# Synthesis and Photochromism of Novel Chromene Derivatives Bearing a Monoazacrown Ether Moiety

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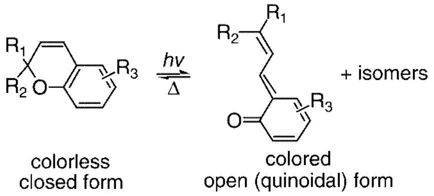
Crowned chromenes – four novel naphthopyrans (chromenes) bearing monoaza-12-crown-4, -15-crown-5, -18-crown-6, and a noncyclic analogue at the 5-position – were synthesized, and their photochromism in acetonitrile was examined in the presence of alkali and alkaline-earth metal ions. Incorporation of crown ether units to chromene moieties facilitated to a great extent both the thermal isomerization and photoisomerization of the chromene moiety, reflecting the metal-ion-binding ability of the crown ether moiety. Comparison of the crowned chromenes with the corresponding crowned spirobenzopyrans reveals that photochromism of the crowned chromene reflects an interaction between the metal ion and the crown ether moiety that is stronger than that of the crowned spirobenzopyran, and shows only positive photochromism with significant red-shifts in the UV/Vis absorption spectra, in contrast to the crowned spirobenzopyrans reported previously.

## Introduction

Photochromism is a reversible photoinduced phenomenon in which a photosensitive substrate is transformed into another isomer exhibiting a different absorption spectrum in the visible region. In the last few decades, the investigation of photochromic molecules[1] has became an important field because of a large number of potential applications, such as optical variable-transmission materials, optical switches, and memories,[2] based on their photoreversibility. The investigated characteristics that have been studied are: (1) coloration by sunlight (heliochromism) and thermal decoloration, (2) absorption in the visible region upon irradiation, (3) rate of decoloration, (4) coloration efficiency upon irradiation (colorability), and (5) resistance to photodegradation (photofatigue resistance).

Pyran compounds such as benzo- and naphthopyrans (chromenes), spiropyrans, and spirooxazines are well-known photochromic materials. Since the discovery of photochromic behavior of the chromene by Becker and coworkers,[3] extensive studies have been devoted to chromenes because of their excellent resistance to photodegradation, which is similar to that of spirooxazines. The photochromic behavior of chromene is based on reversible pyran ring opening, in which its colorless closed form is converted by UV irradiation into a set of corresponding colored open forms that return thermally to the closed form (Scheme 1).[4] Because of the quasi planarity of the open form, extended π-electron conjugation is achieved and a distinct absorption, typically in the visible region, is observed. A noteworthy difference among the pyran compounds is that chromenes[5] and spirooxazines[6] take a quinoidal open form, but spiropyran[7] prefers the zwitterionic open form.



Scheme 1. Photoisomerization of chromene

On the other hand, incorporating the features of both photochromic and metal ion recognition molecules has been reported to afford bifunctional molecules in which the photochromic moiety controls the metal-ion-binding behavior or the metal ion recognition moiety dominates the

