresponding merocyanine form can sometimes be observed if the metal ion complexes of the merocyanine form are sufficiently stable (Scheme 1). In

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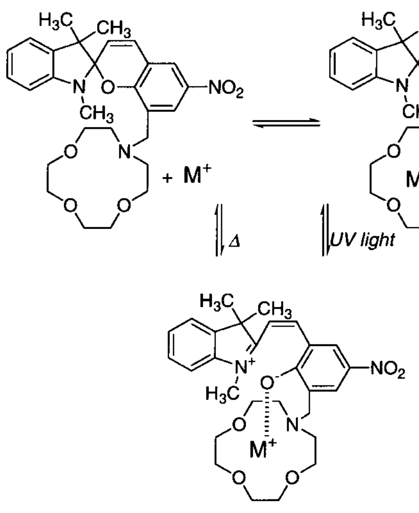
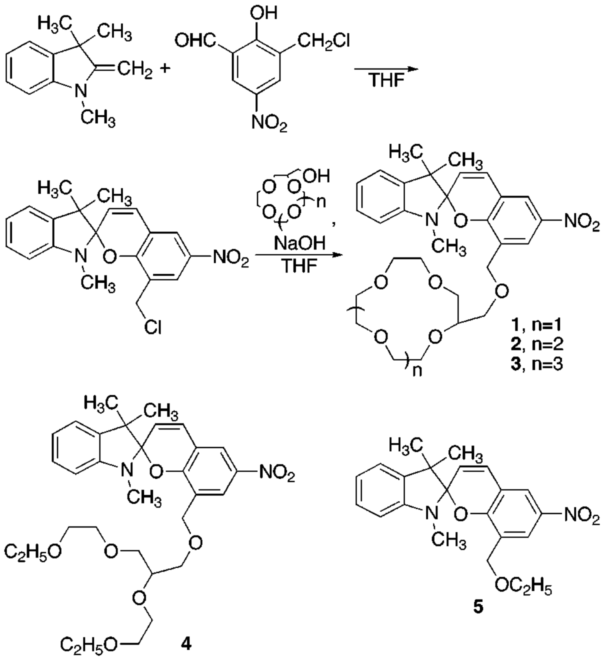
Scheme 1



this paper, we wish to report the synthesis and photochromism of spirobenzopyran derivatives bearing an oxymethylcrown ether moiety, which undergo metal ion complexation-induced switching between positive and negative photochromisms.

Results and Discussion

Scheme 2



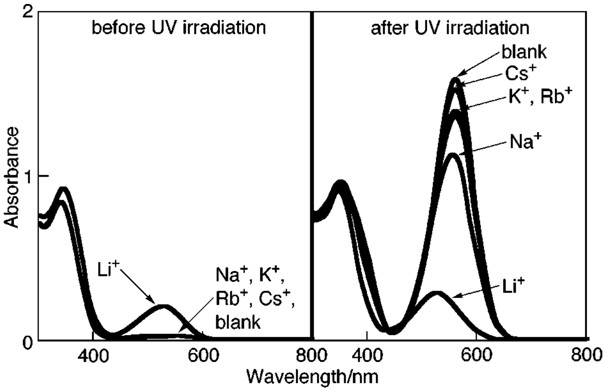


Figure 1. Absorption spectra of **1** (1×10^{-4} mol dm^{-3}) with an alkali metal ion (1×10^{-4} mol dm^{-3}).

Synthesis. The syntheses of oxymethylcrowned spirobenzopyrans **1**−**3** were done according to the synthetic route outlined in Scheme 2. Chloromethyl spirobenzopyran was prepared according to a reported procedure,[4] but THF was used as the solvent instead of ethanol to avoid any side reactions of the chloromethyl group. The reaction of chloromethyl spirobenzopyran with a hydroxymethyl crown ether was attempted with various bases, and powdered NaOH was found to give moderate yields in the presence of excess hydroxymethyl crown ether. For comparison with crowned spirobenzopyrans, noncyclic analogues, **4** and **5**, were prepared in a similar fashion.

