

Synthesis and Photochromism of Spirobenzopyrans and Spirobenzothiopyran Derivatives Bearing Monoazathiocrown Ethers and Noncyclic Analogues in the Presence of Metal Ions

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Spirobenzopyrans bearing monoazathiocrown ethers and noncyclic analogues were synthesized, and their ion-responsive photochromism depending on the dual metal ion interaction with the crown ether and the phenolate anion moieties was examined using alkali and alkaline-earth metal ions, Ag⁺, Tl⁺, Pb²⁺, Hg²⁺, and Zn²⁺. The prepared spirobenzopyrans showed a selective binding ability to Mg²⁺ and Ag⁺ with negative and positive photochromism, respectively. Among the metal ions, only Ag⁺ facilitated photoisomerization to the corresponding merocyanine form. Depending on the ring size of the monoazathiocrown ether moieties, soft metal ions such as Hg²⁺ and Ag⁺ showed significant shifts in the UV–vis absorption spectra, while hard metal ions such as Mg²⁺, Zn²⁺, and Pb²⁺ did not afford any meaningful shift. This result reflects that the monoazathiocrown ether and phenolate anion moieties prefer soft and hard metal ions, respectively. Therefore, the Mg²⁺ and Ag⁺ selectivities are mainly derived from the phenolate anion and monoazathiocrown ether moieties, respectively. On the other hand, a spirobenzothiopyran bearing 3,9-dithia-6-monoazaundecane showed a remarkable selectivity to Ag⁺.

Introduction

Photochromic properties of recently synthesized compounds have been examined extensively to explore their potentiality in optical devices.¹ Spirobenzopyrans are well-known photochromic compounds that isomerize from spiroopyran to merocyanine forms by UV light and vice versa by visible light or heat.¹ It has been recognized that incorporation of a crown ether moiety into a spirobenzopyran affords ion-responsive photochromic materials, reflecting the metal-ion binding ability of the crown ether moieties.²

In our previous work, spirobenzopyrans bearing a crown ether moiety, crowned spirobenzopyrans, showed

photochromism switching between positive and negative, depending on the metal ion.³ There are two metal ion interactions in the merocyanine form of a crowned spirobenzopyran as shown Scheme 1, where the metal ion interaction with the phenolate anion moiety induces the photoisomerization back to the corresponding spiroopyran form upon UV irradiation, resulting in appearance of negative photochromism.⁴

In the case of crowned spirobenzothiopyrans, not only alkali and alkaline-earth metal ions but also Ag⁺ influenced photochromism through a strong affinity of the thiophenolate anion moiety to Ag⁺.⁵ It is well-known that oxygen atoms prefer hard metal ions such as alkali and alkaline-earth metal ions, while sulfur atoms tend to bind with soft metal ions.⁶ Therefore, spirobenzopyrans bearing monoazathiocrown ether moieties were designed and examined for the influence of the combination of a soft metal ion preferred monoazathiocrown ether and a hard metal ion preferred phenolate anion on photochromism.

In this paper, we report the synthesis of spirobenzopyrans and spirobenzothiopyran derivatives bearing mono-

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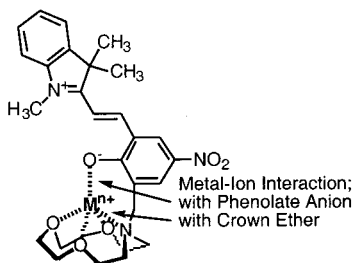
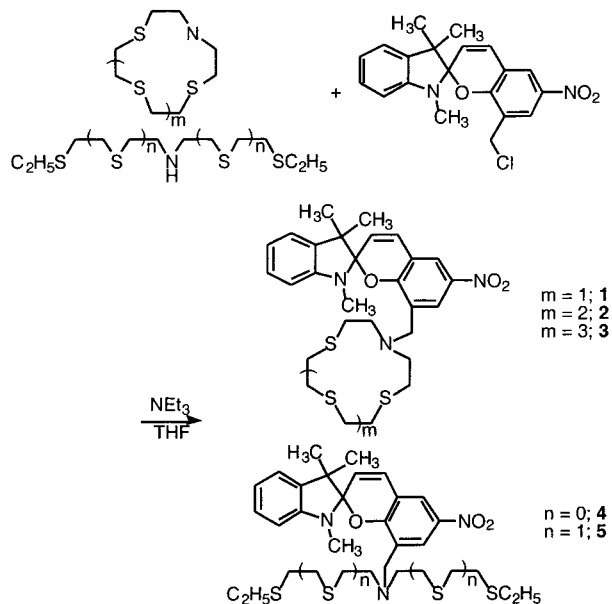
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Scheme 1. Two Metal Interactions**Scheme 2. Synthesis of Spirobenzopyrans**

azathiacyclic crown ethers and noncyclic analogues and their photochromism in the presence of various metal ions.