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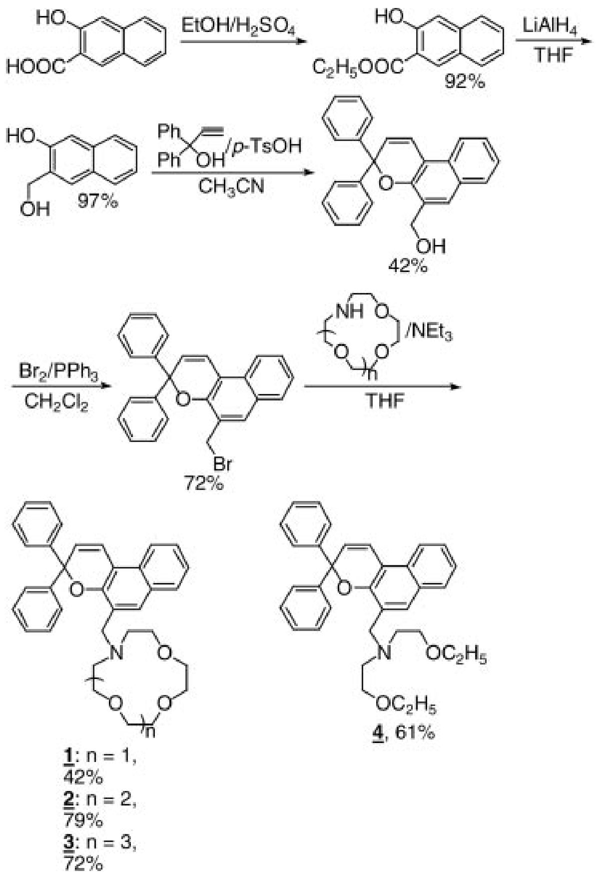
photochromism. The incorporation of crown ether units into azobenzene[8] and diarylethene[9] shows the former tendency, and incorporation into spirooxazine[10] and spirobenzopyran[11,12] indicates the latter behavior. To the best of our knowledge, however, there has been only one report on chromene derivatives bearing a crown ether moiety.[13] In a continuation of our previous work dealing with crowned spirobenzopryran[14,15] and spirooxazine,[16] in this paper we report chromene derivatives bearing a monoazacrown ether moiety, namely crowned chromenes.

## Results and Discussion

**Synthesis:** The synthesis of crowned chromenes **1−3** and their analogue **4** was carried out according to the synthetic route outlined in Scheme 2. 5-Bromomethylchromene was prepared according to a method similar to that found in the literature.[17] The reaction of 5-bromomethylchromene with monoazacrown ethers was undertaken in the presence of triethylamine in dry THF under reflux for 6 h under nitrogen. For comparison with the crowned chromenes, the noncyclic analogue **4** was prepared in a similar fashion. In all cases, the products were isolated by GPC (gel permeation chromatography) in their protonated forms. Deprotonation of the products was carried out by washing with aqueous potassium carbonate solution, and the crowned chromenes **1−3** and the analogue **4** were obtained in moderate to good yields (42−79%).



Scheme 2. Synthetic approach

**Photochromism of Crowned Chromenes:** UV/Vis absorption spectra of the crowned chromenes **1−3** and the analogue **4** were measured in acetonitrile ($1 \times 10^{-4}$ mol·dm$^{-3}$) in the presence of a metal perchlorate ($1 \times 10^{-4}$ mol·dm$^{-3}$) before and after UV irradiation (365 nm, 3 min) at room temperature.[18] As shown in Figure 1, the spectra of **1** are hardly changed by addition of the equimolar amount of an alkali metal ion. This observation means that thermal isomerization to the quinoidal form does not proceed, in contrast to the situation found for the corresponding crowned spirobenzopyran, the pyran ring of which is opened readily without UV irradiation.[19] Upon UV irradiation, the Li$^+$ solution shows the most significant spectral change with a remarkable red-shift, and the Na$^+$ solution indicats a slight spectral change. The facilitated photoisomerization with Li$^+$ is clearly derived from the metal-ion binding ability of the 12-crown-4 moiety. In the case of alkaline-earth metal ions, Ca$^{2+}$ induces a considerable thermal isomerization. On the other hand, the facilitated photoisomerization was observed for all solutions with significant red-shifts (Figure 2).

For the crowned chromene **2**, a slight thermal isomerization is observed in the presence of Li$^+$ (Figure 3), reflecting the strong interaction between Li$^+$ and **2**. Upon UV irradiation, both Li$^+$ and Na$^+$ induce drastic changes in the absorption spectra. This enhancement of photoiso-

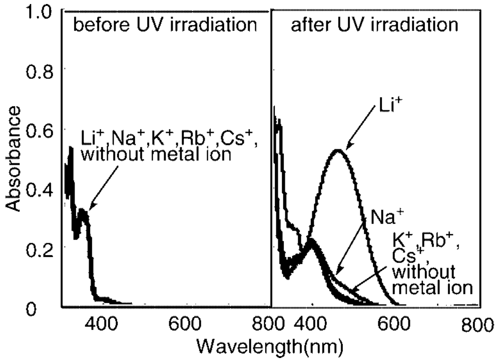


Figure 1. Absorption spectra of **1** in acetonitrile in the presence of alkali-metal ions