Photochromism of Oxymethylcrowned Spirobenzopyrans. The absorption spectra of **1** were measured in acetonitrile in the presence and absence of an alkali metal ion (an equal amount) before and after UV irradiation (Figure 1). Even without UV irradiation, a Li$^+$ solution of **1** showed a significant spectral change, that is, thermal isomerization reflecting the Li$^+$-selective binding ability of 12-crown-4 moiety as reported previously.[4a−d] In the presence of other metal ions, the absorption spectrum was similar to that of the corresponding metal ion free solution. Upon UV irradiation, a drastic spectral change was seen with all of the **1** solutions except for the Li$^+$-containing solution. The

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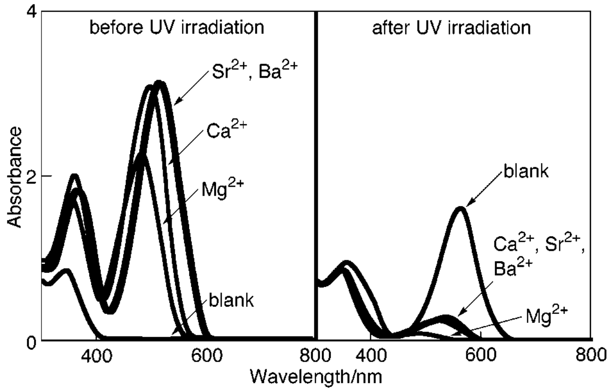

Figure 2. Absorption spectra of **1** (1×10^{-4} mol dm^{-3}) with an alkaline-earth metal ion (1×10^{-4} mol dm^{-3}).

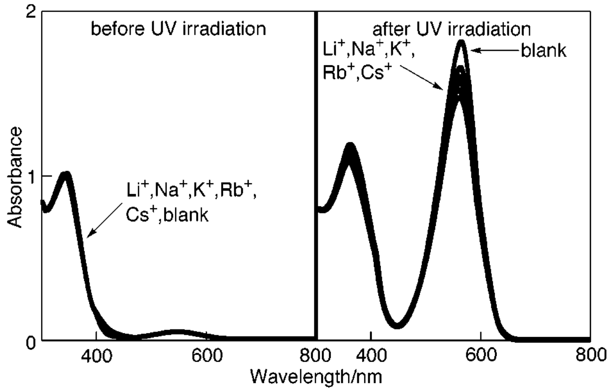

Figure 3. Absorption spectra of **5** (1×10^{-4} mol dm^{-3}) with an alkali metal ion (1×10^{-4} mol dm^{-3}).

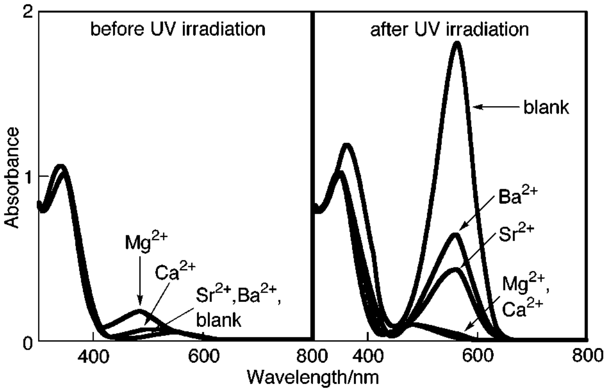

Figure 4. Absorption spectra of **5** (1×10^{-4} mol dm^{-3}) with an alkaline-earth metal ion (1×10^{-4} mol dm^{-3}).

