Cation complexation, isomerization, and photoresponsive ionic conduction of a crown ether derivative carrying two spirobenzopyran units

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Cation complexation and subsequent isomerization of a diaza-18-crown-6 derivative possessing two spirobenzopyran units, crowned bis(spirobenzopyran), were investigated in solution and compared with those of its corresponding derivative incorporating only one spirobenzopyran unit. Complexation of multivalent metal ions, especially Ca^{2+} and La^{3+}, by crowned bis(spirobenzopyran) enhanced the isomerization of the spirobenzopyran moiety to the corresponding merocyanine form due to the effective intramolecular interaction between a crown-complexed cation and two phenolate anions in the cation complexes of the merocyanine form. Significant photoinduced switching of ionic conductivity was realized in composite films containing crowned bis(spirobenzopyran) and a calcium salt.

Spirobenzopyran derivatives are typical photochromic compounds that undergo reversible isomerization to corresponding zwitterionic merocyanine isomers. They can be therefore used in photochemical control systems of physical properties in solutions.

We have already reported spirobenzopyran derivatives incorporating a monoazacrown ether ring at the 8-position, crowned spirobenzopyrans, **2**.[1] The crowned spirobenzopyrans can modulate the cation-complexing property of the crown ether moiety by photoisomerization between the electrically neutral spiropyran and zwitterionic merocyanine forms. In other words, the phenolate anion in the metal ion complexes of the merocyanine form of **2** ($n = 1$–3) can interact intramolecularly with a metal ion captured by their crown moiety to form a six-membered-ring chelate between the oxy anion of the phenolate and the nitrogen atom of the crown ether ring. Photoisomerization of the crowned spirobenzopyrans can, therefore, affect this intramolecular interaction, which in turn results in changes in the cation-complexing ability. Photoinduced switching of ionic conductivity using crowned spirobenzopyran **2** ($n = 1$) and a lithium salt was successfully achieved by taking advantage of the above-mentioned photochemical control of cation complexation by photochromic crown ethers.[2] The photochromic crown compounds were found to be useful materials for photoinduced ionic-conductivity switching.

What will happen if a crown ether derivative has more than one spirobenzopyran unit? As mentioned above, crowned spirobenzopyrans **2** which carry only one spirobenzopyran unit readily complex monovalent alkali metal ions due to the intramolecular interaction of a crown-complexed monovalent cation and a phenolate anion with 1:1 stoichiometry in the merocyanine–metal ion complexes. It can be therefore expected that the incorporation of two or more spirobenzopyran units into a crown ether results in preferable complexation of multi-
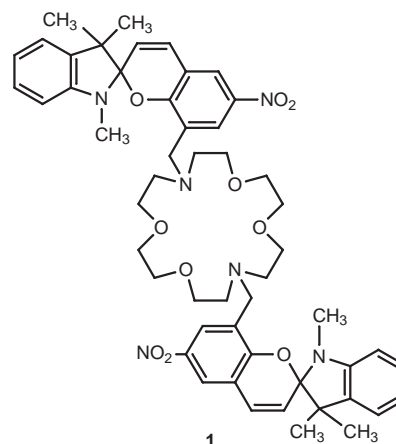
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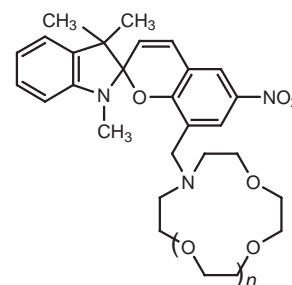
2(n = 1-3)
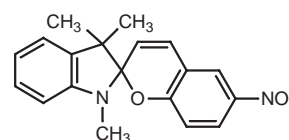
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valent metal cations. Therefore, the crown ethers carrying more than one spirobenzopyran unit are candidates for a material for photochemical complexation control of multivalent metal ions. Also, the crown ether derivatives may allow photoinduced ionic-conductivity switching in the ion-conducting systems containing multivalent ions, which affords higher current density than the systems of monovalent metal ions.

These considerations prompted us to design a diaza-18-crown-6 carrying two spirobenzopyran units at the *N*-position, crowned bis(spirobenzopyran) **1**. We recently communicated the high affinity of the crowned bis(spirobenzopyran) for Ca^{2+} and La^{3+} as compared with alkali metal ions, which is based on the multiple ionic interaction in its merocyanine form.[3,4] Here we report the behavior of metal ion complexation, photochromism, and photoresponsive ionic conduction of the crowned bis(spirobenzopyran).