Results and Discussion

Synthetic procedures are outlined in Scheme 2. Monoazathiacyclic crown ethers and noncyclic analogues were prepared according to the procedures reported elsewhere.⁷ Spirobenzopyrans bearing monoazathiacyclic crown ethers **1–3** were prepared by the reaction of monoazathiacyclic crown ethers with chloromethyl spirobenzopyran derivative in dry THF in the presence of triethylamine under a nitrogen atmosphere. Noncyclic analogues **4** and **5** were also prepared in a similar fashion.

Absorption spectra of **1** in acetonitrile solution with an alkali metal ion before and after 365 nm UV irradiation for 3 min at room temperature are shown in Figure 1. Only Li^+ suppressed the photoisomerization to the merocyanine form slightly through the interaction with the phenolate anion moiety,⁴ and no influence in absorption spectra was observed with other metal ions. Similar results were obtained with other spirobenzopyran derivatives **2–5**. This is consistent with the results of the solvent extraction experiments where monoazathiacyclic crown ethers did not extract alkali metal ions.⁷

In the case of alkaline-earth metal ions (Figure 2), **1** showed significant spectral change before UV irradiation in the presence of Mg^{2+} , reflecting that the Mg^{2+} interaction with **1** induced isomerization even without UV irradiation, namely, thermal isomerization.

The thermal isomerization induced by Mg^{2+} resulted in the appearance of negative photochromism upon UV

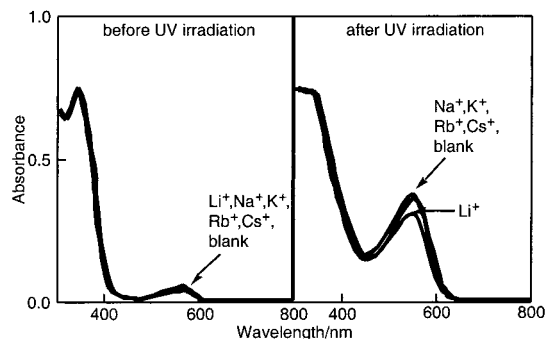


Figure 1. Absorption spectra of **1** in the presence of an alkali metal ion.

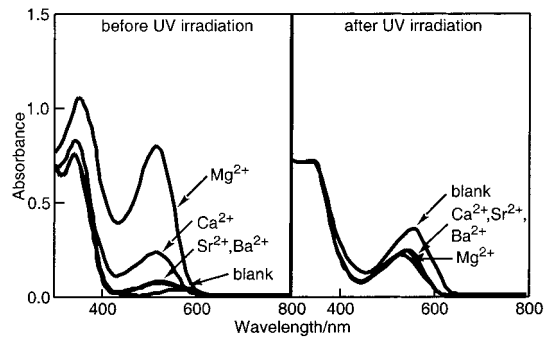


Figure 2. Absorption spectra of **1** in the presence of an alkaline-earth metal ion.

irradiation because of the strong interaction between Mg^{2+} and the phenolate anion moiety in the merocyanine form of **1**.⁴ Similarly, Ca^{2+} induced considerable thermal isomerization to show negative photochromism, but positive photochromism appeared with Sr^{2+} and Ba^{2+} . Negative photochromism induced by Mg^{2+} and Ca^{2+} was observed for **2–5**, but the Mg^{2+} preference over Ca^{2+} was not very drastic compared with that in **1**. The wavelength of maximal absorption for the merocyanine form with Mg^{2+} before UV irradiation was 513, 512, 516, 516, and 514 nm for **1–5**, respectively. These similar values indicate that the Mg^{2+} interaction with the phenolate anion moiety is predominant in **1–5** and causes thermal isomerization,⁸ which is supported by the fact that the phenolate anion in the merocyanine form of spirobenzopyrans prefers metal ions possessing a higher charge density such as Li^+ and Mg^{2+} .⁹ As only the monoazathiacyclic crown ether moiety shows some binding ability to Mg^{2+} in solvent extraction experiments,⁷ the significant Mg^{2+} preference over Ca^{2+} in the binding ability of **1** seems to be derived from the cooperation of the monoazathiacyclic crown ether moiety with the phenolate anion moiety.

