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Tetrahedron

Tetrahedron 60 (2004) 3211–3220

Oxymethylcrowned chromene: photoswitchable stoichiometry of metal ion complex and ion-responsive photochromism

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Received 20 January 2004; revised 10 February 2004; accepted 10 February 2004

Abstract—Chromene derivatives bearing oxymethyl-12-crown-4 (**1**), -15-crown-5 (**2**), -18-crown-6 (**3**) ether moieties, and non-cyclic analogue (**4**) were synthesized, and their metal ion binding properties and photochromism were examined. NMR titration with alkali metal ions revealed that **1** formed a 1:2 complex (metal ion: ligand) with Na^+, while Li^+ afforded a 1:1 complex of **1**. In cases of K^+ and Rb^+, the complexes were a mixture of 1:1 and 1:2 complexes, but the formation of 1:1 complex was observed again with Cs^+. Under UV irradiation, however, the complex stoichiometry of **1** with all alkali metal ions was 1:1. As a comparison of NMR spectra between the Li^+ and Na^+ complexes of **1** indicated considerable upfield shift for the chromene moiety of the Na^+ complex, $\pi-\pi$ stacking of the chromene moiety seems to induce formation of the 1:2 complex. These results indicate that the chromene moiety is not only to show photochromism but also to induce aggregation to form the 1:2 complex resulted in switching of the complex stoichiometry by UV irradiation. The formation of 1:2 complex appeared only with **1** because flexibility of the crown moieties for **2** and **3** interfered the formation of 1:2 complex. Studies on photochromism in the presence of a metal ion demonstrated that the chromene derivatives bearing crown ether moieties show ion-responsive photochromism depending on the metal ion binding ability of their crown ether moieties.

1. Introduction

Photochromism is a reversible photoinduced phenomenon in which a photosensitive compound is converted to another isomer exhibiting a different absorption spectrum in the visible region. For recent several decades, various photochromic compounds have been designed, and their photochromism has been examined.[1] In view of practical application, physical properties such as colorability, decoloration rate, photofatigue resistance and so on, have been widely scrutinized. On the other hand, combination of photochromic compounds with ion-responsive molecules such as crown ether has been reported to afford ion-responsive photochromic compounds. Incorporation of a crown ether moiety to azobenzene,[2] diarylethene,[3] spiropyran,[4] and spirooxadine[5] have been reported to show their fascinating ion-responsive photochromism. In our previous work, chromene derivatives bearing monoazacrown ether[6] and *t*-butylcalix[4]arene[7] moieties also showed ion-responsive photochromism. In this paper, we report chromene derivatives bearing an oxymethylcrown ether moiety, namely, crowned chromene, which show not only ion-responsible photochromism but also photoswitchable stoichiometry of metal ion complexes.

2. Results and discussion

2.1. Synthesis of chromene derivatives

Crowned chromenes **1–3** and non-cyclic analogue **4** for comparison were synthesized according to the outline as shown in Scheme 1. Bromomethylchromene was prepared by following a method in the literature.[8] The reaction of bromomethylchromene with hydroxymethylcrown ethers or non-cyclic analogue was carried out in the presence of powdered sodium hydroxide using THF as a solvent at room temperature. Conventional treatment of the reaction mixture afforded the corresponding products with 59–83% yields after purification by gel permeation chromatography.

2.2. Binding properties with metal ions

The metal ion binding properties of the obtained crowned chromenes and non-cyclic analogue was examined by ^{13}C NMR titration using alkali and alkaline-earth metal perchlorates in acetonitrile-d_3 at room temperature. In control experiments using **1** with Li^+, NMR spectra for

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Keywords: Chromene; Crown ether; Photochromism; Metal ion binding.

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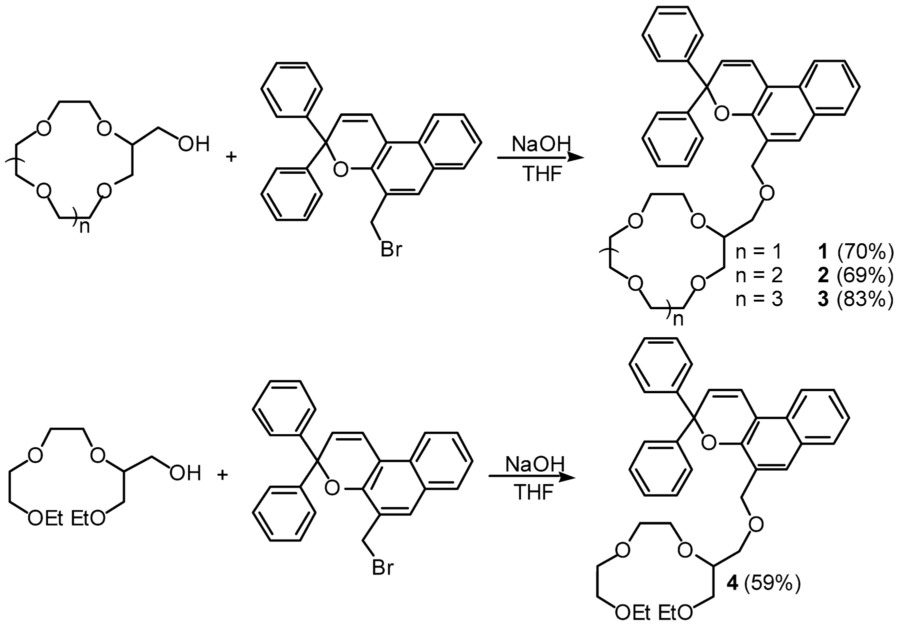
doi:10.1016/j.tet.2004.02.014



Scheme 1. Synthesis outline.

the crown ether moiety showed significant downfield shift upon addition of Li^+, however, there was serious difficulty in assignment. For the chromene moiety, any meaningful change in chemical shift was not observed. On the other hand, the benzyl carbon adjacent to the crown ether moiety was assignable with a considerable change in chemical shift. Therefore, we chose this carbon as an indicator for NMR titration.