Experimental

Synthesis of crowned bis(spirobenzopyran)

7,16-Bis(1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline]-8-ylmethyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane or bis[(spirobenzopyran)methyl]diaza-18-crown-6 **1** was synthesized by the condensation reaction of 1,3,3-trimethyl-2-methyleneindoline and 7,16-bis(2-hydroxy-3-formyl-5-nitrobenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, which was obtained by the reaction of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (diaza-18-crown-6) with 3-chloromethyl-5-nitrosalicylaldehyde in the presence of triethylamine. 3-Chloromethyl-5-nitrosalicylaldehyde was prepared according to a procedure described in the literature.[5] To a dry tetrahydrofuran (THF) solution (5 cm³) of diaza-18-crown-6 (3.8 mmol) and triethylamine (18.8 mmol) was added a dry THF solution (20 cm³) of 3-chloromethyl-5-nitrosalicylaldehyde (9.3 mmol) dropwise while stirring in an ice bath. The stirring was allowed to continue overnight at room temperature and then for 6 h under refluxing conditions. After the reaction was completed, the precipitate was filtered off and washed with dry THF. The precipitate thus obtained was added to 3 mol dm⁻³ HCl aqueous solution (50 cm³) and then stirred for 12 h. After filtration of the mixture, the filtrate was adjusted to about pH 8 to yield a yellow precipitate of 7,16-bis(2-hydroxy-3-formyl-5-nitrobenzyl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane, which was used for the subsequent reaction without further purification. A dry ethanol solution (20 cm³) of 1,3,3-trimethyl-2-methyleneindoline (0.65 mmol) and 7,16-bis(2-hydroxy-3-formyl-5-nitrobenzyl)diaza-18-crown-6 (1.33 mmol) was refluxed for 10 h. After the reaction was complete, the ethanol was evaporated to yield a crude product of the corresponding crowned bis(spirobenzopyran). After removal of a chloroform-insoluble impurity from the crude product, recrystallization from dry ethanol yielded a pale-yellow crystal of pure **1** (yield: 58%): mp 131–133 °C; ¹H-NMR (600 MHz, CDCl₃) δ 1.19 and 1.27 (6H, s, CCH₃), 2.63 (8H, t, *J* = 5.7 Hz, NC*H*₂CH₂O), 2.69 (6H, s, NCH₃), 3.39–3.45 (16H, m, OCH₂), 3.47 (4H, s, PhCH₂), 5.84 (2H, d, *J* = 10.3 Hz, C*H*=CHPh), 6.52 (2H, d, *J* = 7.4 Hz, 7′-H of indoline), 6.85 (2H, dd, *J* = 7.4 Hz, 6′-H of indoline), 6.91 (2H, d, *J* = 10.3 Hz, CH=C*H*Ph), 7.06 (2H, d, *J* = 7.4 Hz, 5′-H of indoline), 7.16 (2H, dd, *J* = 7.4 Hz, 4′-H of indoline), 7.88 (2H, d, *J* = 2.8 Hz, 5-H of benzopyran), 8.22 (2H, d, *J* = 2.8 Hz, 7-H of benzopyran); MS, *m/e* (% relative intensity) 931 (M⁺, 11), 335 (100) (Anal. Calcd. for C₅₂H₆₂N₆O₁₀: C, 67.08; H, 6.71; N, 9.03. Found: C, 66.85; H, 6.70; N, 8.87%).

Other materials

1′,3′,3′-Trimethyl-6-nitro-8-[16-(1,4,7,10,13-pentaoxa-16-azacyclooctadecyl)methyl]spiro[2*H*-1-benzopyran-2,2′-indoline] or monoaza-18-crown-6-methyl spirobenzopyran **2** (*n* = 3) was

prepared according to the literature.[1] 1′,3′,3′-Trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-indoline] **3** and diaza-18-crown-6 were purchased from Tokyo Kasei and Aldrich, respectively. Unless otherwise specified, all the reagents were the best available grade. The solvents for the spectroscopy were spectrograde from Dojindo Lab. Water was deionized. Poly(vinyl chloride) (PVC) (average polymerization degree of 1020) was purified by repeated reprecipitation. *o*-Nitrophenyl octyl ether (NPOE) was prepared as reported elsewhere.[6] Bis[di{*p*-(1,1,3,3-tetramethylbutyl)phenyl}phosphato]calcium (HDOPP-Ca) was employed as received from Dojindo Lab. THF for the preparation of composite films was distilled over LiAlH₄.