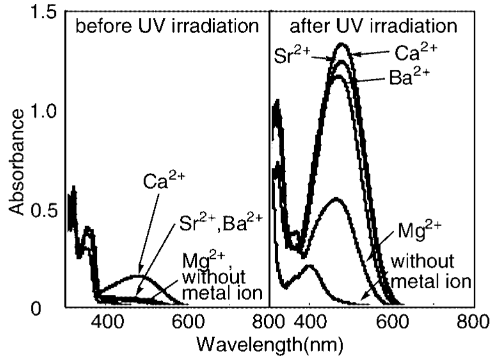


Figure 2. Absorption spectra of **1** in the presence of alkaline-earth metal ions in acetonitrile

merization by $Na^+$ for **2**, compared with that for **1**, may be attributed to the ring-size enlargement of the crown ether moiety. In the presence of alkaline-earth metal ions, the thermal isomerization of **2** is more significant than that of **1**, as shown in Figure 4. Of the alkaline-earth metal ions, $Mg^{2+}$ induces the most significant thermal isomerization and the photoisomerization having the most notable red-shift.

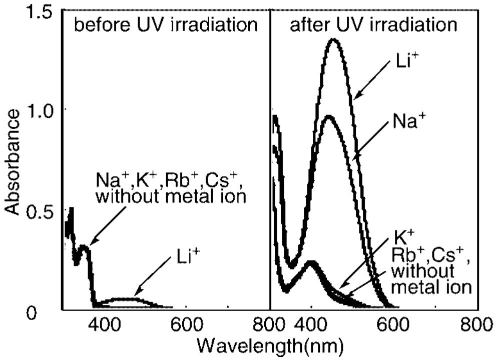


Figure 3. Absorption spectra of **2** in the presence of alkali-metal ions

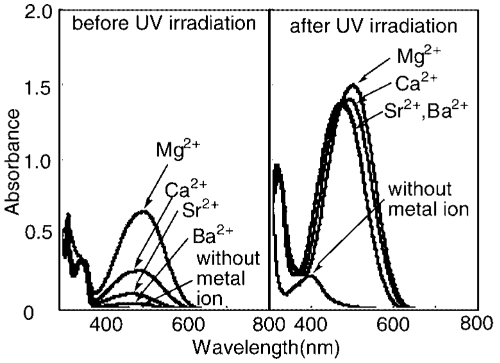


Figure 4. Absorption spectra of **2** in the presence of alkaline-earth metal ions

In the case of **3**, no significant thermal isomerization was observed in the presence of alkali metal ions, an observation similar to that of **1** (Figure 5). UV irradiation induced the most drastic spectral change for the $Na^+$ solution, and the $Li^+$ solution also showed a significant spectral change. Furthermore, $K^+$ facilitated the photoisomerization considerably. With alkaline-earth metal ions (Figure 6), the observed tendency is similar to that for **1** (Figure 2), where $Ca^{2+}$ induces the most significant thermal isomerization and photoisomerization.

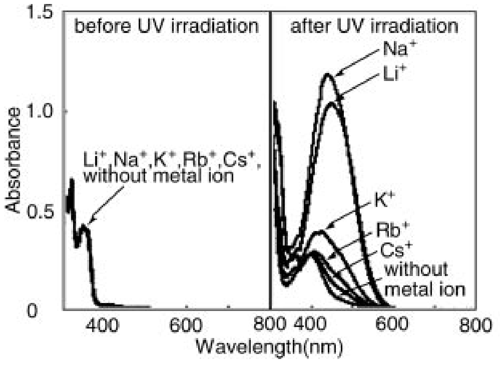


Figure 5. Absorption spectra of **3** in the presence of alkali-metal ions

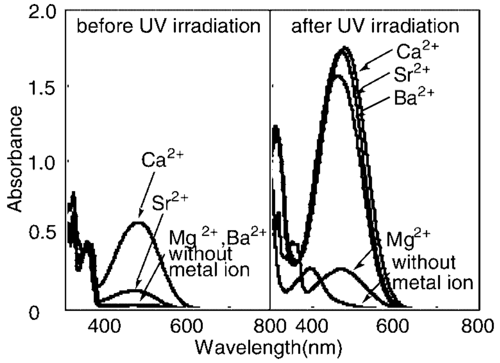


Figure 6. Absorption spectra of **3** in the presence of alkaline-earth metal ions

