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Metal-ion stabilization of photoinduced open colored isomer in crowned spirobenzothiapyran

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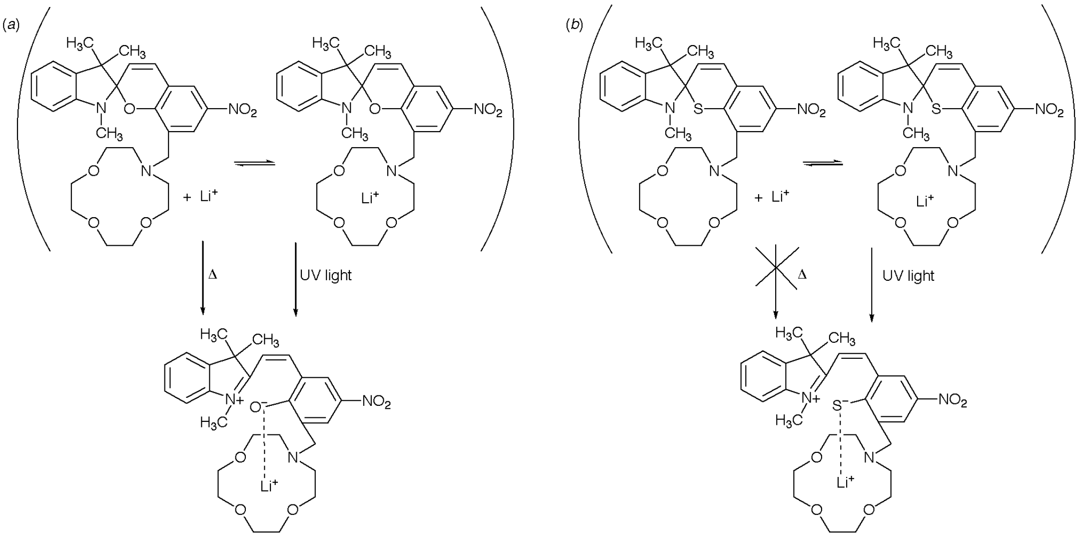
A spirobenzothiapyran derivative bearing a monoaza-12-crown-4 moiety affords significant thermal stability enhancement in the UV light induced colored merocyanine form of its photochromic moiety by metal-ion complexation of its crown ether moiety, although the complexation hardly induces the isomerization without photoirradiation.

Spirobenzopyrans[1] and spirobenzothiapyrans[2] are well-known photochromic compounds that isomerize to their corresponding merocyanine forms under UV light, and *vice versa* under visible light or heat. Such kinds of compounds have been studied extensively in view of photochromic devices.[3] However, the application of spirobenzothiapyrans to photochromic devices does not seem to be very easy due to the poor thermal stability of their open colored form. In our previous studies[4] on spirobenzopyrans bearing a monoazacrown ether moiety, we found that the spiropyran ring opening was facilitated by metal ion complexation of the crown ether moiety in the presence of metal ions. This resulted in the spiropyran ring opening even without UV light irradiation [Scheme 1(*a*)]. This finding prompted us to design spirobenzothiapyrans bearing a crown ether moiety, which we call crowned spirobenzothiapyrans, expecting facilitation of the thiapyran ring opening by metal ion complexation of the crown ether moiety. This in turn may allow the resulting spirobenzothiapyrans to be applicable for photochromic devices. Here we report preliminary results on significant stabilization of the photoinduced open colored isomer of a crowned spirobenzothiapyran in the presence of alkali metal ions, especially Li^+.

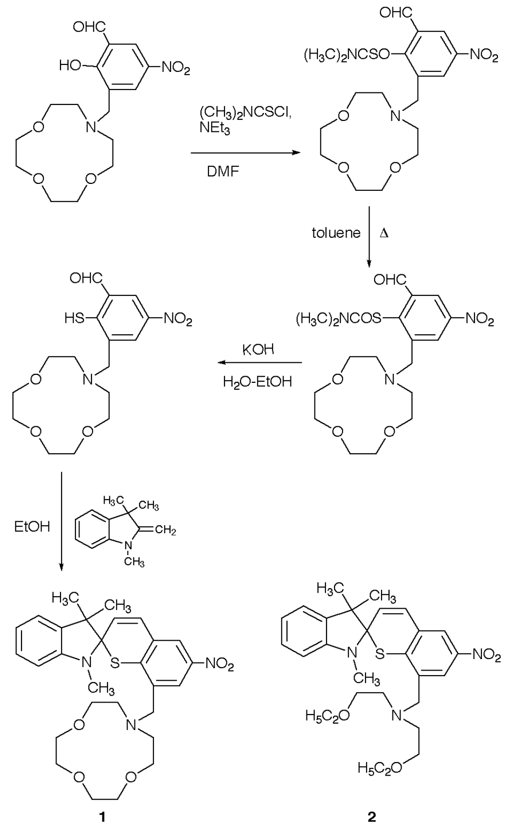
The synthesis of crowned spirobenzothiapyran **1** was carried out in accordance with Scheme 2. The conversion of the phenolic hydroxy group of crowned nitrosalicylaldehyde[4a] to the corresponding thiol group was attained by the reaction with $(CH_3)_2NCSCl$ at 0–25 °C in the presence of NEt_3, by refluxing in toluene, and by hydrolysis with KOH.[2d] The crowned thiosalicylaldehyde was then reacted with 2-methylene-1,3,3-trimethylindoline in refluxing EtOH to yield the spirobenzothiapyran bearing a monoaza-12-crown-4 moiety, **1**, which was purified by recrystallization from EtOH after preparative gel-permeation chromatography.† For comparison, we also synthesized a spirobenzothiapyran derivative bearing an oligooxyethylene moiety, **2**, in a similar way to **1**.