When the molar ratio of Li^+/ligand was greater than 1, the chemical shift of the benzyl carbon of **1** was almost constant. This result suggests formation of a 1:1 complex. To determine the Li^+ complex stoichiometry of **1** precisely, we examined a Job plot as depicted in Figure 1. A clear maximum point was observed at 0.5 in the molar fraction of ligand to indicate a 1:1 stoichiometry of the Li^+ complex. Similarly, ^{13}C NMR titration of **1** was carried out using Na^+. Interestingly, the chemical shift was constant when the molar ratio of Na^+/ligand was greater than 0.5. This tendency implies that the Na^+ complex stoichiometry of **1** is 1:2 (Na^+: ligand). Job plots (Fig. 2) showed a maximum around 0.67 in the molar fraction of ligand which confirms that the Na^+ complex stoichiometry of **1** is 1:2 (Na^+: ligand). In cases of K^+ and Rb^+, Job plots gave a maximum between 0.5 and 0.67. These tendencies suggest that these complexes were a mixture of 1:1 and 1:2 complexes. For Cs^+, Job plots again gave the maximum point at 0.5 in the molar fraction, indicating that complex stoichiometry of **1** with Cs^+ was 1:1. The formation of 1:2 complex is not usual for monomeric (monocyclic) 12-crown-4 derivatives, and this phenomenon will be discussed later in detail. On the other hand, the complex stoichiometries with alkali metal ions for **2** and **3** were always 1:1. For **4**, the spectral change in chemical shift induced by addition of an alkali metal ion was too small to evaluate metal ion binding properties. It is obvious that non-cyclic analogue **4** is lack of metal ion binding ability as compared with other chromene derivatives bearing the crown ether moieties.

When alkaline-earth metal perchlorates were added to the

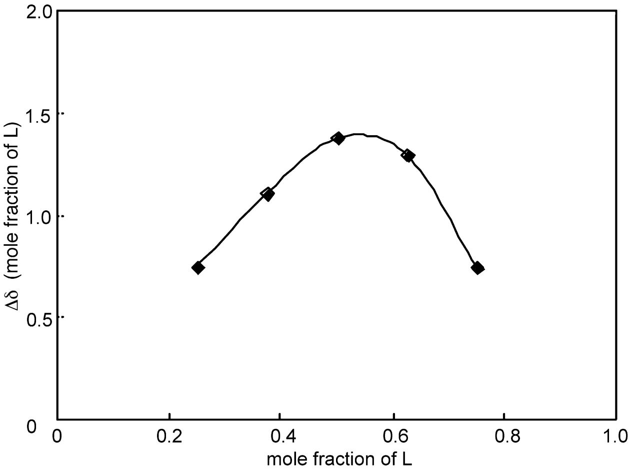


Figure 1. Job plots for Li^+ complex of **1**.

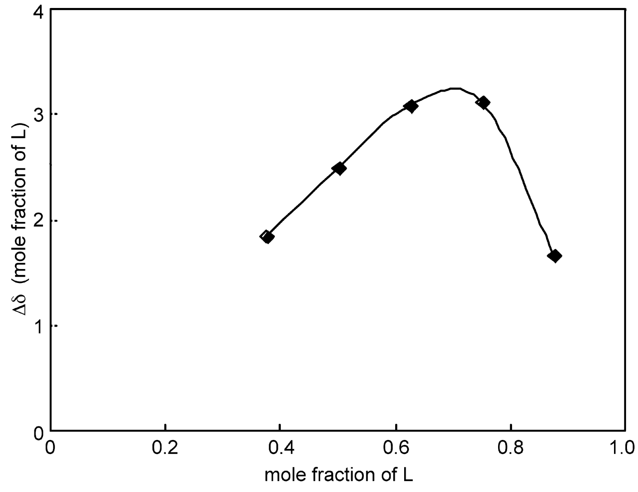


Figure 2. Job plots for Na^+ complex of **1**.

Table 1. Binding constants[a]

	Li^+	Na^+	K^+	Rb^+	Cs^+
1	4.2	(71)	—	—	0.24
2	20	29	16	4.6	2.3
3	0.51	58	75	10	5.9
4	—	—	—	—	—

[a] The units for k_{11} and k_{12} (in parenthesis) are $10^3\,mol^{-1}\,dm^3$ and $10^5\,mol^{-2}\,dm^6$, respectively.

solution of **1**, spectral broadening occurred with coloration of the solution to hamper the measurement. A similar tendency was observed with other chromene derivatives. As the coloration of the solution means that thermal isomerization is induced, alkaline-earth metal ions interacted with the chromene derivatives more strongly enough to induce thermal isomerization than alkali metal ions. Therefore, the binding constants with alkaline-earth metal ions could not be determined by NMR titration.

The binding constants[9] for 1:1 complexes (k_{11}) with alkali metal ions were evaluated through the binding isotherms by non-linear least-square regression using the NMR titration data, and the values are summarized in Table 1. In the case of Na^+ complex of **1**, the binding constant of 1:2 complex (k_{12}) was also evaluated as two molecules of **1** were regarded as one bidentate ligand to form 1:1 complex. The binding constants for **1** showed that Li^+ was far preferable to Cs^+. In cases of K^+ and Rb^+, the binding constants could not be determined because these complexes were a mixture of 1:1 and 1:2 complexes. Crowned chromene **2** showed the binding ability to Na^+, while the complex of **3** with K^+ appeared to be the most stable. Generally, 12-crown-4, 15-crown-5, and 18-crown-6 are known to show the binding ability to Li^+, Na^+, and K^+ depending on their ring size, respectively. As the binding properties of the crowned chromenes were consistent with the binding properties of the parent crown ethers, the lariat effect of the chromene moieties upon the binding properties seems to be negligible.