On the other hand, the non-cyclic analogue **4** did not show any significant thermal isomerization in the presence of any metal ions, as was anticipated from its metal-ion-complexing ability. Similarly, the facilitated photoisomerization was hardly observed in any case, and only $Ca^{2+}$ induced a slight facilitated photoisomerization (Figure 7 and 8).

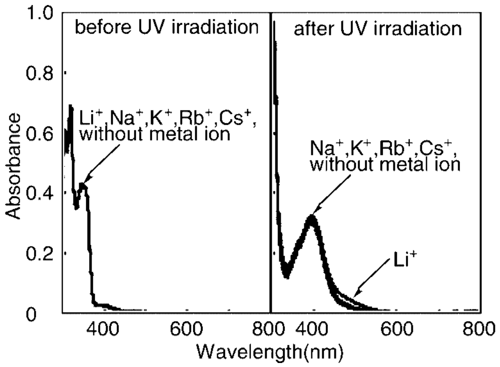


Figure 7. Absorption spectra of **4** in the presence of alkali-metal ions

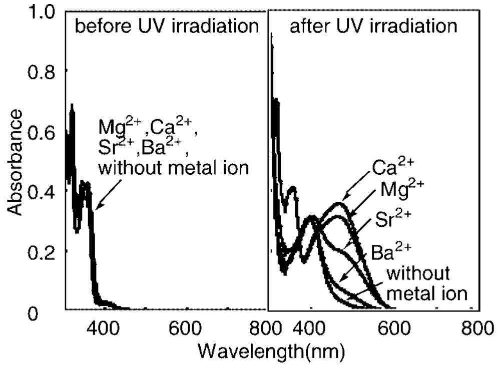
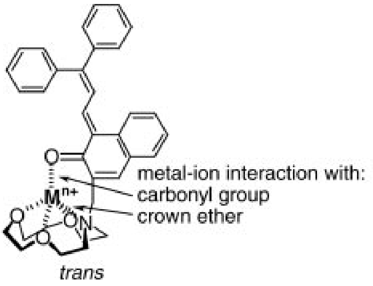


Figure 8. Absorption spectra of **4** in the presence of alkaline-earth metal ions



Scheme 3. Interaction of the metal ion with the carbonyl group and the crown ether unit of the *trans* form.

As depicted in Scheme 3,[4] dual interactions of the metal ion with the crown ether moiety and the carbonyl group are possible in the quinoidal form of the crowned chromene in a similar manner to that in the merocyanine form of the crowned spirobenzopyran.[15] The alkali metal ion that induced the greatest facilitated photoisomerization changed from $Li^+$ to $Na^+$ when the size of the crown ether moiety was increased from 12- to 18-membered rings. In the case of the corresponding crowned spirobenzopyrans, $Li^+$ always induced the most remarkable thermal isomerization, regardless of the ring size of the crown ether moiety, which reflects the strong ionic interaction of $Li^+$ with the phenolate anion moiety in the merocyanine form of the crowned spirobenzopyran.[19] Furthermore, the non-cyclic analogue **4** did not show a thermal isomerization, whereas significant thermal isomerization appeared for the corresponding spirobenzopyran in the presence of $Li^+$. Therefore, this ring-size dependency in the crown ether moiety implies that the interaction of metal ions with the crown ether moiety, rather than with the carbonyl group, is predominant in determining the tendency for photochromism in crowned chromenes. Among alkaline-earth metal ions, $Ca^{2+}$ showed the most significant influence on both the thermal isomerization and photoisomerization of **1**, **3**, and **4**, while $Mg^{2+}$ was the most effective for **2**. A similar independence of the ring size in the crown ether moiety also was observed for the crowned spirobenzopyrans. The charge density of alkaline-earth metal ions is much higher than that of alkali metal ions and, therefore, the effect of alkaline-earth metal ions on the isomerization may be stronger than that of alkali-metal ions through stronger interactions between the metal ion and the carbonyl group, a situation similar to that observed for the phenolate anion moiety of crowned spirobenzopyrans.[15] A comparison of crowned chromenes with the corresponding crowned spirobenzopyrans suggests that the enhanced photochromism of crowned chromenes reflects that the metal-ion-binding ability of their crown ether moieties is stronger than that in the crowned spirobenzopyran, since the interaction of the metal ion with the carbonyl group in the crowned chromene is weaker than that with the phenolate anion moiety in the crowned spirobenzopyran.