Spectrophotometric measurements

Acetonitrile solutions containing a spirobenzopyran derivative (2 × 10⁻⁵ mol dm⁻³) and an appropriate concentration of a metal nitrate were prepared and their absorption spectra were then taken. UV (300–400 nm) and visible (>500 nm) wavelengths were obtained by passing light of a 500-W xenon lamp through Toshiba UV-D35 and V-Y50 color filters, respectively.

Molecular orbital calculation

Calculation by the MNDO-PM3 method[7] was performed with the MOPAC program (ver. 6) using an Iris Indigo R4000 computer. The structural output was recorded by using the MOL-GRAPH program (ver. 2.8) by Daikin Industry Ltd. Na⁺ and Zn²⁺ were adopted as the monovalent and divalent metal ions, respectively.

Composite film fabrication

PVC-based composite films for ionic-conductivity measurements were prepared on indium–tin–oxide-coated (ITO) glasses (2 × 2.5 cm) by a spin coating technique from chloroform solutions, and then dried at 40 °C under a nitrogen stream. In general, 0.2 cm³ of a THF solution (0.6 cm³) containing PVC (60 mg, 50.1 wt%), NPOE (50 mg, 41.7 wt%), crowned bis(spirobenzopyran) (9.3 mg, 7.8 wt%), and Ca(ClO₄)₂ (0.5 mg, 0.4 wt%) was used for each spin coating on an ITO glass, affording a composite film with 4 μm thickness. Composite films containing HDOPP-Ca as a Ca²⁺ salt consisted of PVC (60 mg, 46.4 wt%), NPOE (50 mg, 38.7 wt%), crowned bis(spirobenzopyran) (9.3 mg, 7.2 wt%), and HDOPP-Ca (9.9 mg, 7.7 wt%). On the composite films for ionic-conductivity measurements, gold was evaporated as an electrode (4.5 mm diameter, about 10 nm thickness).

Ionic conductivity measurements

Ac impedance of composite films was measured under an argon stream, as reported previously.[8] Ionic conductivity was determined by the Cole–Cole plot method.[9]

Results and discussion

Metal ion complexation induced isomerization

Crowned spirobenzopyrans **2** form alkali metal ion complexes, as reported elsewhere.[1] The cation complexation of crowned spirobenzopyrans leads to the isomerization of the electrically neutral spirobenzopyran moiety to the corresponding zwitterionic merocyanine form even under dark conditions. In the metal ion complexes of the crowned spirobenzopyran merocyanine forms, the phenolate anion interacts with a metal ion complexed by the crown moiety. The selectivities in the cation complexation and subsequent isomerization of the crowned spirobenzopyrans are quite dependent upon the nature of the crown moiety. In any case, they are selective for monovalent alkali metal ions, especially Li⁺.