The absorption spectra of **1** with a heavy metal ion are depicted in Figure 3 with the wavelength of maximal absorption in parentheses. Significant thermal isomerization of **1** was observed with other divalent metal ions

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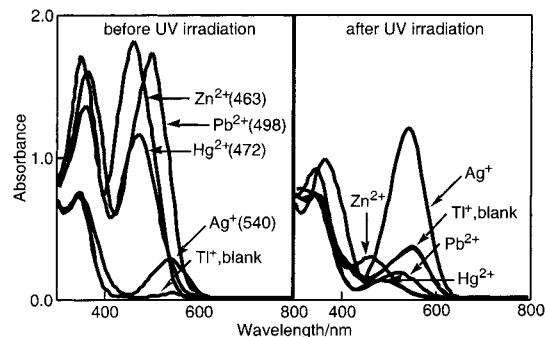


Figure 3. Absorption spectra of **1** in the presence of a heavy metal ion.

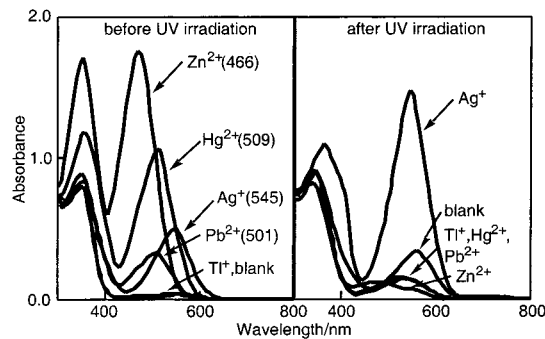


Figure 4. Absorption spectra of **2** in the presence of a heavy metal ion.

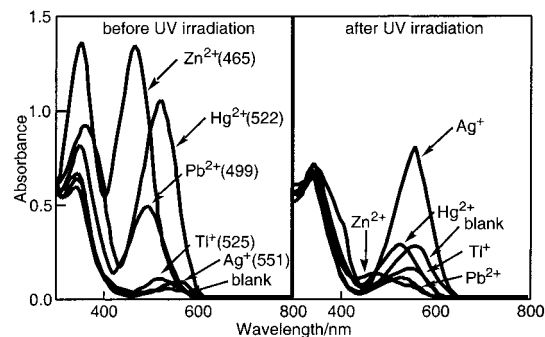


Figure 5. Absorption spectra of **3** in the presence of a heavy metal ion.

such as Hg^{2+} , Pb^{2+} , and Zn^{2+} that induced negative photochromism upon UV irradiation in a similar way to Mg^{2+} . In the case of monovalent metal ions, Ag^+ also showed considerable thermal isomerization, but Ag^+ induced significant facilitation of photoisomerization to the merocyanine form in contrast to the divalent metal ion systems. This tendency might reflect that Ag^+ interacts with the monoazathiacycrown ether moiety much stronger than with the phenolate anion moiety in the merocyanine form of **1**, judging from its longer wavelength of maximal absorption compared with the divalent metal ions. On the other hand, TI^+ did not show any interaction with **1**.

Absorption spectra of **2** and **3** in the presence of a heavy metal ion are shown in Figures 4 and 5. By increasing the ring size of the monoazathiacycrown ether moieties from 12 to 18, we observed a red shift in absorption spectra with Hg^{2+} and Ag^+ , where the wavelengths of maximal absorption were 472, 509, and 522 nm with Hg^{2+} and 540, 545, and 551 nm with Ag^+ for **1–3**, respectively. On the other hand, Zn^{2+} (463, 466, and 465

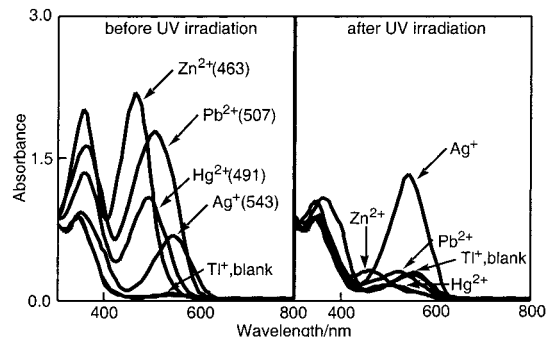


Figure 6. Absorption spectra of **4** in the presence of a heavy metal ion.