2.3. Ion-responsive photochromism

The photochromism of the chromene derivatives was evaluated in the presence of alkali and alkaline-earth metal ions. Without UV irradiation, no spectral change of **1** solution was observed in the presence of an alkali metal ion as shown in Figure 3. This indicates that there is no thermal isomerization induced by the metal ion complexation of its crown ether moiety. Upon UV irradiation, the most significant change in spectra was induced with Li^+, reflecting that Li^+ formed the most stable complex. In cases of alkaline-earth metal ions, Ca^{2+} induced slight thermal isomerization, and the other alkaline-earth metal ions induced significant spectral change under UV irradiation (Fig. 4). Considerable red-shift in the spectra[10] was induced by metal ions as was observed in the chromene derivatives bearing monoazacrown ether[6] and *t*-butylcalix[4]arene[7] moieties.

In the case of solution of **2** (Fig. 5), thermal isomerization was not observed in the presence of any alkali metal ions similar to the solution of **1**. When UV light was irradiated on the solution of **2**, the most significant spectral change was induced with Na^+. Among alkaline-earth metal ions, Ca^{2+}, Sr^{2+}, and Ba^{2+} induced significant spectral change for the solution of **2**, but Mg^{2+} showed no influence on photoisomerization (Fig. 6).

In Figure 7, the solution of **3** with K^+ afforded the most spectral change upon UV irradiation, but the influence of alkali metal ions on photoisomerization was not remarkable. Contrary to alkali metal ions, all alkaline-earth metal ions induced distinguished spectral change for the solution of **3** upon UV irradiation as shown in Figure 8. Especially, the Mg^{2+} influence on photoisomerization was notable compared with the Mg^{2+} solutions of **1** and **2**. This tendency

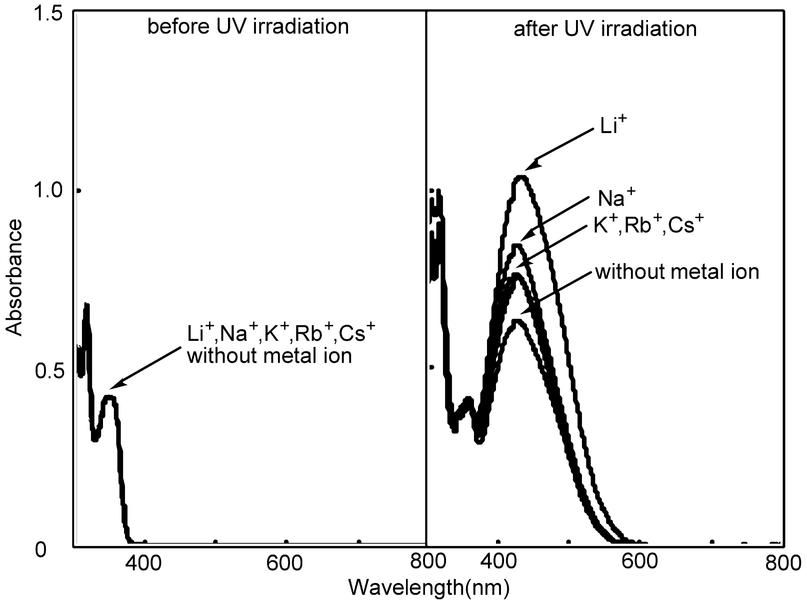


Figure 3. Absorption spectra of **1** in the presence of alkali metal ions.

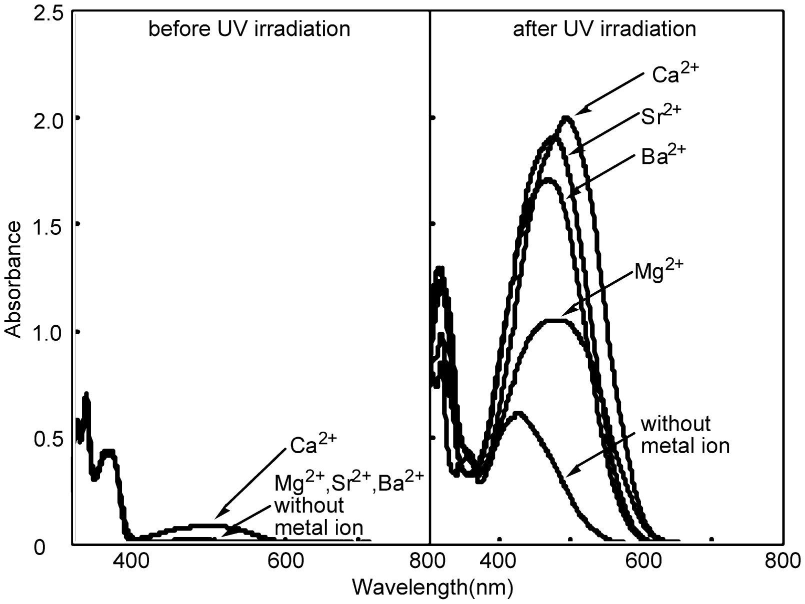


Figure 4. Absorption spectra of **1** in the presence of alkaline-earth metal ions.

might be derived from the flexibility of the 18-crown-6 moiety, which may capture two small metal ions. For non-cyclic analogue **4**, any influence of alkali metal ions on photochromism was hardly observed, but significant spectral changes were induced by alkaline-earth metal ions similar to the crowned chromenes (the data not shown).