Crowned bis(spirobenzopyran) **1** is expected to show selectivity for divalent metal ions in the cation complexation and
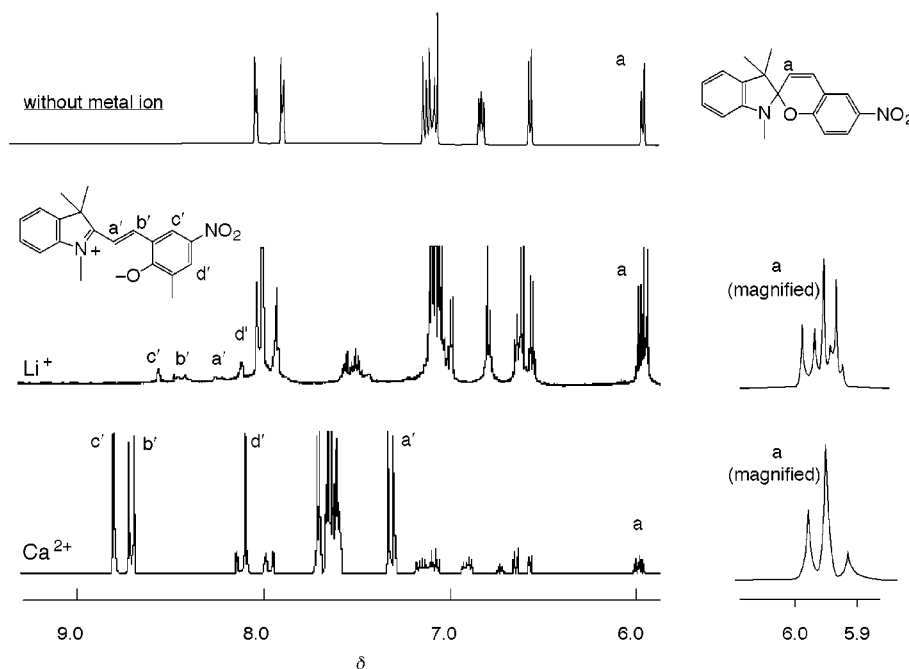
subsequent isomerization. The stoichiometry of the **1**–metal ion complex formed is 1:1. The cation-complexation induced isomerization of crowned bis(spirobenzopyran) **1** to its corresponding merocyanine form was studied spectrophotometrically in acetonitrile solutions containing an equimolar amount of **1** and a metal salt under dark conditions, using various nitrates of mono-, di-, and trivalent cations. Fig. 1 summarizes the absorption-spectral data for the merocyanine isomer of **1** together with the data for the corresponding crowned mono-(spirobenzopyran) **2** ($n = 3$) for comparison. The solutions of the crowned spirobenzopyrans without any metal salt had no
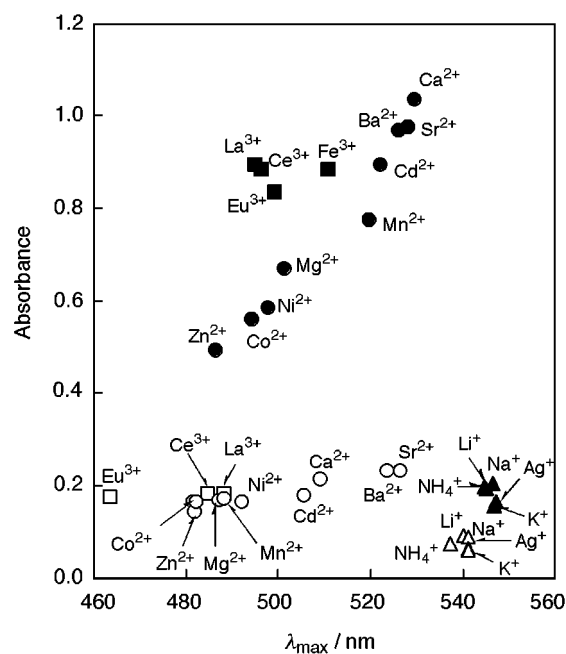
detectable absorption in the visible region, assignable to their merocyanine form. Also, an acetonitrile solution of spirobenzopyran derivative without the crown ether moiety **3** exhibited negligible spectral changes on addition of metal salts under identical conditions. This convinces us that the isomerization of crowned bis(spirobenzopyran) to its merocyanine form in the presence of metal salts is derived from the cation complexation by its crown ether moiety. It appears that the system of crowned bis(spirobenzopyran) with multivalent metal ions can induce isomerization of the spirobenzopyran moiety to its merocyanine form more efficiently than monovalent cations. Multivalent metal ions also gave absorption peaks of the merocyanine form at lower wavelengths than monovalent cations did in both the crowned mono- and bis(spirobenzopyran).

