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COMMUNICATION

Highly calcium-ion-accelerated coloration of bis(spirobenzopyran) bridged by diaza-18-crown-6 moiety at the 8-position

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Complexation of metal ions, especially of polyvalent metal ions, by a spirobenzopyran dimer bridged by a diaza-18-crown-6 moiety at the 8-position induced remarkable isomerization of its spiropyran moiety to the corresponding merocyanine even under dark conditions. Crowned bis(spirobenzopyran) can bind Ca^{2+} to form stable metal ion complexes of its merocyanine isomer, which in turn brings about the high rate constant of its thermal coloration after visible-light irradiation.

Spirobenzopyran derivatives can photoisomerize between their electrically neutral spiropyran and zwitterionic merocyanine forms.[1] We have already synthesized spirobenzopyran derivatives incorporating a monoazacrown ether moiety at the 8-position. We call these compounds crowned spirobenzopyrans, which permit photochemical control of cation-complexing ability.[2,3] The complexation of monovalent metal ions such as Li^+ by the crown ether moiety of crowned spirobenzopyrans can be modulated photochemically due to the efficient interaction between a monovalent metal ion captured by their crown ether moiety and side arm. Complexation involves the phenolate anion of the merocyanine moiety formed by the photoisomerization of the spirobenzopyran, which is in turn derived from the chelate formation of 6-membered ring by the nitrogen atom of the crown ether moiety and the phenolate oxy anion. It occurred to us that crown ether derivatives possessing two spirobenzopyran moieties may exhibit photocontrolled complexation of divalent metal ions due to the intramolecular interaction of the ion with the two phenolate anions of the merocyanine-containing sidearms.

The condensation reaction of 1,3,3-trimethyl-2-methylene-indoline 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[4] in the presence of triethylamine, afforded bis[(spirobenzopyran)-

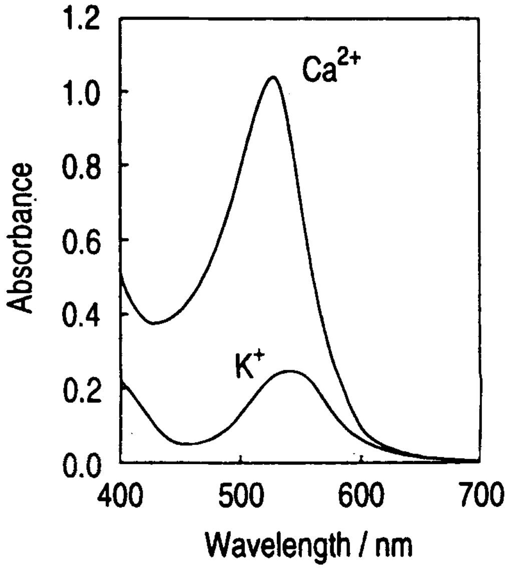

Figure 1 Absorption spectra of crowned bis(spirobenzopyran) **1** in acetonitrile in the presence of a metal ion.

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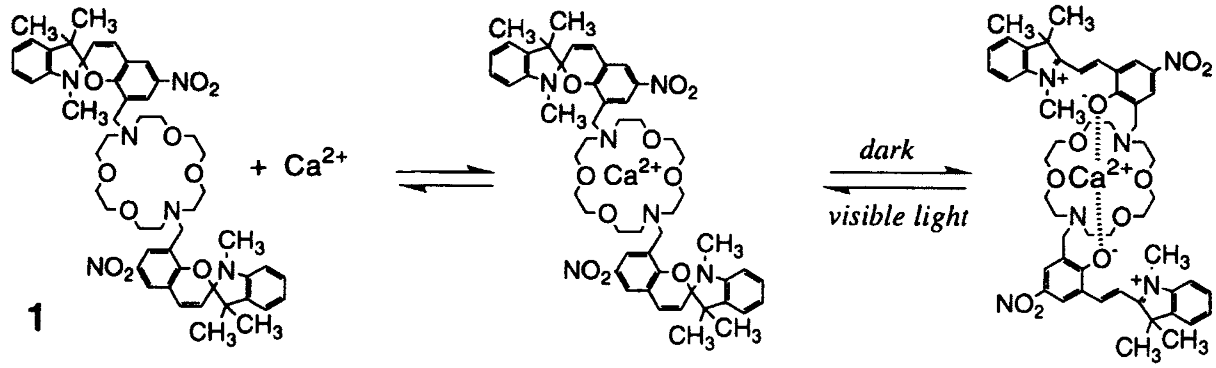
Table 1 First-order rate constants (*k*) of thermal coloration for crowned bis(spirobenzopyran) 1 in the presence of metal ions.