It is reported that chromene is converted to the open (quinoidal) form by UV irradiation[11] in which there is a carbonyl group to interact with a metal ion (Scheme 2). In previous work,[6] we pointed out that there are two interactions with a metal ion derived from the crown ether moiety and the carbonyl group in the open form (Scheme 3) similar to the crowned spiropyrans.[12] Among alkali metal ions, the most significant influence on photoisomerization was induced with Li^+, Na^+, and K^+ for the solution of **1**, **2**, and **3**, respectively. This tendency seems to reflect the metal ion binding ability of the crown ether moieties as 12-crown-4, 15-crown-5, and 18-crown-6 to Li^+, Na^+, and K^+ depending on their ring size, respectively. However, alkaline-earth metal ions did not show such tendency depending on the ring size of the crown ether moieties. This difference might reflect that alkali metal ions interact with the crown ether moieties predominantly, while alkaline-earth metal ions tend to interact with the carbonyl group[13] more strongly than with the crown ether moiety in the open form. This is supported by the tendency of non-cyclic analogue **4** where alkali metal ions did not show any influence on photochromism, but alkaline-earth metal ions induced significant spectral change upon UV irradiation.

In order to estimate the conversion (%) of chromene derivatives to the open form from the closed form upon UV irradiation, extinction coefficient, ε for the open form was

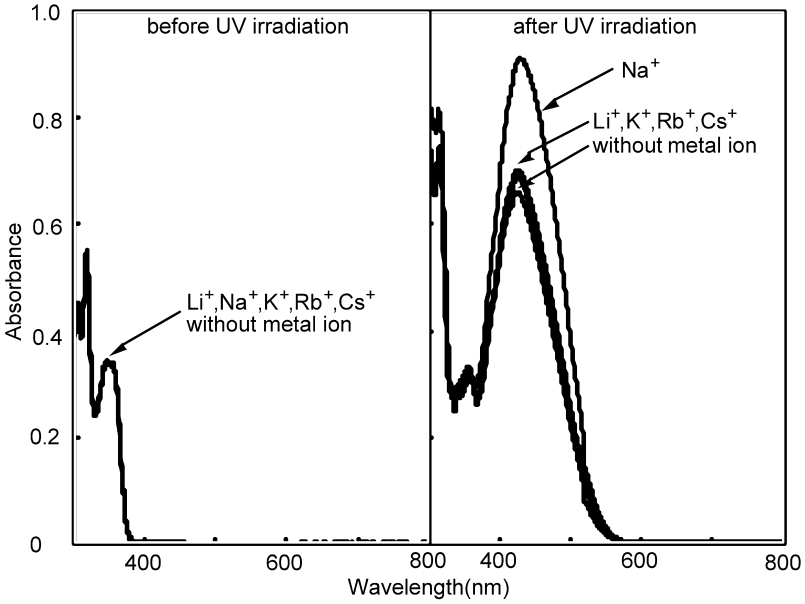


Figure 5. Absorption spectra of **2** in the presence of alkali metal ions.

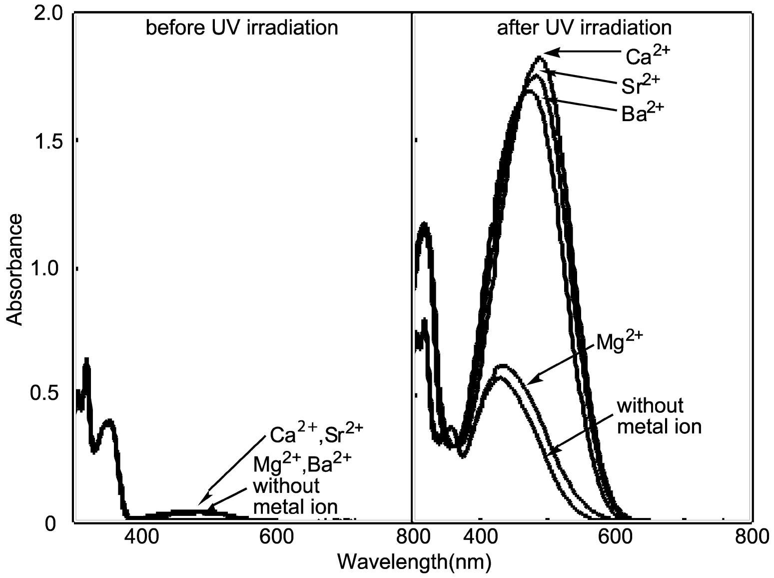


Figure 6. Absorption spectra of **2** in the presence of alkaline-earth metal ions.

evaluated. When the interaction of a metal ion with the chromene derivatives is strong enough, the conversion is regarded as 100% in the presence of excess amount of the metal ion upon UV irradiation. As Ca^{2+} showed notable interaction with all of the chromene derivatives, their absorption spectra were measured in the presence of tenfold excess amount of Ca^{2+} to evaluate ε for the open form. The obtained ε values were 2.0, 1.8, 1.7, and 2.0×10^4 mol^{-1} dm^3 for **1**, **2**, **3**, and **4**, respectively. Therefore, the conversion in the absence of a metal ion was evaluated as 32, 37, 36, and 31% for **1**, **2**, **3**, and **4**, respectively. In the presence of Li^+, **1** was converted to the open form in 69%. The conversion for **2** and **3** was 51 and 47% in the presence of Na^+ and K^+, respectively. These tendencies reflect the influence of metal ions on the photoisomerization equilibrium. In the case of **4**, the conversion in the presence of alkali metal ions was between 31 and 35% and any meaningful influence on the conversion ratio was not observed. Among alkaline-earth metal ions, Ca^{2+}, Sr^{2+}, and Ba^{2+} afforded high conversion with more than 85% for **1**, **2**, and **3**, and the conversion was more than 80% even for **4**. This result indicates that the influence on photoisomerization equilibrium by alkaline-earth metal ions is far greater than that by alkali metal ions.