For the crowned chromenes, the wavelengths at the maximum absorption point for the solutions undergoing facilitated photoisomerizations show significant red-shifts, whereas blue-shifts appeared for the crowned spirobenzopyran. It has been reported that both red- and blue-shifts can be induced by solvation,[20] and the quinoidal form of chromene shows a slight red-shift in polar solvents.[21] The most significant red-shift (104 nm), when compared with the solution absent the metal ion, was observed for the $Mg^{2+}$ solution of **2**, indicating a strong interaction between $Mg^{2+}$ and the quinoidal form. A $^1H$ NMR spectrum of a solution of **2** ($1 \times 10^{-2}$ mol·dm$^{-3}$) in the presence of an excess of $Mg^{2+}$ ions ($1 \times 10^{-1}$ mol·dm$^{-3}$) showed a significant downfield shift (ca. 0.4 ppm) for the protons of the crown ether moiety resulting from the formation of a complex with $Mg^{2+}$. In the previous study on photochromism of the crowned spirobenzopyran, negative photochromism was induced when a strong interaction was observed between the metal ion and the crowned spirobenzopiran.[15] An attempt, however, to induce negative photochromism for **2** ($1 \times 10^{-4}$ mol·dm$^{-3}$) in the presence of a high concentration of $Mg^{2+}$ ($5 \times 10^{-3}$ mol·dm$^{-3}$) was not successful, again showing different behavior than that of the crowned spirobenzopyran.

**Stabilization Effect of Metal Ions on the Quinoidal Form:** To evaluate the stabilization effect of metal ions on the quinoidal form of the crowned chromenes, we determined rate constants for thermal decoloration in a similar fashion as that reported earlier.[18] Unfortunately, the crowned chromenes **1−3**, as well as the non-cyclic analogue **4**, showed poor resistance to photodegradation in the absence of metal ions, which hampered determination of the rate constants. Similarly, the serious photodegradation resulted in a failure to determine reliable rate constants when no significant facilitated photoisomerization was observed, even in the presence of metal ions. In contrast, reliable rate constants were obtained for the solutions that showed notable facilitated photoisomerization, namely, those with a strong interaction between the metal ions and the quinoidal form. This tendency implies that the strong interaction of metal ions with the crowned chromene enhances the resistance to photodegradation as well as the facilitated photoisomerization. The

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

| | Without metal ion[a] | $Li^+$ | $Na^+$ | $K^+$ | $Rb^+$ | $Cs^+$ | $Mg^{2+}$ | $Ca^{2+}$ | $Sr^{2+}$ | $Ba^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| **1** | n.d. | 4.5 | n.d. | n.d. | n.d. | n.d. | n.d. | 0.097 | 0.40 | 0.45 |
| **2** | n.d. | 0.063 | 1.6 | n.d. | n.d. | n.d. | 0.0069 | 0.019 | 0.063 | 0.11 |
| **3** | n.d. | 1.8 | 1.7 | 4.9 | n.d. | n.d. | n.d. | 0.0075 | 0.038 | 0.23 |
| **4** | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |

[a] n.d.: Reliable constant was not determined.

smaller rate constants for decoloration mean that there are greater stabilization effects on the quinoidal form of the crowned chromenes. The rate constants are summarized in Table 1.