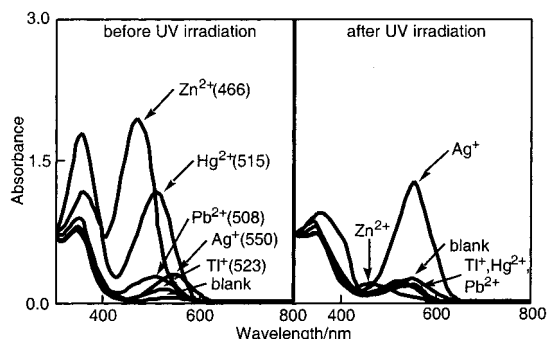


Figure 7. Absorption spectra of **5** in the presence of a heavy metal ion.

nm for **1–3**, respectively) and Pb^{2+} (498, 501, and 499 nm for **1–3**, respectively) did not show such a shift in absorption spectra. It is well-known that Mg^{2+} , Zn^{2+} , and Pb^{2+} are hard metal ions, while Hg^{2+} and Ag^+ are soft metal ions. Furthermore, the strong affinity of the monoazathiacycrown ether rings for Hg^{2+} and Ag^+ was observed in the solvent extraction experiments.⁷ Therefore, this red shift in absorption spectra clearly reflects that soft metal ions such as Hg^{2+} and Ag^+ are separated from phenolate anion moieties by monoazathiacycrown ether moieties with increasing their ring size. In the case of Pb^{2+} , thermal isomerization depended significantly on the ring size of the monoazathiacycrown ether moieties, although the Pb^{2+} interaction with the phenolate anion moiety was predominant, as is the case with Mg^{2+} . This phenomenon suggests that the weak Pb^{2+} interaction with the monoazathiacycrown ether moiety also contributes to thermal isomerization. A similar tendency was observed with **4** and **5** as shown in Figures 6 and 7, respectively. The close similarity in photochromism between the spirobenzopyrans bearing monoazathiacycrown ethers and noncyclic analogues with heavy metal ions¹⁰ suggests that the combination of sulfur and oxygen atoms around the spiropyran moiety is a predominant factor in controlling heavy metal ion-responsive photochromism.

Taking the above results into account, we designed a spirobenzothiapyran bearing 3,9-dithia-6-monoazaundecane **6** as a Ag^+ -responsive photochromic material (Scheme 3). The absorption spectra of **6** in the presence of a heavy metal ion are shown in Figure 8. In the presence of Ag^+ ,

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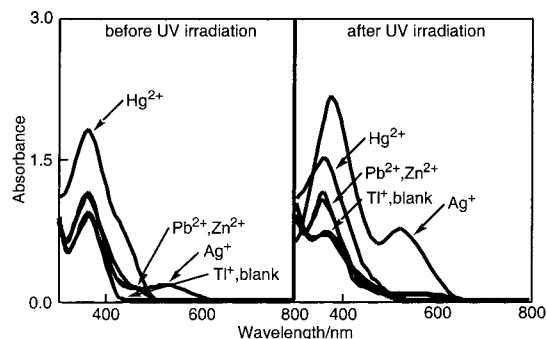
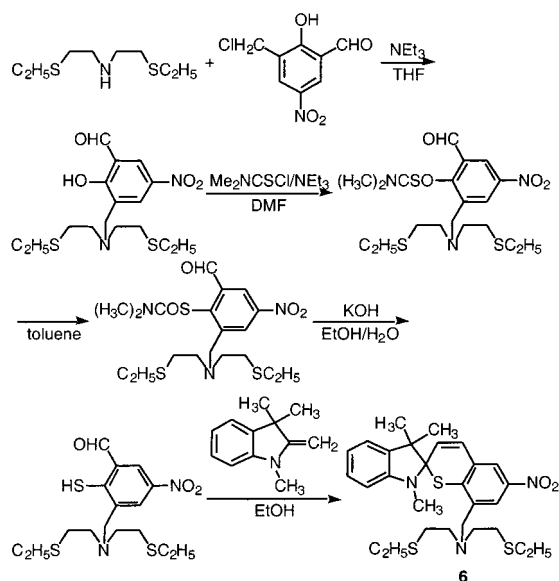


Figure 8. Absorption spectra of **6** in the presence of a heavy metal ion.

Scheme 3. Synthesis of Spirobenzothiapyran



thermal isomerization and facilitated photoisomerization to the merocyanine form were observed. By contrast, other metal ions did not show meaningful effects on photochromism. Among alkali and alkaline-earth metal ions, only Mg^{2+} facilitated the photoisomerization to the merocyanine form slightly. The results show that the Ag^+ interaction with 3,9-dithia-6-monoazaundecane and the thiophenolate anion moieties is strong enough to induce thermal isomerization of spirobenzothiapyran, although spirobenzothiapyran is notorious for its thermal instability in the merocyanine form.