Chromene, which is colorless in the closed form, is colored upon UV irradiation by adopting the open form (Scheme 2).[11] The colored open form restores to the colorless closed form thermally. If there is any specific interaction between a metal ion captured by the crown ether moiety and the carbonyl group in the open form, the open form of the crowned chromene should be stabilized, resulting in a significant delay of the decoloration process (Scheme 3). Therefore, the decoloration rate constants reflect the thermal stability of the crowned chromene complex with a metal ion under UV irradiation.

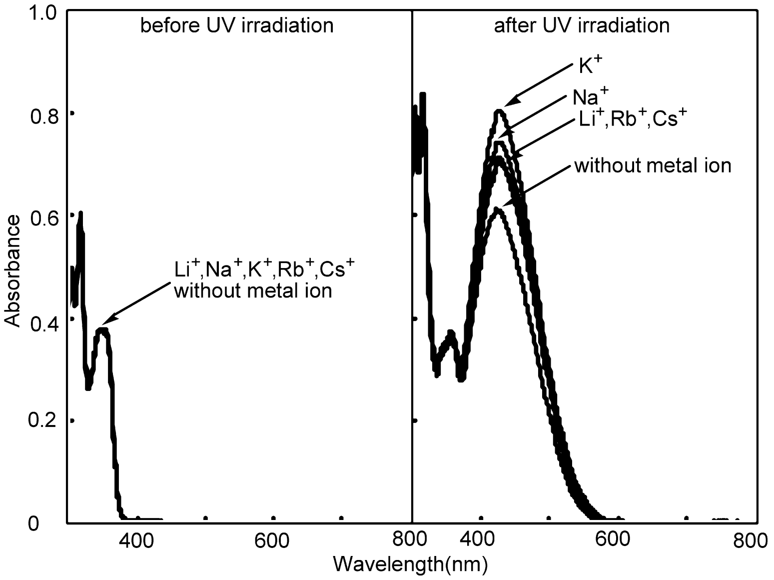


Figure 7. Absorption spectra of **3** in the presence of alkali metal ions.

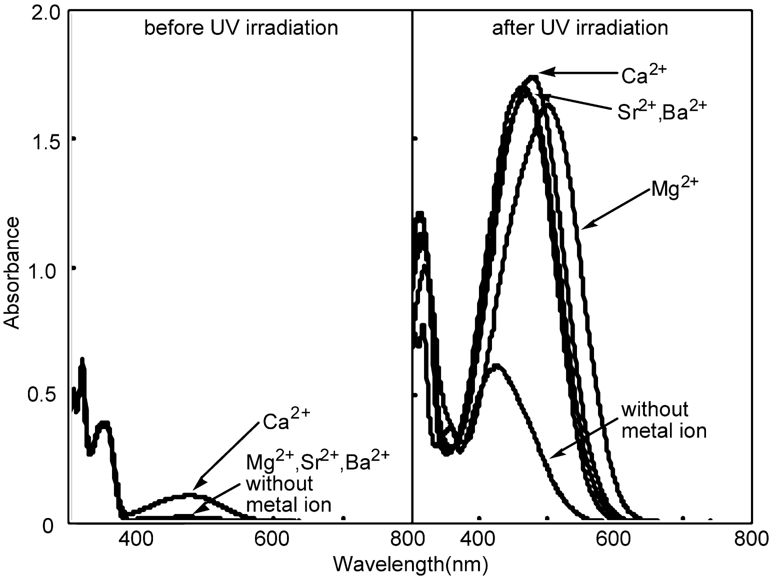
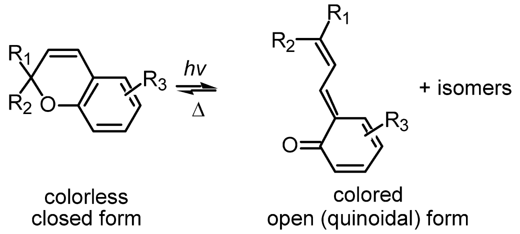
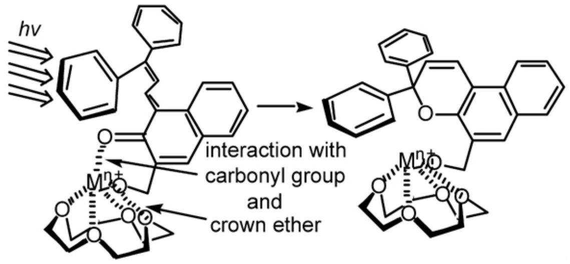


Figure 8. Absorption spectra of **3** in the presence of alkaline-earth metal ions.



Scheme 2. Photoisomerization of chromene.



Scheme 3. Photoisomerization of crowned chromene.