With respect to the systems containing Li^+, Ca^{2+}, Zn^{2+}, and La^{3+}, the isomerization of the spirobenzopyran moiety of **1**, **2** ($n = 3$), and **3** to the corresponding merocyanine form on the metal salt addition was also followed by ^{1}H-NMR spectroscopy. Fig. 2 displays the ^{1}H-NMR spectra for the Li^+ and Ca^{2+} systems of crowned bis(spirobenzopyran) **1**, together with that in the absence of metal ions. On equimolar addition of a metal salt to an acetonitrile-d_3 solution of crowned bis-(spirobenzopyran) **1**, the doublet signals assignable to the protons at the 3-position of the spirobenzopyran moiety (H_a) decreased, while another doublet for the corresponding protons of the merocyanine form ($H_{a'}$) appeared at the higher frequencies. These results again indicate that the isomerization of **1** from its spirobenzopyran to its merocyanine isomer is caused by cation complexation with its crown ether moiety. It should be noted that three pairs of doublets were clearly observed for the proton at the 3-position of the spirobenzopyran moiety in the Li^+ system. By contrast, only two pairs of doublets were found for the proton in the Ca^{2+} system. This means that on Li^+ complexation by crowned bis(spirobenzopyran) **1**, one of the two spirobenzopyran units isomerized to its merocyanine form, while the other remained unchanged. On the contrary, Ca^{2+} complexation by **1** can bring about concurrent isomerization of its two spirobenzopyran units. This is the case with the systems of **1** with Zn^{2+} and La^{3+}. This is probably because a monovalent cation captured by the crown ether moiety of **1** interacts intramolecularly with only one phenolate anion of its
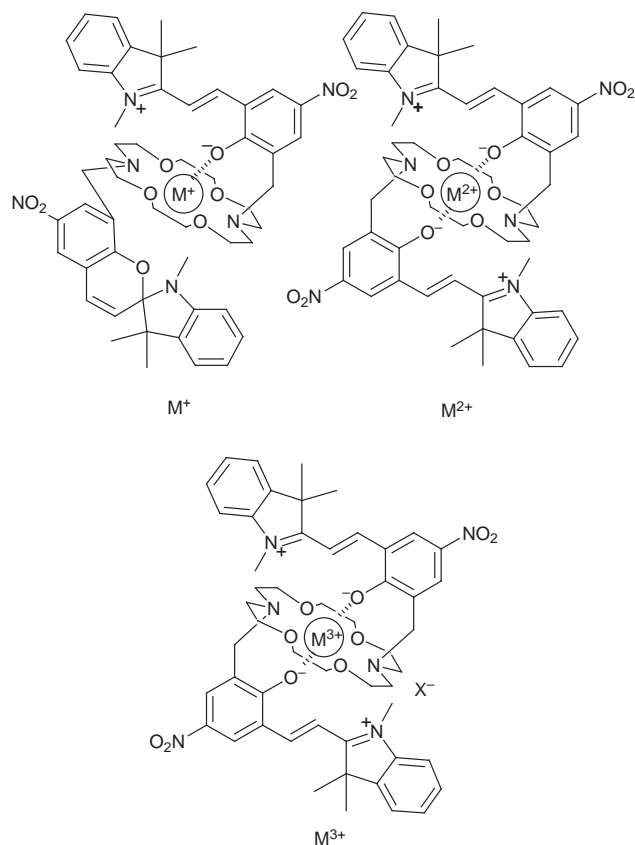

Fig. 1 Absorption-spectral data in visible region for crowned spirobenzopyrans **1** (full symbols) and **2** ($n = 3$) (empty symbols) in the presence of metal ions [monovalent (triangle); divalent (circle); trivalent (square)] under dark conditions. Concentration of **1** and **2**: 2×10^{-5} mol dm^{-3} in acetonitrile; concentration of salt: 2×10^{-5} mol dm^{-3} in acetonitrile.

Fig. 2 ^{1}H-NMR spectra for crowned bis(spirobenzopyran) **1** in the presence of Li^+ and Ca^{2+} and without metal ions. Concentration of **1** and metal salt: 2×10^{-3} mol dm^{-3} each in acetonitrile-d_3. The proton of a (H_a) for the spirobenzopyran moiety and those of a' through d' ($H_{a'}$, $H_{b'}$, $H_{c'}$, and $H_{d'}$) for the merocyanine form are as shown in the structure.
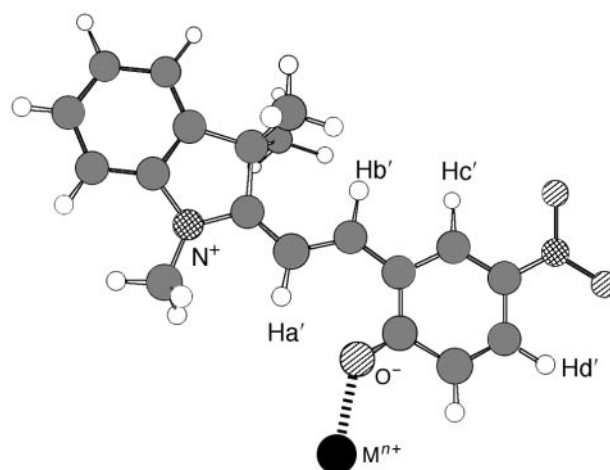
Scheme 1

Table 1 Isomerization percentage of spirobenzopyran derivatives on equimolar addition of metal ions and their complex formation constants

	Isomerization percentage (complex formation constant in 10^3 dm^3 mol^{-1})		
Metal ion	**1**	**2** ($n = 3$)	**3**
Li$^+$	17(3.9)	11(0.69)	0
Ca^{2+}	87(260)	92(720)	0
Zn^{2+}	29(2.9)	22(1.8)	0
La^{3+}	>97(>5400)	90(450)	0

Concentrations for spirobenzopyran derivatives and metal nitrates: 2×10^{-4} mol dm^{-3} each in CH$_3$CN.