To evaluate complex formation ability with various metal ions, the decoloration and coloration rate constants were determined for the positive and negative photochromism systems, respectively. While a smaller value for the positive photochromism system means more stable complex formation, a greater value for the negative photochromism indicates more stable complex formation. The constants are summarized in Table 1.

Among alkali metal ions, the stabilization of the merocyanine form was observed only with Li^+ for **1**. In the case of alkaline-earth metal ions, significant stabilization by Mg^{2+} was observed, especially for **1** and **6**. The stabilization effect of heavy metal ions decreased on increasing the ring size of the monoazathiacycrown ether moieties for **1–3**, and the effect decreased on increasing the monoazathiacycrown ether moiety for **4** and **5**. On the other hand, Ag^+ showed remarkable stabilization of the

merocyanine form for **6**. This significant stabilization effect of Ag^+ for **6** is evidently derived from the cooperation of sulfur atoms in 3,9-dithia-6-monoazaundecane and thiophenolate anion moieties.

Conclusions

In conclusion, spirobenzopyran derivatives bearing a monoazathiacycrown moiety showed selective binding abilities to Mg^{2+} and Ag^+ with negative and positive photochromism, respectively. Among all metal ions, only Ag^+ facilitated the photoisomerization to the merocyanine form. As the monoazathiacycrown ether rings and the phenolate anion moieties prefer soft and hard metal ions, respectively, Mg^{2+} selectivity is derived mainly from the phenolate anion moiety and Ag^+ selectivity from the monoazathiacycrown ether moiety.

Experimental Section

All chemicals for the synthesis were of available purity and used without further purification. For measurements, spectroscopic-grade acetonitrile was used as the solvent for the absorption spectra, while all metal salts were of the highest available purity and used without further purification. The preparation of monoazathiacycrown ethers and noncyclic analogues were carried out according to the method reported in ref 7. Procedures for the absorption-spectral measurement and the determination of the decoloration and coloration rate constants are described in refs 4 and 3, respectively. Chloromethyl spirobenzopyran was prepared with the method in ref 3.

Synthesis of Monoazathiacycrown Spirobenzopyrans and Derivatives. Monoazatrithia-12-crown-4 Spirobenzopyran (1). Under a nitrogen atmosphere, monoazatrithia-12-crown-4 (223 mg, 1 mmol), chloromethylspirobenzopyran (741 mg, 2 mmol), triethylamine (1.11 g, 11 mmol), and dry THF (100 mL) were put into a three-necked flask, and the reaction mixture was refluxed for 6 h. The product obtained by solvent evaporation was purified by gel permeation chromatography to give an 11% yield of **1** as a red-purple solid: mp 123–125 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 1.20 (3H, s, CH_3), 1.28 (3H, s, CH_3), 2.43 (4H, t, $J = 7.0$ Hz, $\text{SCH}_2\text{CH}_2\text{N}$), 2.58 (4H, t, $J = 7.0$ Hz, NCH_2), 2.7–2.8 (8H, m, SCH_2), 2.71 (3H, s, NCH_3), 3.3–3.5 (2H, m, PhCH_2), 5.88 (1H, d, $J = 10.4$ Hz, $\text{CH}=\text{C}$), 6.55 (1H, d, $J = 7.6$ Hz, ArH), 6.89 (1H, t, $J = 7.4$ Hz, ArH), 6.94 (1H, d, $J = 10.4$ Hz, $\text{CH}=\text{C}$), 7.08 (1H, d, $J = 6.8$ Hz, ArH), 7.20 (1H, t, $J = 8.2$ Hz, ArH), 7.94 (1H, s, ArH), 8.17 (1H, s, ArH); m/z 557 (M^+); IR (neat, cm^{-1}) 2960 ($-\text{CH}_2-$), 1520 (NO_2), 1180 (C–N), 750 (C=C). Anal. Calcd for $\text{C}_{28}\text{H}_{35}\text{N}_3\text{O}_3\text{S}_3$: C, 60.32; H, 6.28; N, 7.54; S, 17.24. Found: C, 60.05; H, 5.97; N, 7.19; S, 17.46.