When the complex stoichiometry of the crowned chromene with a metal ion is 1:1, the decoloration process from the open form (O) to the closed form (C) is expressed as a first-order reaction. The decoloration rate constant (*k*) is defined by Eq. 1 in Scheme 4 with the elapsed time (*t*), initial concentration of O at $t=0$ ($[\mathrm{O}]_0$), and concentration of C at a given time ($[\mathrm{C}]_t$). $[\mathrm{O}]_0$ and $[\mathrm{C}]_t$ are expressed with the initial absorbance of a crowned chromene solution (A_0), final absorbance at $t=\infty$ (A_∞), absorbance at a given time (A_t), and the molar absorption coefficient of O (ε). Eq. 1 is then converted to Eq. 2 in Scheme 4. According to Eq. 2, the thermal decoloration rate constants of the crowned chromene under UV irradiation can be determined, where the smaller value means the more stable complex formation.

$$\frac{d[\mathrm{C}]_t}{dt} = k([\mathrm{O}]_o - [\mathrm{C}]_t) \,, \qquad kt = \ln \frac{[\mathrm{O}]_o}{[\mathrm{O}]_o - [\mathrm{C}]_t} \quad \cdots\cdots\cdots \quad \text{Eq. 1}$$

$$[\mathrm{O}]_o = \frac{A_o - A_\infty}{\varepsilon} \qquad [\mathrm{C}]_t = \frac{A_o - A_t}{\varepsilon}$$

$$kt = \ln \frac{A_o - A_\infty}{A_t - A_\infty} \quad \cdots\cdots\cdots \quad \text{Eq. 2}$$

Scheme 4. Equations for decoloration rate constant.

To determine the decoloration rate constants, time-course absorption-spectral changes of the crowned chromene acetonitrile solutions in the presence of a metal ion were followed at room temperature after turning off UV light.[14] The decoloration rate constants are summarized in Table 2. Among the alkali metal ion complexes of **1**, the Li^+ complex was the most stable one, while Na^+ forms the most stable complex with **2**. However, the complexes of **3** and **4** did not show clear stabilization effect with alkali metal ions. On the other hand, alkaline-earth metal ions showed remarkable stabilization effect in all of the chromene derivatives, even in non-cyclic analogue **4**. This tendency also suggests that the interaction of the carbonyl group with alkaline-earth metal ions[13] seems to be stronger than that with alkali metal ions, resulting in the stabilization of the complexes regardless of ring size of the crown ether moieties.

2.4. Complex stoichiometry of 1

The metal ion binding ability of 12-crown-4 to Li^+ is well known to form 1:1 complex.[15] On the other hand, bis(12-crown-4) derivatives generally show a high binding ability to Na^+ by formation of a sandwich type complex, namely, 1:2 (metal ion: crown ether ring) complex.[16] In the case of polymers carrying a 12-crown-4 moiety at the side chain, their binding ability towards Na^+ is also attained through formation of a similar sandwich type complex.[17] On the other hand, it has been reported that various lariat crown

Table 2. Decoloration rate constants (10^{-2} s^{-1})

	Without metal ion	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
1	6.1	4.4	5.7	6.2	6.2	6.2	1.6	0.029	0.10	0.28
2	6.0	6.2	4.6	5.8	5.7	5.9	2.6	0.051	0.033	0.086
3	6.7	6.5	6.3	6.0	6.1	6.2	0.25	0.021	0.063	0.060
4	5.8	5.8	5.4	5.9	5.9	5.6	2.7	0.17	0.34	0.61

ethers form metal ion complexes in which the lariat moiety interacts with the metal ion captured by the crown ether moiety intramolecularly.[18] To the best of our knowledge, however, the sandwich type complex formation of monomeric (monocyclic) 12-crown-4 derivatives seems to be possible only in the presence of a large excess of crown ether. In the case of the sandwich type Na^+-complex formation of our crowned chromene, therefore, the chromene moiety must play an essential role to induce an intermolecular interaction resulting in the 1:2 complex formation of its 12-crown-4 moiety with Na^+.

In order to investigate the 1:2 complex structure of **1**, ^1H NMR measurement was conducted in the presence of Li^+ and Na^+. The concentrations for **1** and metal ions were 2 and 4×10^{-2} mol dm^{-3}, respectively. Li^+ induced significant downfield shifts (<ca. 0.2 ppm) for the crown ether ring protons and slight downfield shifts (<0.02 ppm) for the chromene moiety and the benzyl protons. In the case of Na^+, the crown ether moiety protons indicated moderate downfield shifts (<0.06 ppm), but the chromene moiety and the benzyl protons exhibited moderate upfield shifts (<0.05 ppm). As upfield shifts are induced by diamagnetic anisotropy of aromatic rings,[19] $\pi-\pi$ stacking of the chromene moieties is strongly suggested. However, further attempts to obtain information about the 1:2 complex structure by X-ray crystallography was failed.

The formation of 1:2 complex was only observed in the case of **1**. With increasing metal ion radius from Li^+ to Cs^+, the complex stoichiometry of **1** changed from 1:1 to 1:2, between 1:1 and 1:2, and finally, returned to 1:1. It is well known that Na^+ is the most suitable to form 1:2 complex with 12-crown-4, but Li^+ and Cs^+ have significant disadvantage to form 1:2 complex with 12-crown-4, where Li^+ and Cs^+ are too small and large in size, respectively. This tendency implies that not only $\pi-\pi$ stacking of the chromene moiety but also the size fitness of the metal ion to the crown ether moiety promotes the formation of 1:2 complex. Although the formation of 1:2 complex is also reported with various 15-crown-5 and 18-crown-6 derivatives in the presence of K^+ and Cs^+, respectively, the corresponding crowned chromenes, **2** and **3**, did not form 1:2 complex. The fact that 15-crown-5 and 18-crown-6 are more flexible than 12-crown-4 implies that flexibility of the crown ether moieties hampers $\pi-\pi$ stacking of the chromene moieties. Probably due to rigidity of the 12-crown-4 moiety, the formation of 1:2 complex occurs only for **1** in the presence of appropriate metal ion.