Absorption spectra of **1** and **2** were measured in MeCN in the presence and absence of an alkali metal perchlorate. The spectra of **1** and **2** were hardly changed by adding an equimolar amount of Li^+, Na^+, and K^+, unless irradiated by UV light. This means that isomerization to their merocyanine form by the thiapyran ring opening cannot proceed by metal ion complexation of their crown ether ring under dark conditions [Scheme 1(*b*)]. This isomerization behavior of **1** is very different from that of the spirobenzopyran bearing a monoaza-12-crown-4 moiety, the pyran ring of which can be opened readily by metal ion complexation even without UV light irradiation[4] [Scheme 1(*a*)], probably due to the polarity increase induced by the metal ion binding.

It should be noted that irradiation of 365 nm UV light‡ on the **1** solution containing Li^+ causes a drastic change in the absorption spectrum (Fig. 1). On the other hand, hardly any significant spectral change was observed in the **1** solution without any metal ion and with an equimolar amount of K^+. The Na^+ addition afforded only a slight spectral change (Fig. 1). Definitely, the metal ion complexing ability of the crown ether



Scheme 1



1 **2**

Scheme 2

moiety of **1** stabilizes the colored merocyanine isomer that is formed only on UV light irradiation, owing to the polarity enhancement. It is worth noting that the stabilization is highly selective for Li^+. In addition to the selective Li^+ binding with a monoaza-12-crown-4 moiety of **1**, some interaction between the thiolate anion and Li^+ complexed by the crown ether moiety probably contributes to the stabilization of the colored merocyanine isomer of **1,** as is the case with the Li^+ complex for merocyanine form of crowned spirobenzopyran (Scheme 1).[4c] This Li^+-specific stabilization of the photoinduced colored form of **1** is also supported by photochromism for a model compound carrying a linear oligooxyethylene moiety instead of a crown ether moiety, **2**. Since the linear oligooxyethylene moiety of **2** cannot bind a metal ion very powerfully, the presence of a metal ion, even Li^+, scarcely induced such UV light-induced isomerization to the open colored isomer as seen in the **1** system.

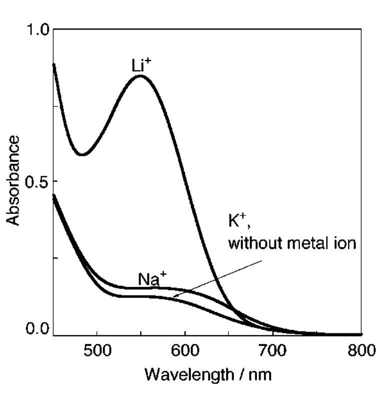


Fig. 1 Absorption spectra of crowned spirobenzothiapyran **1** under UV irradiation in the absence and presence of an alkali metal ion. **1** and alkali metal perchlorate: 2×10^{-4} mol dm^{-3} in acetonitrile.

In order to elaborate the thermal stability of the open colored form of crowned spirobenzothiapyran **1** in MeCN, thermal decoloration of the **1** solution in the presence or absence of Li^+ was followed at room temperature by turning off UV the light.§ In the absence of Li^+, the thermal isomerization back to the spiropyran form was complete within 5 s. On the contrary, the thermal back-isomerization in the presence of Li^+ was very sluggish even by visible light irradiation, the half-life of the UV-induced merocyanine isomer being about 2 min. This again proves the Li^+ complexation-induced high stability of the colored merocyanine form in crowned spirobenzothiapyran **1**.

In conclusion, the crowned spirobenzothiapyran **1** exhibits characteristic photochromism as follows: i) the isomerization of **1** to its corresponding colored merocyanine form does not proceed even in the presence of any crown ether complexing metal ion, unless otherwise irradiated by UV light; ii) the Li^+-selective complexation of the crown ether moiety facilitates UV light induced isomerization (thiapyran ring opening) dramatically; and iii) the metal ion complexation stabilizes the colored merocyanine isomer thus formed to a great extent. Thus the photochromic crown ether seems to be promising for applications such as photochromic devices.

Notes and references

† *Selected data* for **1** : mp 146–148 °C; δ_H($CDCl_3$, 500 Hz) 1.23 (3H, s, CH_3), 1.37 (3H, s, CH_3), 2.68 (3H, s, NCH_3), 2.71 (4H, t, *J* 4, NCH_2), 3.53–3.77 (14H, m, OCH_2 and $PhCH_2N$), 5.98 (1H, d, *J* 6, CH=), 6.50 (1H, d, *J* 7.5, ArH), 6.85 (1H, t, *J* 7, ArH), 6.93 (1H, d, *J* 6, CH=), 7.06 (1H, d, *J* 6.5, ArH), 7.17 (1H, t, *J* 7.5, ArH), 7.93 (1H, s, ArH), 8.73 (1H, s, ArH). Calc. for $C_{28}H_{35}N_{30}O_5S$: H, 6.67, C, 64.00; N, 8.00; S, 6.10. Found: H, 6.63; C, 63.86; N, 7.86; S, 5.84%.

‡ The UV light, obtained by passing light of a 250 W Hg lamp through a light filter (wavelength 363.25 nm, $\Delta\mu/2$ 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 absorption spectra were therefore taken, while irradiating the measurement cell in the perpendicular direction to the measuring incident light.

§ The thermal coloration was followed by measuring the absorbance at 550 nm after UV light irradiation for 1.5 min.

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