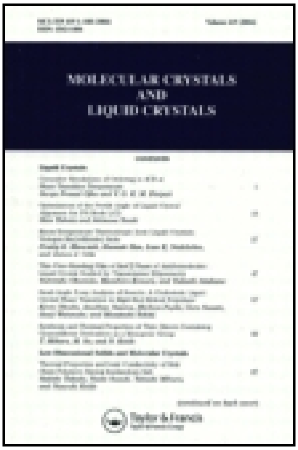

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High Affinity of Crowned Bis(Spirobenzopyran) for Multi-Valent Metal Ions Based on Doubly Armed Ionic Interaction

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High Affinity of Crowned Bis(Spirobenzopyran) for Multi-Valent Metal Ions Based on Doubly Armed Ionic Interaction

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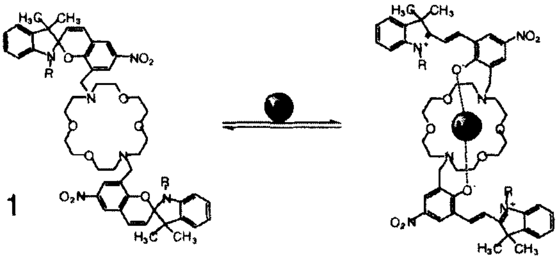
Crowned bis(spirobenzopyran) **1** can bind a divalent metal ion Ca^{2+} more powerfully than monovalent alkali metal ions due to the doubly armed ionic interaction. The Ca^{2+} complexation and selectivity between Ca^{2+} and K^+ can be controlled by turning on and off visible light.

Keywords: crown ether; spirobenzopyran; double ionic interaction; calcium ion complexation; ion selectivity; photocontrol

Spirobenzopyran derivatives are typical photochromic compounds that undergo reversible isomerization to their corresponding zwitterionic merocyanine form. We have studied on crown ether derivatives that can switch their metal-ion complexing ability photochemically. We have already reported 1,3,3-trimethylindolino-6'-nitrobenzopyryrospiran derivatives incorporating a monoazacrown ether at 8'-position, which we call crowned spirobenzopyran. A phenolate anion in the metal ion complexes of merocyanine form of crowned spirobenzopyran can interact by a monovalent metal ion complexed with its crown ether moiety selectively.

Such a phenomenon prompted us to design crowned bis(spirobenzopyran) **1**, which is an 18-crown-6 derivative bearing two spirobenzopyran units at the nitrogen atoms. We determined the complexing ability of **1** with monovalent, divalent and trivalent metal ions by using ^{1}H-

Scheme 1



NMR and electrospray-ionization mass spectroscopy (ESI-MS), and found that **1** binds much more strongly multivalent ions than monovalent ions.[1,2] A significant peak assigned to the merocyanine form was observed in visible absorption spectra of solution containing equimolar amounts of **1** and a metal ion in acetonitrile under dark conditions. This implies that isomerization from the spiropyran form into the merocyanine form is induced by complexation of a multivalent metal ion by the crown ether moiety, the two phenolate anions interacting the central metal ion (Scheme 1). We have already reported that the crowned bis(spirobenzopyran) binds a trivalent metal ion La^{3+} more powerfully than monovalent metal ions such as alkali metal ions.[1] The metal ion complexation can be switched by visible-light irradiation. ESI-MS under dark conditions afforded a huge peak assigned to $[LaNO_3\text{-}\mathbf{1}]^{2+}$ as compared to that for $[K\text{-}\mathbf{1}]^{+}$. Visible-light irradiation increased the peak intensity of the La complex, while decreasing that of the K complex.

Here we report the higher affinity of crowned bis(spirobenzopyran) **1** to a divalent metal ion Ca^{2+} than alkali metal ions and photoinduced control of metal ion complexation and ion selectivity between the divalent metal ion and an alkali metal ion. Addition of an equimolar amount of an alkali or alkaline-earth metal salt to an acetonitrile solution of crowned bis(spirobenzopyran) **1** allowed the solution to turn dark red. This means that cation complexation of **1** by its crown ether moiety induced the isomerization of its spirobenzopyran moiety to the merocyanine isomer.