The complex stoichiometry of **1** with Li^+ and Na^+ under UV irradiation was examined by Job plot method using the absorption spectra data at 420 nm, where there was no absorbance derived from the closed form, as shown in Figure 9. As the chromene derivatives are converted to the open form by UV irradiation in the absence of a metal ion, the absorbance difference between the chromene solutions with and without a metal ion was applied to Job plots to evaluate the complex stoichiometry for the open form under UV irradiation. Both plots afforded the maximum points at

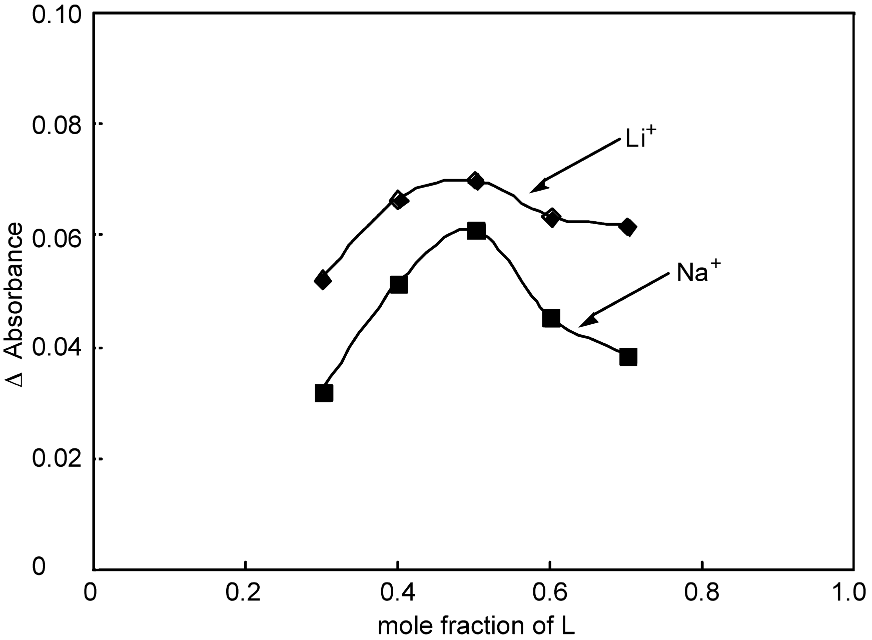
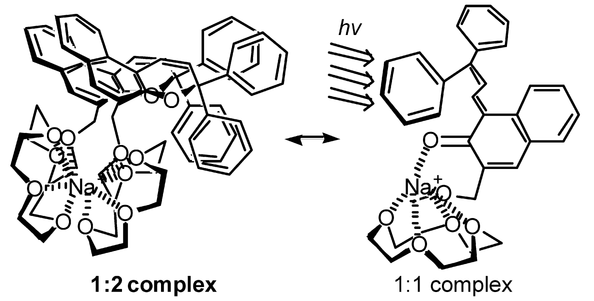
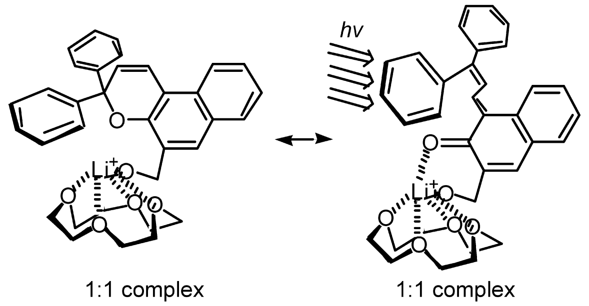


Figure 9. Job plots for Li^+ and Na^+ complexes of **1** under UV irradiation.

0.5, indicating that both complex stoichiometries with Li^+ and Na^+ were 1:1 under UV irradiation. Therefore, it is clear that the Na^+ complex of **1** changed its stoichiometry form 1:2 to 1:1 (Na^+: ligand) by UV irradiation (Scheme 5). On the other hand, the Li^+ complex of **1** adopted 1:1 stoichiometry regardless of UV irradiation (Scheme 6).



Scheme 5. Photoisomerization of Na^+ complex of **1**.



Scheme 6. Photoisomerization of Li^+ complex of **1**.

3. Conclusions

In summary, the Na^+ complex of **1** showed a drastic change in the complex stoichiometry by UV irradiation. The complex stoichiometry of **1** with Na^+ was 1:2 (Na^+: ligand) for the closed form (without UV irradiation), but it turned out to 1:1 for the open form (with UV irradiation) (Scheme 5). On the contrary, Li^+ formed 1:1 stoichiometry complexes regardless of UV irradiation (Scheme 6). This phenomenon indicates that the chromene moiety in the crowned chromenes is a unique functional group not only to show a photochromism but also to switch the complex stoichiometry of its crown ether upon UV irradiation in the presence of a metal ion. Furthermore, the chromene derivatives bearing crown ether moieties showed ion-responsive photochromism depending on the metal ion binding ability of their crown ether moieties.

4. Experimental

4.1. General

All chemicals for synthesis were of available purity and used without further purification. For spectral measurements, spectroscopic grade acetonitrile was used as a solvent, while all metal perchlorates were of the commercially highest purity.

4.2. Synthesis of chromene derivatives: general procedures

Under nitrogen atmosphere, a THF solution (20 mL) of 5-bromomethylchromene (427 mg, 1 mmol) with hydroxymethyl crown ether or non-cyclic analogue (3 mmol) was placed to a three-necked flask at room temperature. Powdered sodium hydroxide (360 mg, 9 mmol) was added, 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 the product was extracted with chloroform. The crude product obtained by solvent evaporation was purified by gel permeation chromatography.