Among alkali-metal ions, distinct stabilization effects were observed with $Li^+$ for **1**, $Li^+$ and $Na^+$ for **2**, and $Li^+$, $Na^+$ and $K^+$ for **3**. This tendency clearly reflects the metal-ion-binding ability of the crown ether moiety depends on the ring size. Pronounced stabilization effects were observed when the crowned chromenes interacted with alkaline-earth metal ions. Specifically, $Ca^{2+}$ showed a strong stabilization effect for all the crowned chromenes. The trends in the rate constants for decoloration are consistent with those in the UV/Vis absorption spectra.

## Conclusion

The metal-ion-binding ability of the crown ether moiety in crowned chromenes drastically influences photochromism in a similar way to that observed for crowned spirobenzopyran. A comparison of the crowned chromene with the corresponding crowned spirobenzopyran revealed the following three features: (1) the photochromism of the crowned chromenes reflects an interaction between the metal ions and the crown ether moieties that is stronger than that of the crowned spirobenzopyran because the metal ion interacts more weakly with the carbonyl group in the crowned chromenes than with the phenolate anion moiety in the crowned spirobenzopyran; (2) a strong interaction between the metal ion and the crowned chromene caused a significant red-shift in the UV/Vis absorption spectrum in contrast to the blue-shift observed for the crowned spirobenzopyran; (3) the crowned chromene did not show the negative photochromism that was observed with the crowned spirobenzopyran.

## Experimental Section

**General Remarks:** All chemicals for synthesis were of available purity and used without further purification. For spectral measurements, spectroscopic-grade acetonitrile was used as the solvent, while all metal perchlorates were the highest grade available and were employed as received. The procedures for the spectral measurement and the determination of the rate constants for decoloration are described in reference [18]. 5-Bromomethylchromene and 3,9-dioxa-6-monoazaundecane were prepared according to the methods reported in ref.[17] and ref.[18], respectively. For the measurement of NMR spectra, [D$_3$]acetonitrile and magnesium perchlorate were used at room temperature.

**Synthesis of Chromenes. General Procedure:** Under nitrogen, monoaza-crown ether (0.5 mmol), 5-bromomethylchromene (214 mg, 0.5 mmol), triethylamine (150 mg, 1.5 mmol), and dry THF (50 mL) were placed into a three-necked flask, and the reaction mixture was refluxed for 6 h. The product obtained by solvent evaporation was purified by GPC (gel permeation chromatography) in its protonated form. The chloroform solution obtained by GPC was washed with 5-wt% aqueous potassium carbonate, and the organic phase was dried overnight on anhydrous sodium sulfate. The solids were filtered off and the product was obtained by evaporation of the solvent.

**Monoaza-12-crown-4-chromene (1):** The preparation of **1** was carried out according to the general procedure described above, and the product (0.211 mmol, 110 mg, 42%, $C_{34}H_{35}NO_4$, MW 521.65) was obtained as a viscous, yellow-brown oil: $^1H$ NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 2.83 (t, $J$ = 4.6 Hz, 4 H, $NCH_2$), 3.6−3.8 (m, 12 H, $OCH_2$), 3.94 (s, 2 H, $PhCH_2$), 6.20 (d, $J$ = 9.6 Hz, 1 H, CH=), 7.2−7.5 (m, 13 H, ArH, CH=), 7.72 (d, $J$ = 8.0 Hz, 1 H, ArH), 7.93 (d, $J$ = 8.0 Hz, 1 H, ArH), 8.02 (s, 1 H, ArH) ppm. IR (neat): $\tilde{\nu}$ = 2855 ($CH_2$), 1110 ($OCH_2$), 753 (C=C) $cm^{-1}$. MS: $m/z$ = 521 [$M^+$]. $C_{34}H_{35}NO_4 \cdot H_2O$: calcd. C 75.67, H 6.91, N 2.60; found C 76.07, H 6.58, N 2.47.