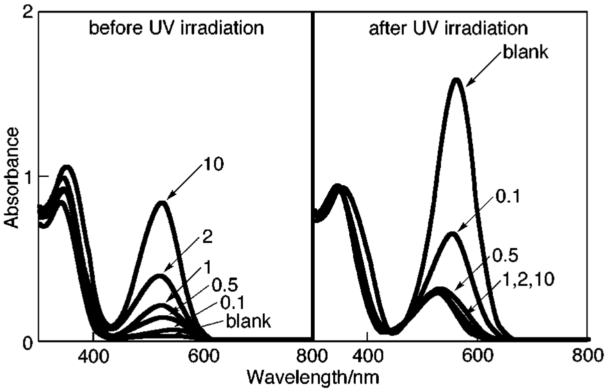

Figure 5. Li^+ concentration ($\times 10^{-4}$ mol dm^{-3}) dependence of absorption spectra of **1** (1×10^{-4} mol dm^{-3}).

photoisomerization of **1** was suppressed in the presence of Li^+, although the interaction between the 12-crown-4 moiety and a Li^+ facilitated photoisomerization of its spiropyran moiety to the merocyanine form in previous studies.[4a-d] Irradiation of 350- and 380-nm UV lights on a solution of **1** brought about similar results. The photoisomerization suppression appeared more clearly in cases of alkaline-earth metal ion solutions, as shown in Figure 2. All alkaline-earth metal ions seem to interact with **1** strongly enough to cause thermal isomerization of its spiropyran moiety to the merocyanine form. Upon UV irradiation, however, the merocyanine form was converted to the original spirobenzopyran form. That is to say, a negative photochromism appeared upon UV irradiation.

To evaluate the effect of metal ion complexation of different crown ether moieties on the photochromism of crowned spirobenzopyrans, absorption spectra of **2**−**5** were measured under conditions identical to the **1** system. In the case of **2**, Na^+ caused a slight thermal isomerization, and moderate suppression of the photoisomerization was observed in the presence of Li^+ and Na^+. Such a drastic photoisomerization suppression as seen in the **1** system was found in the presence of Li^+, not only with **3** but also with noncyclic analogue **4**. However, **5** did not show any meaningful photoisomerization suppression by alkali metal ions (Figure 3). In a way similar to the **1** system, alkaline-earth metal ions induced a remarkable thermal isomerization and a strong suppression of photoisomerization with the **2**−**4** systems, which showed a negative photochromism. In the case of **5**, however, a slight thermal isomerization was observed with Mg^{2+} as shown in Figure 4. This may indicate some affinity of the phenolate anion in the merocyanine form to Mg^{2+}.[6] Therefore, a negative photochromism was found only with Mg^{2+} in **5**. These results suggest that the negative photochromism is induced by a combination of the intense interaction between the phenolate anion in the merocyanine form and a metal ion and the metal ion complex formation of the crown ether moiety.

Absorption spectra of **1** were also measured in the presence of various concentrations of Li^+ (Figure 5). With an increasing Li^+ concentration, the thermal isomerization was enhanced by Li^+ complex formation of the crown ether moiety. On the contrary, the photoisomerization was drastically suppressed by an increase in the Li^+ concentration, which in turn resulted in a negative photochromism. Therefore, the metal ion complex formation of the crown ether moiety enhances the thermal isomerization and suppresses the photoisomerization, thus leading to a negative photochromism. The photochromism of **5** was also examined in solutions with various Li^+ concentrations. The photoisomerization was similarly suppressed at higher Li^+ concentrations as shown in Figure 6, but the suppression was not very drastic compared with the **1** system. However, any negative photochromism was not observed with the **5** system due to the lack of any remarkable thermal isomerization. This result may suggest that the photoisomerization of the spirobenzopyrans is essentially suppressed by the interaction of the phenolate anion in

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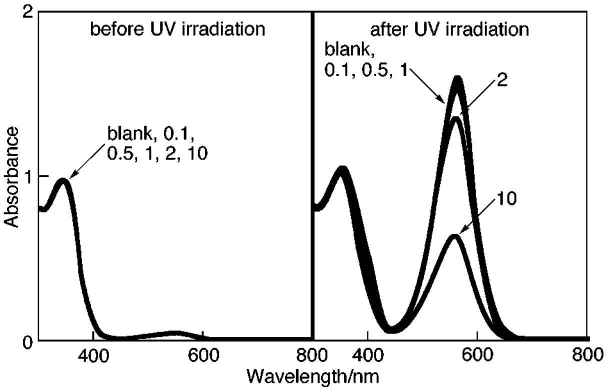

Figure 6. Li^+ concentration ($\times 10^{-4}$ mol dm^{-3}) dependence of absorption spectra of **5** (1×10^{-4} mol dm^{-3}).