The coloration was more remarkable with Ca^{2+} than monovalent metal ions such as K^+.[2,3] ^1H-NMR spectroscopy indicated that the isomerization degree was much greater in the complexation with Ca^{2+} than with K^+.[2] Also, 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. The coloration reaction rates for various metal ions were measured spectrophotometrically by following the absorbance for the merocyanine isomer.[3] The rate constant of thermal coloration is much higher for Ca^{2+} than for alkali metal ions. Also, the thermal coloration rate for the other divalent metal ions, Mg^{2+}, Sr^{2+}, and Ba^{2+} are considerably lower than for Ca^{2+}. This may show that the size fit of the metal ions into the crown ether moiety also contributes to the high rate constants of thermal coloration. Probably, the fast thermal coloration is reflected in the high stability of metal ion complexes of **1**. Thus, the absorption spectroscopy under dark conditions, NMR spectroscopy, and the thermal coloration rate measurements suggests that crowned bis(spirobenzopyran) **1** forms much more stable complexes with Ca^{2+} than the other alkaline-earth metal ions and alkali metal ions. Thus, the high coloration rate and therefore the high complex stability for crowned bis(spirobenzopyran) **1** – Ca^{2+} system can be attributed to a combination of the relatively high Ca^{2+} affinity of its crown ether moiety itself and the counterbalance of the positive charges of Ca^{2+} with two negative charges of **1** merocyanine form. The complex formation in turn causes efficient intramolecular interaction of the metal ion with two phenolate anions of the merocyanine moiety, probably, one above and the other below the crown ether ring, as demonstrated in the scheme 1.

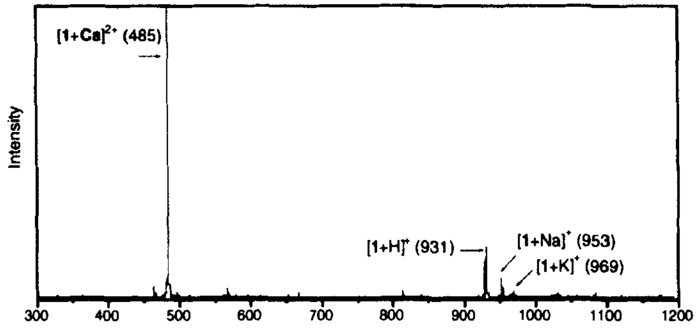


Fig. 1. ESI-MS *for acetonitrile solution containing* **1** *and mixture of* Ca^{2+} *and alkali* metal ions (Li^+, Na^+, K^+) under dark conditions.
[**1**] : 1 X 10^{-5} M; [metal nitrate]: 1 X 10^{-5} M each.

ESI-MS for an acetonitrile solution containing a mixture of Ca^{2+} and alkali metal ions confirms the high stability of the **1**-Ca^{2+} complex (Fig. 1). The mass spectrum shows an intense peak for Ca^{2+} complex ([**1**+Ca]$^{2+}$) and only tiny peaks for the alkali metal complexes ([**1**+M]$^{+}$), although the system contains an equal amount of metal ions.

Visible-light irradiation on an acetonitrile solution containing an equal amount of crowned bis(spirobenzopyran) **1** and Ca^{2+} caused isomerization of the merocyanine form of **1** back to the spirobenzopyran form. Turning off the light again allowed the spiropyran to merocyanine forms. That is to say, the crowned bis(spirobenzopran) is photoisomerized between the spiropyran and merocyanine forms even in the presence of Ca^{2+}. Since the photoisomerization of crowned bis(spirobenzopyran) **1** can proceed almost reversibly, photochemical control of Ca^{2+} complexation is expected to be feasible with **1**. ESI-MS for an acetonitrile solution containing **1** and Ca^{2+} was measured under dark conditions and after visible-light irradiation (Fig. 2). There is a significant peak for **1**-Ca^{2+} complex under dark conditions, which shows that **1** binds Ca^{2+} powerfully. The photoirradiation decreased dramatically the peak intensity for the Ca^{2+} complex, thus resulting in metal ion