Table 2 Point charges obtained by molecular orbital calculation

Atom	M$^+$	M^{2+}	Without metal ion
H$_{a'}$	0.1468	0.1292	0.0978
H$_{b'}$	0.1046	0.1619	0.1410
H$_{c'}$	0.1230	0.1569	0.1105
H$_{d'}$	0.1315	0.1755	0.1189
N$^+$	0.2512	0.6343	0.1530
O$^-$	−0.5688	−0.1481	−0.5320

Fig. 3 Optimized structure for the merocyanine–metal ion complex in its conjugate system.

merocyanine moiety so as to compensate for the single positive charge, as shown in Scheme 1. The complexation of divalent and trivalent metal cations by **1**, on the other hand, forces two of the spirobenzopyran units to isomerize for the intramolecular interaction between a multivalent cation and two phenolate anions. For the La^{3+} complex of **1**, a nitrate anion as well as the two phenolate anions takes part in the compensation of the metal ion positive charge. This was confirmed by electrospray-ionization mass spectrometry.[4]

The isomerization percentages of spirobenzopyran to merocyanine units were determined from ratios of protons at the 3-position or the 4′-, 5′-, 6′-, and 7′-position of the spirobenzopyran unit to their corresponding protons of the merocyanine form, which in turn allowed us to calculate metal ion complex formation constants for **1**, on the assumption that any molecule of the crowned merocyanine of **1** forms a metal ion complex with 1:1 stoichiometry of metal ion and **1**. The isomerization percentages are summarized in Table 1, together with the complex formation constants. The high isomerization percentage in the Ca^{2+} and La^{3+} systems of **1** and **2** ($n = 3$) suggests that the metal ions can fit into the 18-crown-6 moiety of crowned spirobenzopyrans. The high complex formation constants with Ca^{2+} and La^{3+} must arise from some intramolecular interaction of the crown-complexed metal ions with phenolate anion(s) in the metal ion complexes of crowned bis(spirobenzopyran) **1**. The extremely high affinity of **1** for La^{3+} is noteworthy as compared with the other metal ion complexes.

In order to obtain some information about the intramolecular interaction of the crown-complexed metal ions with phenolate anion(s) in the metal ion complexes of crowned bis(spirobenzopyran) **1**, a molecular orbital calculation was carried out with a simple model of metal ion complexes with a merocyanine moiety. Fig. 3 depicts the optimized structure of a merocyanine metal ion complex and Table 2 summarizes the net point charges for main protons on its conjugate system containing the N$^+$ and O$^-$ at the ends for the free and metal-ion-complexed merocyanines. The relationship between the net

point charges and the ^{1}H-NMR chemical shifts of the given protons (Fig. 2) is worth noting. In comparing the monovalent and divalent cation systems, one can see that the point charges of the M^{2+} system have higher positive values at H$_{b'}$, H$_{c'}$, and H$_{d'}$, and lower positive values at H$_{a'}$ than for the M$^+$ system. In the NMR spectra, the signals for H$_{b'}$, H$_{c'}$, and H$_{d'}$ shifted to the higher frequencies and the signal for H$_{a'}$ shifted to the lower frequency in the M^{2+} system as compared to the M$^+$ system. Taking account of the rule that lower electron density on protons shifts their signals to a higher frequency, the data for the net point charge obtained by the molecular orbital calculation are consistent with the NMR data. Thus, a comparison in the net point charge between the M$^+$- and M^{2+}-complexed merocyanines and its free merocyanine is quite reliable. There is distinct deviation in the net point charges of the metal ion-complexed merocyanines from those of the free merocyanine. Furthermore, on comparing the net point charge for the N$^+$ and O$^-$, the M^{2+} system deviates more significantly in the net charge from the free system than the M$^+$ system. For the metal ion complexes of **1**, the metal ions captured by the crown ether moiety undergo an electrostatic interaction intramolecularly with phenolate anion(s). The electrostatic interaction is more powerful in the systems of multivalent metal ions than in those

of monovalent cations. Thus, the structures for the monovalent and multivalent cation complexes of crowned bis(spirobenzopyran) **1** illustrated in Scheme 1 are plausible.