Monoazatetrathia-15-crown-5 Spirobenzopyran (2). Under a nitrogen atmosphere, monoazatetrathia-15-crown-5 (283 mg, 1 mmol), chloromethylspirobenzopyran (741 mg, 2 mmol), triethylamine (1.11 g, 11 mmol), and dry THF (100 mL) were put into a three-necked flask, and the reaction mixture was refluxed for 36 h. The product obtained by solvent evaporation was purified by gel permeation chromatography to give a 44% yield of **2** as a red-purple solid: mp 58–61 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 1.18 (3H, s, CH_3), 1.27 (3H, s, CH_3), 2.39 (4H, t, $J = 7.8$ Hz, $\text{SCH}_2\text{CH}_2\text{N}$), 2.56 (4H, t, $J = 7.6$ Hz, NCH_2), 2.8–2.9 (15H, m, SCH_2 , NCH_3), 3.3–3.5 (2H, m, PhCH_2), 5.86 (1H, d, $J = 10.4$ Hz, $\text{CH}=\text{C}$), 6.54 (1H, d, $J = 7.6$ Hz, ArH), 6.87 (1H, t, $J = 7.4$ Hz, ArH), 6.92 (1H, d, $J = 10.4$ Hz, $\text{CH}=\text{C}$), 7.07 (1H, d, $J = 6.8$ Hz, ArH), 7.18 (1H, t, $J = 7.8$ Hz, ArH), 7.91 (1H, s, ArH), 8.12 (1H, s, ArH); m/z (intensity) 507 ($\text{M}^+ - 110$, 60), 336 ($\text{M}^+ - 281$, 100); IR (neat, cm^{-1}) 2920 ($-\text{CH}_2-$), 1520 (NO_2), 1182 (C–N), 750 (C=C). Anal. Calcd for $\text{C}_{30}\text{H}_{39}\text{N}_3\text{O}_3\text{S}_4$: C, 58.34; H, 6.32; N, 6.81; S, 20.75. Found: C, 58.44; H, 5.94; N, 6.84; S, 20.41.

Monoazatetrathia-18-crown-6 Spirobenzopyran (3). Under a nitrogen atmosphere, monoazapentathia-18-crown-6

Table 1. Rate Constants for Decoloration or Coloration^a

	blank	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺	Ag ⁺	Tl ⁺	Pb ²⁺	Hg ²⁺	Zn ²⁺
1	3.0	1.7	2.9	3.0	3.2	2.8	(0.59)	(0.37)	nd	nd	0.33	2.4	(0.84)	(0.13)	(0.31)
2	1.6	1.5	1.7	1.5	1.7	1.6	(0.19)	(0.18)	nd	nd	0.48	1.2	nd	nd	(0.36)
3	1.4	1.3	1.6	1.1	1.4	1.5	(0.29)	(0.28)	nd	nd	1.2	nd	nd	nd	(0.23)
4	1.8	1.1	1.8	1.8	1.8	1.6	(0.26)	(0.24)	nd	nd	0.54	1.2	(0.27)	(0.16)	(0.20)
5	1.3	1.0	1.3	1.4	1.3	1.3	(0.32)	(0.25)	nd	nd	0.90	1.3	nd	(0.10)	(0.16)
6	nd	nd	nd	nd	nd	nd	1.0	nd	nd	nd	<0.1	nd	nd	nd	nd

^a Values in parentheses are coloration rate constants, and "nd" indicates that the constant was not determined due to a small change in spectra.

(343 mg, 1 mmol), chloromethylspirobenzopyran (741 mg, 2 mmol), triethylamine (1.11 g, 11 mmol), and dry THF (100 mL) were put into a three-necked flask, and the reaction mixture was refluxed for 48 h. The product obtained by solvent evaporation was purified by gel permeation chromatography to give a 35% yield of **3** as a red-purple liquid: ¹H NMR (CDCl₃, 400 MHz) δ 1.19 (3H, s, CH₃), 1.27 (3H, s, CH₃), 2.4–2.9 (27H, m, SCH₂, NCH₂, NCH₃), 3.3–3.5 (2H, m, PhCH₂), 5.87 (1H, d, *J* = 10.4 Hz, CH=), 6.55 (1H, d, *J* = 7.6 Hz, ArH), 6.89 (1H, t, *J* = 7.4 Hz, ArH), 6.93 (1H, d, *J* = 10.8 Hz, CH=), 7.09 (1H, d, *J* = 7.2 Hz, ArH), 7.20 (1H, t, *J* = 7.6 Hz, ArH), 7.93 (1H, s, ArH), 8.18 (1H, s, ArH); *m/z* (intensity) 507 (M⁺ – 170, 30), 223 (M⁺ – 454, 100); IR (neat, cm⁻¹) 2920 (–CH₂–), 1520 (NO₂), 1182 (C–N), 750 (C=C). Anal. Calcd for C₃₂H₄₃N₃O₃S₅: C, 56.72; H, 6.35; N, 6.20; S, 23.63. Found: C, 56.81; H, 6.09; N, 6.13; S, 23.36.