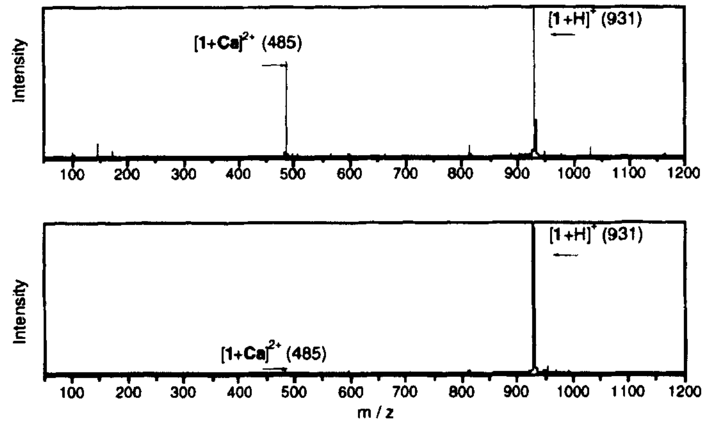


Fig. 2. Photoinduced change in ESI-MS for acetonitrile solution containing **1** and Ca^{2+}. **a**: under dark conditions; **b**:after visible-light (>400 nm) irradiation for 20 min. [**1**] : 1 X 10^{-5} M; [$Ca(NO_3)_2$]: 1 X 10^{-5} M .

release from the complex. This verifies the photochemical control of Ca^{2+} complexation by **1**.

The spiropyran and merocyanine isomers of **1** are very different in the metal-ion comeplexation and selectivity. The spiropyran isomer prefers monovalent metal ions like K^+ to divalent metal ions because the spirobenzopyran moiety hardly participates in the metal ion binding. The ion selectivity of the spiropyran isomer is essentially based on that for the parent crown ether, diaza-18-crown-6. On the other hand, the merocyanine isomer of **1** binds divalent metal ions like Ca^{2+} more strongly than monovalent ions due to the powerful interaction with its two phenolate anions. Photoinduced selectivity switching between divalent and monovalent metal ions was thus realized with crowned bis(spiro-benzopyran) **1** (Scheme 2) . The photoinduced change of ESI-MS for a solution of Ca^{2+}, K^+, and **1** is indicative of the ion selectivity switching between Ca^{2+} and K^+. Photoirradiation decreased the peak intensity for the **1**-Ca^{2+} complex, while increasing that for **1**-K^+ complex.

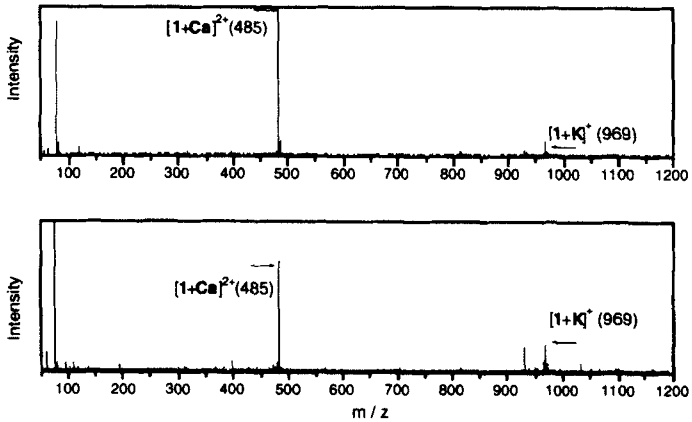
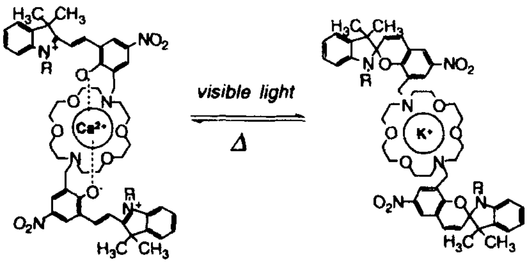


Fig. 3. Photoinduced change in ESI-MS for acetonitrile solution containing **1**, Ca^{2+} and K^{+}. **a**: under dark conditions; **b**: after visible-light (>400 nm) irradiation for 20 min. [**1**] : 1 X 10^{-5} M; [$Ca(NO_3)_2$]: 1 X 10^{-5} M ; [KNO_3]: 1 X 10^{-3} M.

Scheme 2



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References

[1] K. Kimura, T. Utsumi, T.Teranishi, M. Yokoyama, H. Sakamoto, M. Okamoto, R. Arakawa, H. Moriguchi, and Y. Miyaji, *Angew. Chem. Int. Ed. Engl.*, **36**, 2452 (1997).

[2] K. Kimura, T. Teranishi, M. Yokoyama, S. Yajima, S. Miyake, H. Sakamoto, and M. Tanaka, *J. Chem. Soc. Perkin Trans. 2*, ***1999***, *199*.

[3] K. Kimura, T. Teranishi, M. Yokoyama, *Supramol. Chem.*, **7**, 11 (1996).