4.2.1. Oxymethyl-12-crown-4-chromene 1. The reaction of bromomethylchromene with hydroxymethyl-12-crown-4 by the general procedures afforded the compound in 70% yield as yellow-orange viscous oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.5–3.9 (17H, m, OCH_2), 4.81 (2H, s, $PhCH_2$), 6.20 (1H, d, *J*=10.0 Hz, CH=), 7.2–7.5 (13H, ArH, CH=), 7.70 (1H, d, *J*=8.4 Hz, ArH), 7.73 (1H, s, ArH), 7.93 (1H, d, *J*=8.4 Hz, ArH); IR (neat, cm^{-1}): 3019 (CH_2), 1221 (OCH_2), 752 (C=C); m/z 552 (M^+). Anal. Calcd for $C_{35}H_{36}O_6$: C 76.06, H 6.57, Found: C 76.15, H 6.37.

4.2.2. Oxymethyl-15-crown-5-chromene 2. The reaction of bromomethylchromene with hydroxymethyl-15-crown-5 afforded the compound in 69% yield as yellow-orange viscous oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.6–3.9 (21H, m, OCH_2), 4.82 (2H, s, $PhCH_2$), 6.19 (1H, d, *J*=10.0 Hz, CH=), 7.1–7.5 (13H, ArH, CH=), 7.70 (1H, d, *J*=8.0 Hz, ArH), 7.75 (1H, s, ArH), 7.91 (1H, d, *J*=8.4 Hz, ArH); IR (neat, cm^{-1}): 3019 (CH_2), 1211 (OCH_2), 769 (C=C); *m/z* 596 (M^+). Anal. Calcd for $C_{37}H_{40}O_7$: C 74.47, H 6.76, Found: C 74.28, H 6.73.

4.2.3. Oxymethyl-18-crown-6-chromene 3. The reaction of bromomethylchromene with hydroxymethyl-18-crown-6 afforded the compound in 83% yield as yellow-brown viscous oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.6–3.9 (25H, m, OCH_2), 4.82 (2H, s, $PhCH_2$), 6.21 (1H, d, *J*=9.6 Hz, CH=), 7.2–7.5 (13H, ArH, CH=), 7.71 (1H, d, *J*=8.0 Hz, ArH), 7.74 (1H, s, ArH), 7.94 (1H, d, *J*=8.4 Hz, ArH); IR (neat, cm^{-1}): 3019 (CH_2), 1209 (OCH_2), 727 (C=C); *m/z* 640 (M^+). Anal. Calcd for $C_{39}H_{44}O_8$: C 73.10, H 6.92, Found: C 72.93, H 6.95.

4.2.4. Non-cyclic analogue-chromene 4. The reaction of bromomethylchromene with non-cyclic analogue afforded the compound in 59% yield as yellow viscous oil: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.16 (3H, t, *J*=7.0 Hz, CH_3), 1.17 (3H, t, *J*=6.2 Hz, CH_3), 3.4–3.9 (17H, m, OCH_2), 4.83 (2H, s, $PhCH_2$), 6.20 (1H, d, *J*=10.0 Hz, CH=), 7.2–7.5 (13H, ArH, CH=), 7.71 (1H, d, *J*=7.6 Hz, ArH), 7.75 (1H, s, ArH), 7.93 (1H, d, *J*=8.0 Hz, ArH); IR (neat, cm^{-1}): 3019 (CH_2), 1221 (OCH_2), 781 (C=C); *m/z* 582 (M^+). Anal. Calcd for $C_{37}H_{42}O_6$: C 76.26, H 7.26, Found: C 76.30, H 7.24.

4.3. NMR titration

The solutions for NMR titration were prepared by solvent substitution. For the determination of binding constants with Li^+ and Na^+, the concentration range of metal ions was $5–40\times10^{-3}$ mol dm^{-3}, and the concentration of the chromene derivatives were fixed on 2×10^{-2} mol dm^{-3}. On the other hand, the concentrations for K^+, Rb^+, and Cs^+ were between $0.5–7\times10^{-3}$ mol dm^{-3}, and the concentration for the chromene derivatives were constant at 5×10^{-3} mol dm^{-3}. For the Job plots, the sum of concentrations for the crowned chromenes and metal perchlorates was 4×10^{-2} mol dm^{-3} for Li^+ and Na^+, while that was 1×10^{-2} mol dm^{-3} with K^+, Rb^+, and Cs^+. In order to determine the binding constants, the binding isotherms by non-linear least-square regression were applied, and the chemical shifts for the complexes were evaluated experimentally by extrapolation.

4.4. Absorption spectra measurement

Absorption spectra measurement was carried out using acetonitrile as the solvent at room temperature. The absorption spectra before UV irradiation were taken after allowing a measuring solution to stand overnight under dark condition. The absorption spectra measurements after UV irradiation were carried out after photoirradiation for 3 min, while irradiating the UV light on the measurement cell in the perpendicular direction to the measuring incident light. The UV light (525 mW/cm^2), obtained by passing light of a 200-W Hg–Xe lamp through a light filter (central wavelength; 363 nm, half width; 9.5 nm, transmittance 0.53), was introduced to the cell compartment of a spectrophotometer by using a glass fiber guide and was irradiated on the quartz cell containing a solution. The concentrations for the chromene derivatives and alkali metal perchlorates were 1×10^{-4} and 5×10^{-4} mol dm^{-3}, respectively. In the case of alkaline-earth metal perchlorates, the concentration was 1×10^{-4} mol dm^{-3}. For the Job plots, the sum of concentrations for the crowned chromenes and metal perchlorates was 1×10^{-4} mol dm^{-3}.

Acknowledgements

We are very much indebted to Japan Society for Promotion of Science (JSPS) for the financial support of this work by a Grant-in-Aid for JSPS fellows. Also, financial support by a Grant-in-Aid-for Scientific Research (B) (No. 15350043) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan is gratefully acknowledged.

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