3,9-Dithia-6-monoazaundecane Spirobenzopyran (4). Under a nitrogen atmosphere, 3,9-dithia-6-monoazaundecane (193 mg, 1 mmol), chloromethylspirobenzopyran (741 mg, 2 mmol), triethylamine (1.11 g, 11 mmol), and dry THF (100 mL) were put into a three-necked flask, and the reaction mixture was refluxed for 3 h. The product obtained by solvent evaporation was purified by gel permeation chromatography to give a 24% yield of **4** as a red-purple liquid: ¹H NMR (CDCl₃, 400 MHz) δ 1.19 (6H, t, *J* = 7.4 Hz, CH₂CH₃), 1.20 (3H, s, CH₃), 1.28 (3H, s, CH₃), 2.3–2.5 (8H, m, SCH₂), 2.5–2.6 (4H, m, NCH₂), 2.71 (3H, s, NCH₃), 3.3–3.5 (2H, m, PhCH₂), 5.86 (1H, d, *J* = 10.4 Hz, CH=), 6.54 (1H, d, *J* = 7.6 Hz, ArH), 6.88 (1H, t, *J* = 7.4 Hz, ArH), 6.93 (1H, d, *J* = 10.0 Hz, CH=), 7.08 (1H, d, *J* = 7.2 Hz, ArH), 7.19 (1H, t, *J* = 7.4 Hz, ArH), 7.92 (1H, s, ArH), 8.17 (1H, s, ArH); *m/z* 527 (M⁺); IR (neat, cm⁻¹) 2960 (–CH₂–), 1520 (NO₂), 1180 (C–N), 750 (C=C). Anal. Calcd for C₂₈H₃₇N₃O₃S₂: C, 63.76; H, 7.02; N, 7.97; S, 12.14. Found: C, 63.86; H, 6.81; N, 7.94; S, 12.35.

3,6,12,15-Tetrathia-9-monoazaheptadecane Spirobenzopyran (5). Under a nitrogen atmosphere, 3,6,12,15-tetrathia-9-monoazaheptadecane (313 mg, 1 mmol), chloromethylspirobenzopyran (741 mg, 2 mmol), triethylamine (1.11 g, 11 mmol), and dry THF (100 mL) were put into a three-necked flask, and the reaction mixture was refluxed for 3 h. The product obtained by solvent evaporation was purified by gel permeation chromatography to give a 27% yield of **5** as a red-purple liquid: ¹H NMR (CDCl₃, 400 MHz) δ 1.0–1.2 (12H, m, CH₂CH₃, CH₃), 2.4–2.8 (23H, m, SCH₂, NCH₂, NCH₃), 3.3–3.5 (2H, m, PhCH₂), 5.86 (1H, d, *J* = 10.4 Hz, CH=), 6.55 (1H, d, *J* = 7.6 Hz, ArH), 6.89 (1H, t, *J* = 7.6 Hz, ArH), 6.93 (1H, d, *J* = 10.4 Hz, CH=), 7.08 (1H, d, *J* = 7.2 Hz, ArH), 7.20 (1H, t, *J* = 7.6 Hz, ArH), 7.93 (1H, s, ArH), 8.17 (1H, s, ArH); *m/z* (intensity) 507 (M⁺ – 140, 10), 252 (M⁺ – 375, 100); IR (neat, cm⁻¹) 2960 (–CH₂–), 1520 (NO₂), 1180 (C–N), 750 (C=C). Anal. Calcd for C₃₂H₄₅N₃O₃S₄: C, 59.35; H, 6.96; N, 6.49; S, 19.78. Found: C, 59.20; H, 6.71; N, 6.48; S, 19.78.

***N*-(2'-Hydroxy-3'-formyl-5'-nitrobenzyl)-3,9-dithia-6-monoazaundecane.** Under a nitrogen atmosphere, 3,9-dithia-6-monoazaundecane (463 mg, 2.4 mmol), triethylamine (485 mg, 4.8 mmol), and dry THF (20 mL) were put into a three-necked flask at 0 °C, and a dry THF solution (10 mL) of 3-chloromethyl-5-nitrosalicylaldehyde (518 mg, 2.4 mmol) was added to the mixture dropwise. The reaction mixture was stirred at 0 °C for 3 h and then at room temperature for 12 h under a nitrogen atmosphere. The reaction mixture was poured into water and extracted with chloroform twice. The

crude brown liquid product (>95%) obtained by solvent evaporation was used for the subsequent preparation after drying.