**Monoaza-15-crown-5-chromene (2):** The preparation of **2** was carried out according to the general procedure described above, and the product (0.394 mmol, 223 mg, 79%, $C_{36}H_{39}NO_5$, MW 565.71) was obtained as a viscous, yellow-brown oil: $^1H$ NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 2.88 (t, $J$ = 6.0 Hz, 4 H, $NCH_2$), 3.6−3.7 (m, 16 H, $OCH_2$), 3.94 (s, 2 H, $PhCH_2$), 6.20 (d, $J$ = 9.6 Hz, 1 H, CH=), 7.2−7.6 (m, 13 H, ArH, CH=), 7.71 (d, $J$ = 8.0 Hz, 1 H, ArH), 7.83 (s, 1 H, ArH), 7.91 (d, $J$ = 8.4 Hz, 1 H, ArH) ppm. IR (neat): $\tilde{\nu}$ = 2867 ($CH_2$), 1121 ($OCH_2$), 753 (C=C) $cm^{-1}$. MS: $m/z$ = 565 [$M^+$]. $C_{36}H_{39}NO_5$: calcd. C 76.43, H 6.95, N 2.48; found C 76.05, H 7.09, N 2.51.

**Monoaza-18-crown-6-chromene (3):** The preparation of **3** was carried out according to the general procedure described above, and the product (0.349 mmol, 213 mg, 70%, $C_{38}H_{43}NO_6$, MW 609.74) was obtained as a viscous, yellow-brown oil: $^1H$ NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 2.87 (t, $J$ = 6.0 Hz, 4 H, $NCH_2$), 3.5−3.8 (m, 20 H, $OCH_2$), 3.93 (s, 2 H, $PhCH_2$), 6.21 (d, $J$ = 10 Hz, 1 H, CH=), 7.2−7.5 (m, 13 H, ArH, CH=), 7.71 (d, $J$ = 8.4 Hz, 1 H, ArH), 7.82 (s, 1 H, ArH), 7.92 (d, $J$ = 8.4 Hz, 1 H, ArH) ppm. IR (neat): $\tilde{\nu}$ = 2905 ($-CH_2-$), 1106 ($OCH_2$), 755 (C=C) $cm^{-1}$. MS: $m/z$ = 609 [$M^+$]. $C_{38}H_{43}NO_6 \cdot H_2O$: calcd. C 72.70, H 7.22, N 2.23; found C 72.99, H 7.05, N 2.24.

**3,9-Dioxa-6-monoazaundecane-chromene (4):** Preparation was of **4** carried out according to the general procedure described above, and the product (0.305 mmol, 155 mg, 61%, $C_{34}H_{37}NO_3$ , MW 507.67) was obtained as a viscous, dark-yellow oil: $^1H$ NMR ($CDCl_3$, 400 MHz, 25 °C): δ = 1.14 (t, $J$ = 7.0 Hz, 6 H, $CH_3$), 2.84 (t, $J$ = 6.2 Hz, 4 H, $NCH_2$), 3.38 (q, $J$ = 7.1 Hz, 4 H, $OCH_2$), 3.51 (t, $J$ = 6.2 Hz, 4 H, $OCH_2$), 3.96 (s, 2 H, $PhCH_2$), 6.20 (d, $J$ = 9.6 Hz, 1 H, CH=), 7.2−7.6 (m, 13 H, ArH, CH=), 7.70 (d, $J$ = 8.4 Hz, 1 H, ArH), 7.83 (s, 1 H, ArH), 7.92 (d, $J$ = 8.4 Hz, 1 H, ArH) ppm. IR (neat): $\tilde{\nu}$ = 2864 ($CH_2$), 1110 ($OCH_2$), 749 (C=C) $cm^{-1}$. MS: $m/z$ = 507 [$M^+$]. $C_{34}H_{37}NO_3 \cdot 1/2H_2O$: calcd. C 79.04, H 7.41, N 2.71; found C 79.24, H 7.37, N 2.62.

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[19] The supporting information shows the UV/Vis absorption spectra indicating the thermal isomerization tendencies of the corresponding crowned spirobenzopyrans, for supporting information see also the footnote on the first page of this article.

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