Metal ion	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Mn^{2+}	Zn^{2+}	Ni^{2+}	La^{3+}	Ce^{3+}
k (10^{-3} s^{-1})	1.45	3.04	3.08	0.322	8.17	2.25	1.07	0.355	0.211	0.237	2.51	2.02



Scheme 1

methyl] diaza-18-crown-6 1[*]. Addition of an equimolar amount of a metal salt to an acetonitrile solution of crowned bis(spirobenzopyran) 1 promoted the isomerization of its spirobenzopyran moiety to the merocyanine isomer by the cation complexation of its crown ether moiety, allowing the solution to turn dark red. The coloration was remarkable with polyvalent metal cations, especially alkaline-earth metal ions such as Ca^{2+}, as demonstrated by the absorption-spectral changes in Figure 1. ^1H-NMR spectroscopy indicated that both of the two spirobenzopyran units in a crowned bis(spirobenzopyran) molecule isomerize to the corresponding merocyanine moiety in the Ca^{2+} system, while only a spirobenzopyran unit does so in the K^+ system. Visible-light irradiation led to the isomerization of the merocyanine moiety back to its corresponding spirobenzopyran form. Turning off the visible light caused the thermal coloration reaction based on the isomerization to the merocyanine form under dark conditions. The coloration reaction rates for various metal ions were measured spectrophotometrically by following the absorbance for the merocyanine isomer[$]. The first-order plots of thermal coloration gave straight lines with slopes of rate constants, which are summarized in Table 1. A remarkable observation is the much higher rate constant of thermal coloration for Ca^{2+} than for the other metal ions, even the other alkaline-earth metal ions. The reaction rate in the presence Ca^{2+} is followed by those in the presence of K^+, Na^+, La^{3+}, and Ce^{3+} However, the other polyvalent metal cations do not necessarily show high coloration rates, even though their polyvalent charges were anticipated to be canceled out effectively by two phenolate anions of the merocyanine isomers. However, the rates for Mg^{2+}, Mn^{2+}, Zn^{2+}, and Ni^{2+} are considerably lower than expected. This means that the high cation-binding ability to the crown ether moiety of 1, derived from the size-fit concept, also contributes to the high rate constants of thermal coloration. Actually, Na^+ and K^+ are quite high in the rate constant due to the high cation-binding ability of the 18-crown-6 ring in spite of their monovalency. Thus, the high coloration rate for crowned bis(spirobenzopyran) 1–Ca^{2+} system can be attributed to a good combination of the relatively high Ca^{2+} affinity of its crown ether moiety itself[5] and the neutralization of the two charges. The complex formation in turn causes efficient intramolecular interaction of the cation with two phenolate anions of the merocyanine moiety, probably,

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[*] A dry ethanol solution of 1,3,3-trimethyl-2-methylene-indoline (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. The ethanol was evaporated off to afford a crude product of crowned bis(spirobenzopyran). After removal of chloroform-insoluble impurity from the crude product, recrystallization from dry ethanol afforded a pale-yellow crystal of pure 1 (yield: 58%): ^1H-NMR ($CDCl_3$) δ 1.19 and 1.27(6H,s,CCH_3), 2.63(8H,t,J = 5.7Hz, NCH_2CH_2O), 2.69(6H,s,NCH_3), 3.39–3.45(16H,m,OCH_2), 3.47(4H,s,$PhCH_2$), 5.84(2H,d,J = 10.3Hz, C*H* = CHPh), 6.52(2H,d,J = 7.4Hz,7'-H of indoline), 6.85 (2H,dd,J = 7.4Hz,6'-H of indoline), 6.91(2H,d,J = 10.3Hz, CH = C*H*Ph), 7.06 (2H,d,J = 7.4Hz,5'-H of indoline), 7.16 (2H,dd,J = 7.4Hz,4'-H of indoline), 7.88(2H,d,J = 2.8Hz,5-H of benzopyran), 8.22(2H,d,J = 2.8Hz,7-H of benzopyran).

[$] An acetonitrile solution of an equimolar amount (2×10^{-5} mol cm^{-3}) of 1 and a metal nitrate was irradiated by visible light for 5 min. Immediately after the photoirradiation was stopped, the absorbance for the corresponding merocyanine form at 460–560 nm was followed with time at room temperature. The first-order rate constants of thermal coloration (*k*) were determined from the slope in the plots of $-\log(A_t-A_\infty/A_0-A_\infty)$ vs. time (T), where A_t, A_0, A_∞ are the absorbance at T = t, at T = 0, and at T = ∞, respectively.

one above and the other below the crown ether ring, as shown schematically in Scheme 1.

Since photoisomerization of the crowned bis(spirobenzopyran) **1** can proceed reversibly even in the presence of Ca^{2+}, photochemical control of Ca^{2+} complexation is expected to be feasible with **1**. In a preliminary potentiometric experiment in acetonitrile using an ion sensor, visible-light-induced isomerization in the Ca^{2+} complex of merocyanine moiety of **1** allowed some release of free Ca^{2+} from the complex. Studies are under way to apply the crowned bis(spirobenzopyran) to photoresponsive ion-conducting films using polyvalent metal ions as the carrier.

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