Photochromism in the presence of metal ions

Photoisomerization of crowned bis(spirobenzopyran) **1** proceeds reversibly even in the presence of metal ion. Although isomerization of the spirobenzopyran moiety occurs on addition of metal salts, as mentioned above, UV-light irradiation of the acetonitrile solutions of a 1:1 mixture of **1** and a metal salt enhances the isomerization to the merocyanine form. Visible-light irradiation, on the other hand, caused isomerization back to the corresponding spirobenzopyran form to a great extent. Fig. 4 illustrates the photoisomerization for the crowned bis(spirobenzopyran)–Ca²⁺ system. If the visible light was turned off, the isomerization to the merocyanine form occurred together with coloration of the solution, the isomerization percentage being restored to the initial values under dark conditions.

Photoinduced switching of ionic conductivity

Since the photoisomerization of crowned bis(spirobenzopyran) proceeds even in the presence of Ca^{2+}, the intramolecular inter-

action of a crown-complexed Ca^{2+} with two phenolate anions of its merocyanine moiety can be controlled photochemically, as shown in Scheme 2. This suggests that the Ca^{2+}-complexing ability of **1** can be modified by photoirradiation. Attempts were made to apply the photochemical cation-complexing control system of the crowned bis(spirobenzopyran) to produce a photoinduced ionic-conductivity switching, using a divalent cation, Ca^{2+}, as the ion-conducting carrier. Composite films consisting of plasticized PVC, **1**, and $Ca(ClO_4)_2$ were first fabricated for the photoresponsive ion-conducting system. A typical profile for photoinduced changes of ionic conductivity is depicted in Fig. 5a. Visible-light irradiation of the composite films increased the ionic conductivity and the following UV-light irradiation decreased it. Similar ionic-conductivity changes were also found by alternation of visible-light irradiation and heating in the dark, but the switching magnitude is smaller than that on alternate irradiation with UV and visible light. Conceivably, this photoinduced ionic-conductivity switching is based on the mechanism in Scheme 2. That is to say, visible-light-induced isomerization from the merocyanine to its spirobenzopyran forms in the Ca^{2+} complex of **1** releases some Ca^{2+} due to the decreased cation-complexing ability. The resulting free Ca^{2+} contributes to the enhanced ionic conductivity in the ion-conducting composite films. Following UV-light irradiation
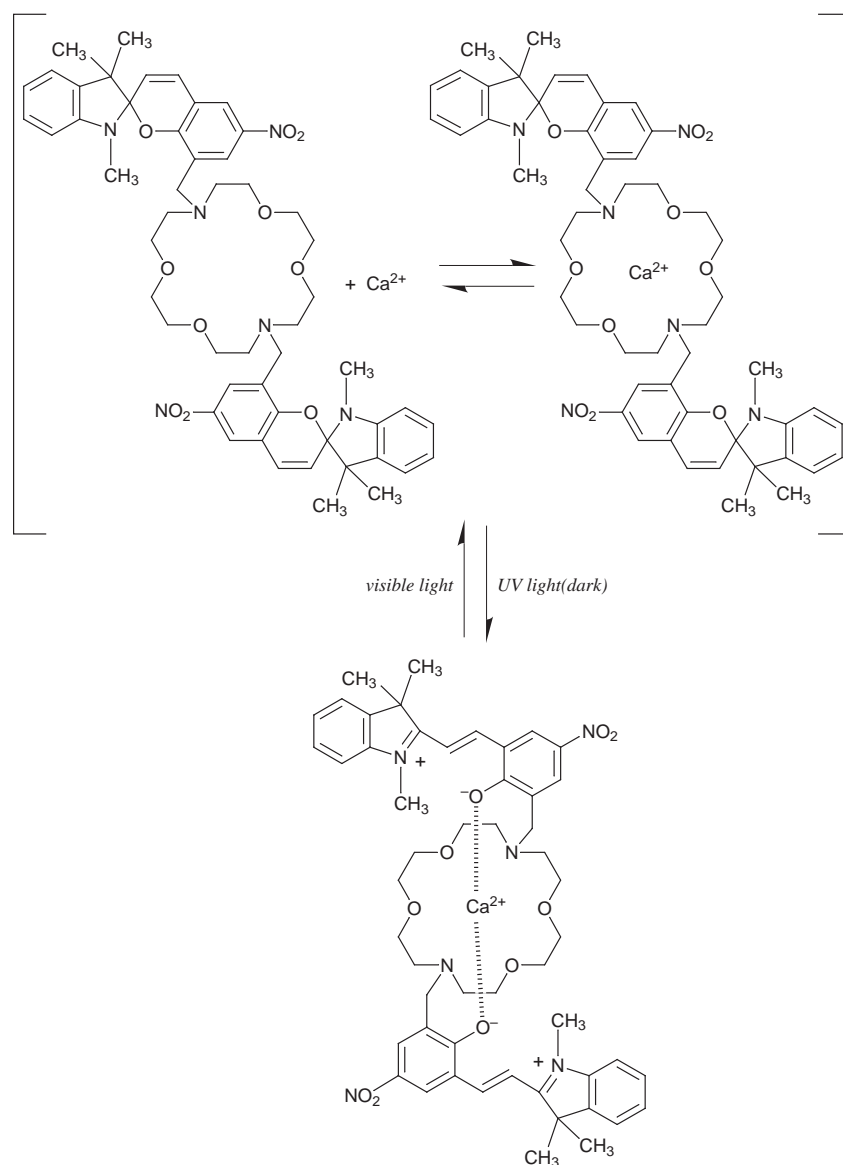
Scheme 2
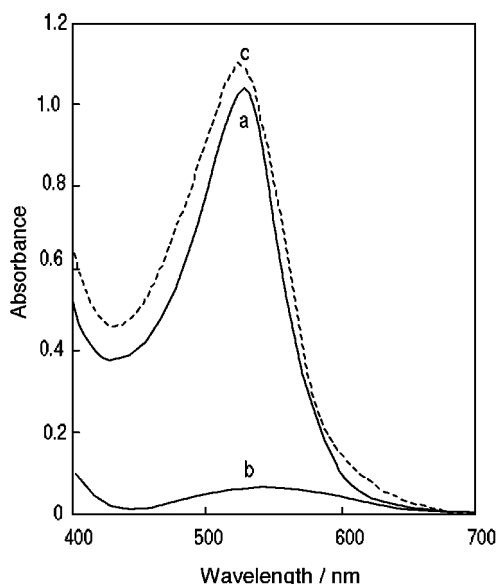
Fig. 4 Absorption-spectral changes of crowned bis(spirobenzopyran) **1**–Ca²⁺ system on photoirradiation. Concentration of **1**: 2×10^{-5} mol dm⁻³ in acetonitrile; concentration of salt: 2×10^{-5} mol dm⁻³ in acetonitrile. a: in the dark; b: visible-light irradiation for 5 min; c: UV-light irradiation for 3 min after b.
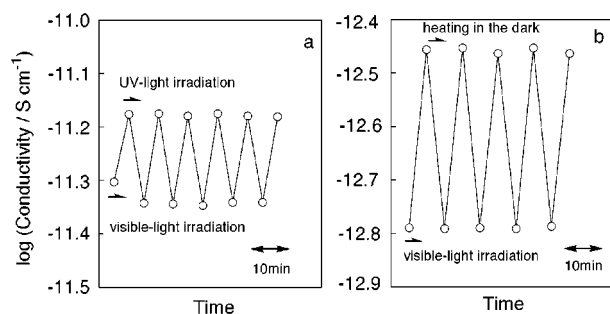
Fig. 5 Photoinduced ionic-conductivity changes for composite films of crowned bis(spirobenzopyran) **1** containing Ca(ClO₄)₂ (**a**) and HDOPP-Ca (**b**). Visible-light irradiation: 5 min; UV-light irradiation: 3 min; heating: 3 min at 50 °C.