***N*-(2'-*N,N*-Dimethylthiocarbamoyloxy-3'-formyl-5'-nitrobenzyl)-3,9-dithia-6-monoazaundecane.** Under a nitrogen atmosphere, *N*-(2'-hydroxy-3'-formyl-5'-nitrobenzyl)-3,9-dithia-6-monoazaundecane (860 mg, 2.4 mmol), triethylamine (727 mg, 7.2 mmol), and dry DMF (60 mL) were put into a three-necked flask at 0 °C, and a dry DMF solution (30 mL) of *N,N*-dimethylcarbonyl chloride (890 mg, 7.2 mmol) was added to the mixture dropwise. The reaction mixture was stirred at 0 °C for 3 h and then at room temperature for 12 h. The reaction mixture was poured into water and extracted with chloroform twice. The crude brown liquid product (>95%) obtained by solvent evaporation was used for the subsequent preparation after drying.

***N*-(2'-*N,N*-Dimethylthiocarbamoylthio-3'-formyl-5'-nitrobenzyl)-3,9-dithia-6-monoazaundecane.** Under a nitrogen atmosphere, *N*-(2'-*N,N*-dimethylthiocarbamoyloxy-3'-formyl-5'-nitrobenzyl)-3,9-dithia-6-monoazaundecane (1.06 g, 2.4 mmol) and dry toluene (50 mL) were put into a three-necked flask, and the reaction mixture was refluxed for 6 h. The product (32%) obtained by solvent evaporation was purified by gel permeation chromatography.

(2'-Mercapto-3'-formyl-5'-nitrobenzyl)-3,9-dithia-6-monoazaundecane. Under a nitrogen atmosphere, *N*-(2'-*N,N*-dimethylthiocarbamoylthio-3'-formyl-5'-nitrobenzyl)-3,9-dithia-6-monoazaundecane (340 mg, 0.77 mmol) and ethanol (50 mL) were put into a three-necked flask, and the aqueous solution (50 mL) of KOH (431 mg, 7.7 mmol) was added to the mixture. The reaction mixture was stirred at room temperature for 2 h under a nitrogen atmosphere. Acetic acid (462 mg, 7.7 mmol) was added to the reaction mixture, and stirring was continued for 10 min. The reaction mixture was poured into water and extracted with chloroform twice. The crude brown liquid product (>95%) obtained by solvent evaporation was used for the subsequent preparation after drying.

3,9-Dithia-6-monoazaundecane Spirobenzothiapyran (6). Under nitrogen atmosphere, (2'-mercapto-3'-formyl-5'-nitrobenzyl)-3,9-dithia-6-monoazaundecane (286 mg, 0.77 mmol), 2-methylene-1,3,3-trimethylindoline (133 mg, 0.77 mmol), and dry ethanol (50 mL) were put into a three-necked flask, and the reaction mixture was refluxed for 12 h. The product obtained by solvent evaporation was purified by gel permeation chromatography to give a 56% yield of **6** as a red-brown liquid: ¹H NMR (CDCl₃, 500 MHz) δ 1.20 (6H, t, *J* = 7.25 Hz, CH₂CH₃), 1.23 (3H, s, CH₃), 1.37 (3H, s, CH₃), 2.47 (4H, q, *J* = 7.33 Hz, SCH₂CH₃), 2.5–2.6 (4H, m, NCH₂), 2.6–2.8 (7H, s, SCH₂, NCH₃), 3.5–3.7 (2H, m, PhCH₂), 6.00 (1H, d, *J* = 11.0 Hz, CH=), 6.50 (1H, d, *J* = 7.5 Hz, ArH), 6.86 (1H, t, *J* = 7.75 Hz, ArH), 6.93 (1H, d, *J* = 11.0 Hz, CH=), 7.06 (1H, d, *J* = 8.0 Hz, ArH), 7.17 (1H, t, *J* = 8.25 Hz, ArH), 7.95 (1H, s, ArH), 8.30 (1H, s, ArH); *m/z* 543 (M⁺); IR (neat, cm⁻¹) 2960 (–CH₂–), 1520 (NO₂), 1060 (C–N), 750 (C=C). Anal. Calcd for C₂₈H₃₇N₃O₂S₃·1/2H₂O: C, 60.87; H, 6.88; N, 7.61; S, 17.39. Found: C, 60.98; H, 6.81; N, 7.75; S, 17.55.

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