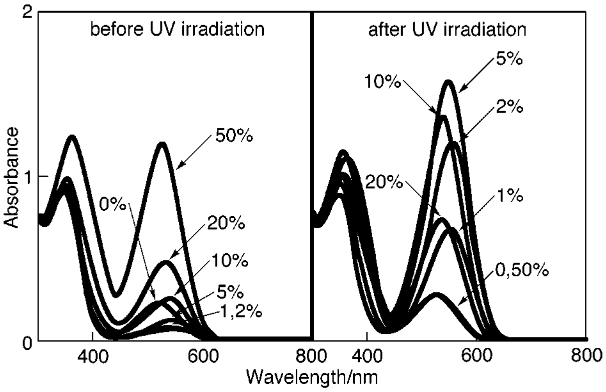

Figure 7. H_2O concentration (vol %) dependence of absorption spectra of **1** (1×10^{-4} mol dm^{-3}).

the merocyanine form with a metal ion. Also, the crown ether moiety not only enhances the thermal isomerization but also suppresses the photoisomerization by the interaction of a complexed metal ion with the phenolate anion, thus resulting in a negative photochromism.

Polar media generally cause thermal isomerization,[6] and metal ion complex formation of the crown ether moiety in crowned spirobenzopyrans is considered to afford a certain polar atmosphere around its spiropyran moiety. Therefore, the influence of solvent polarity on photochromism was evaluated by adding water to a Li^+-containing solution of **1**. The spectral changes on adding water are depicted in Figure 7. When a small amount of water was added to the solution, the thermal isomerization almost disappeared. This suggests that Li^+ hydration depresses the interaction of the crown ether moiety with Li^+. With increasing amounts of water, the thermal isomerization again occurred, because the merocyanine form is stabilized under polar conditions.[6] On the other hand, the photoisomerization was enhanced with an increase in the amount of water up to 5%, but it was suppressed when the amount was greater than 5%. Finally, the water contents of 50% led to a negative photochromism. Thus, the polarity in media to solvate the phenolate anion in the merocyanine form is a fundamental factor to control the photoisomerization, and the interaction of its crown ether moiety of crowned spirobenzopyran with a metal ion produces a certain polar atmosphere around its phenolate anion. This enhances or suppresses the photoisomerization, depending on the degree of metal ion complexation.

Table 1. Thermal Decoloration Rate Constants (10^{-3} s^{-1})

	without metal ion	Li^+	Na^+	K^+	Rb^+	Cs^+
1	6.9	1.2	4.5	5.9	5.4	4.9
2	6.7	2.9	1.5	4.2	4.5	4.1
3	5.9	1.7	3.6	3.7	3.5	4.3
4	6.0	2.9	6.0	6.1	6.0	6.2

Table 2. Thermal Coloration Rate Constants (10^{-3} s^{-1})

	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
1	0.030	0.47	0.34	0.22
2	0.18	0.84	0.65	0.25
3	0.052	2.0	0.64	0.53
4	0.017	0.44	0.16	0.12

Thermal Stability of Merocyanine Form. For the present crowned spirobenzopyrans, a positive photochromism was observed in the presence of an equal amount of alkali metal ions, while a negative photochromism appeared with an equal amount of alkaline-earth metal ions. Therefore, the thermal stability of colored merocyanine form of **1**−**4** was evaluated by determination of rate constants for thermal decoloration and coloration, which are summarized in Tables 1 and 2, respectively. The smaller decoloration rate constant means the higher stability in the metal ion complexes of crowned spirobenzopyrans in Table 1, and the greater coloration rate constant also represents the higher complex stability in Table 2. The small decoloration rate constants for **1** with Li^+ and for **2** with Li^+ and Na^+ reflect the ion selectivity of their crown ether moieties themselves. However, the small coloration rate constants for **3** and **4** with Li^+ seem to reflect a high affinity of the phenolate anion to a high charge-density cation, Li^+, rather than the ion selectivities of the crown ether moieties. This result supports the fact that the formation of stable metal ion complex by crowned spirobenzopyrans suppresses photoisomerization of their spiropyran moieties. Table 2 indicates that Ca^{2+} forms the most stable complex with any of the crowned spirobenzopyrans regardless of the size of their crown ether moieties. This tendency seems to be derived from the combination of the phenolate anion affinity of the merocyanine form to Ca^{2+} with the Ca^{2+}-binding ability of its crown ether moiety.