causes the isomerization back to the merocyanine form, thus promoting Ca²⁺ binding by **1** due to the intramolecular interaction of a crown-complexed metal ion and two phenolate anions. The decreased concentration of free Ca²⁺ lowers the ionic conductivity. However, since not only Ca²⁺ but also its counteranion takes part in ionic conduction in the ion-conducting composite films containing Ca(ClO₄)₂, the contribution of the photoinduced changes of cation-complexing ability to the ionic-conductivity changes might be lowered by that of the counteranion. If a Ca²⁺ salt with a large anion is employed, the contribution of anion conduction may be alleviated, leading to more remarkable photoinduced ionic-conductivity changes. Composite films containing HDOPP-Ca instead of Ca(ClO₄)₂ were used as the photoresponsive ion-conducting films. The photoinduced switching profile in Fig. 5b shows an enhanced switching magnitude in the ionic-conductivity changes by alternation of visible-light irradiation and heating in the dark, as expected. In both of the ion-conducting systems containing Ca(ClO₄)₂ and HDOPP-Ca, the photoinduced ionic-conductivity switching is reversible.

In conclusion, crowned bis(spirobenzopyran) **1** allows photochemical control of complex formation toward multivalent metal cations such as Ca²⁺ and La³⁺, and enables us to design a photochemical switching system of ionic conductivity, using multivalent cations as the ion-conducting carrier.

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