In conclusion, the metal ion complex formation of the crown ether moiety in crowned spirobenzopyrans dramatically affects the photoisomerization of their spiropyran moiety. When the interaction of the crown ether moiety with a metal ion is strong enough to cause the thermal isomerization and suppresses the photoisomerization, a negative photochromism appears. On the other hand, the relatively weak interaction of the crown ether moiety with a metal ion facilitates the photoisomerization, affording a positive photochromism. In other words, the interaction of the phenolate anion with a metal ion can shift the isomerization equilibrium between the spiropyran and merocyanine forms even under UV-irradiated conditions, thus resulting in the apparent suppression of photoisomerization. This phenomenon allows the metal-ion-induced control of the photochromic behavior, that is, the switching between positive and negative photochromisms. This finding might pave the way for a new application of the crowned spirobenzopyrans.

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 metal salts were of the highest available purity and used without further purification.

Synthesis of Oxymethylcrowned Spirobenzopyrans

Chloromethyl Spirobenzopyran. Under N_2 atmosphere, 3-chloromethyl-5-nitrosalycylaldehyde (1.08 g, 5 mmol) and dry THF (90 mL) were put in a three-necked flask. A THF solution (10 mL) of 1,3,3-trimethyl-2-methyleneindolin (0.87 g, 5 mmol) was added to the flask, and then the reaction mixture was refluxed for 4 h under N_2 atmosphere. The reaction mixture was used for the subsequent reaction without further treatment.

Compound 1. A THF solution (20 mL) of chloromethyl spirobenzopyran (370 mg, 1 mmol) and hydroxymethyl-12-crown-4 (618 mg, 3 mmol) were placed to a three-necked flask. Powdered NaOH (360 mg, 9 mmol) was added to the flask, and the reaction mixture was stirred for 1 h at room temperature. Then, acetic acid (540 mg, 9 mmol) was added to the reaction mixture. The reaction mixture was poured into water and extracted with $CHCl_3$. The product was separated by gel-permeation chromatography in 40% yield.

Compounds 2−5. Compounds **2**−**5** were prepared according to a procedure similar to **1**. Hydroxymethyl-15-crown-5 and -18-crown-6, hydroxymethyl triethyleneglycol diethyl ether, and ethanol were used instead of hydroxymethyl-12-crown-4, and the yields were 41, 27, 16, and 34%, respectively.

Absorption-Spectral Measurements. The absorption spectra were measured at room temperature using acetonitrile as the solvent. The concentrations of metal ions and spirobenzopyrans were 1×10^{-4} mol dm^{-3}. Perchlorate salts of alkali and alkaline-earth metal ions were used as the metal salts. The absorption spectra before UV irradiation were taken after allowing a measuring solution to stand under dark conditions overnight. The absorption-spectral measurements under irradiated conditions were carried out after UV irradiation for 3 min, while irradiating the light on the measurement cell in the perpendicular direction to the 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 a quartz cell containing a solution.

Determination of Thermal Decoloration and Coloration Rate Constants. The thermal decoloration and coloration of crowned spirobenzopyrans were followed in acetonitrile in the absence and presence of an equimolar amount of a metalion, by measuring the absorbance after UV irradiation for 3 min. The UV irradiation conditions were the same as for the absorption-spectral measurements.[5c]

Acknowledgment. We thank Mr. Masakatsu Ukon (JSR Corp.) for his assistance in absorption-spectral measurements. Partial financial support by Yamada Science Foundation is acknowledged.

Supporting Information Available: Data about properties and identification (^{1}H NMR, IR, mass spectra, and elemental analyses) for newly synthesized compounds **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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