CHEMISTRY LETTERS, pp. 965-968, 1991.

Photochemical Control of Ionic Conduction by Crowned Spirobenzopyran

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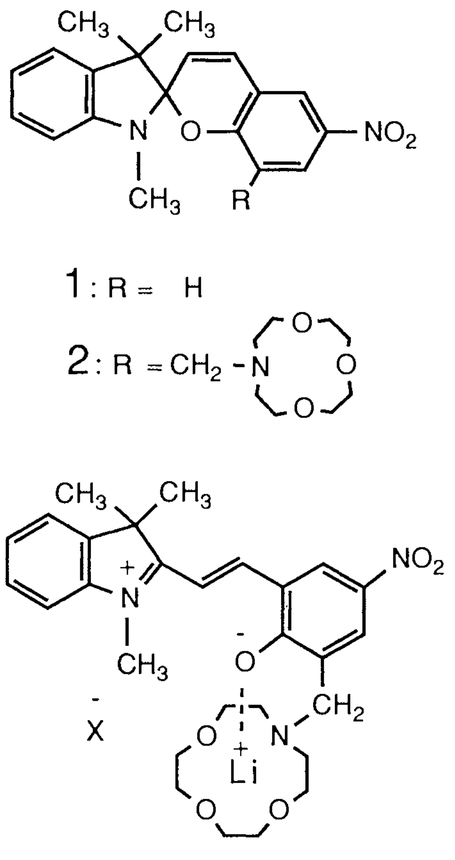
Ionic conduction in composite films incorporating a crowned spirobenzopyran and $LiClO_4$ was controlled photochemically. UV light irradiation, which promotes the isomerization of spirobenzopyran to its corresponding merocyanine form, depressed Li^+ conduction due to its enhanced Li^+ complexation, while visible light irradiation restored the initial ionic conduction.

Spirobenzopyran derivatives,1) such as **1**, generally isomerize to their corresponding merocyanine forms by UV light, and *vice versa* by visible light. The isomerization to the merocyanine form brings about ionic or polar circumstance, since the merocyanine form is most likely to be a zwitter ion. Several attempts have been made to control photochemically transport of amino acids2) and transition metal ions3) and membrane potentials4) in bilayers or liquid membranes containing spirobenzopyran derivatives and to modulate rheological properties of spirobenzopyran-pendant polymers,5) taking advantage of their photo-isomerization between the electrically-neutral spiropyran and ionic merocyanine forms. Inouye *et al.*,6) Akabori *et al.*,6) and we7) independently synthesized spirobenzopyran derivatives incorporating a crown ether moiety which isomerize to their corresponding merocyanine forms to some extent even in the dark when their crown moieties bind alkali metal ions. In our spirobenzopyran with monoazacrown moiety at the 8-position, **2**, the phenolate anion in the merocyanine isomer of crowned spirobenzopyran was found to interact intramolecularly with a Li^+ complexed by its crown moiety (Scheme 1). This led us to envisage photo-responsive ionic conductivity in composite films containing the crowned spirobenzopyran. It was thus expected that photo-induced isomerization of the crowned spirobenzopyran to its merocyanine isomer promotes its Li^+ binding by the cooperative action of the crown moiety and phenolate anion, in turn suppressing the ion conduction remarkably. Photo-reversion to the spiropyran isomer tends to release the bound ion, assisting the ion conduction. This communication reports photochemical control of ion mobility and, thereby, ionic conductivity in ion-conducting composite films containing the crowned spirobenzopyran.

Composite films consisting of 51.9% (in weight) poly(vinyl chloride) (PVC), 43.3% bis(2-ethylhexyl) sebacate (DOS), 4.4% crowned spirobenzopyran, and 0.4% $LiClO_4$ were prepared by spin coating from tetrahydrofuran on glass substrates. The films of about 2 μm thickness were dried at 40 °C under a nitrogen stream overnight. Ac impedance of the ion-conducting composite films was measured on photo-irradiation under an argon atmosphere.8) UV light (300-400 nm) irradiation on the composite film diminished its ionic conductivity significantly (Fig. 1).9) The decreased ionic conductivity was restored to the initial value by visible light (>490 nm) irradiation. The photo-induced change of ionic conductivity for the crowned-spirobenzopyran-containing film was quite reversible, as demonstrated in Fig. 1. Absorption spectra of the UV-light-irradiated composite film exhibited a strong absorption around 520 nm that is attributable to the merocyanine isomer of **2** (Fig. 2). The absorption peak was decreased remarkably by visible light irradiation. The photo-induced ionic conductivity change of the composite film containing the crowned spirobenzopyran is thus synchronized with its photo-isomerization.

It should be noted that the absorption peak of the merocyanine isomer in the composite film shifted to the shorter wavelength as compared with that (around 580 nm) for the film without the salt. The marked blue shift clearly indicates that electron localization in the merocyanine form of the crowned spirobenzopyran is enhanced in the presence of the lithium salt, supporting the intramolecular powerful interaction between the Li^+ complexed by its crown moiety and the resulting phenolate anion in the merocyanine isomer as shown schematically in Scheme 1. In the opposite sense, this intramolecular interaction of the crown-complexed Li^+ with the phenolate anion accelerates the Li^+ binding of the crown moiety in the merocyanine isomer due to a sort of lariat ether effect10) or chelate effect11) of the phenolate anion. The enhancement in the Li^+ binding of the crowned spirobenzopyran on its photo-isomerization from spiropyran to merocyanine forms was verified qualitatively by ^7Li-NMR spectroscopy in an acetonitrile solution.7) A peak assigned to **2** - Li^+ complex illustrated in the scheme appeared at a higher frequency on UV light irradiation, *i.e.* under merocyanine-rich conditions, whereas the peak almost disappeared on visible light irradiation, *i.e.* under spiropyran-rich conditions.

Transference numbers for Li^+ on the ionic conduction, determined by isothermal transient ionic current method,12) offered good information about Li^+ mobility in the composite film on UV- and visible-light irradiation. The transference number for Li^+ in the **2**-containing film was decreased significantly under merocyanine-rich conditions (0.71), as compared with that under spiropyran-rich conditions (0.80). Obviously, the UV-light-induced isomerization of the crowned spirobenzopyran retards Li^+ conduction in



Scheme 1.

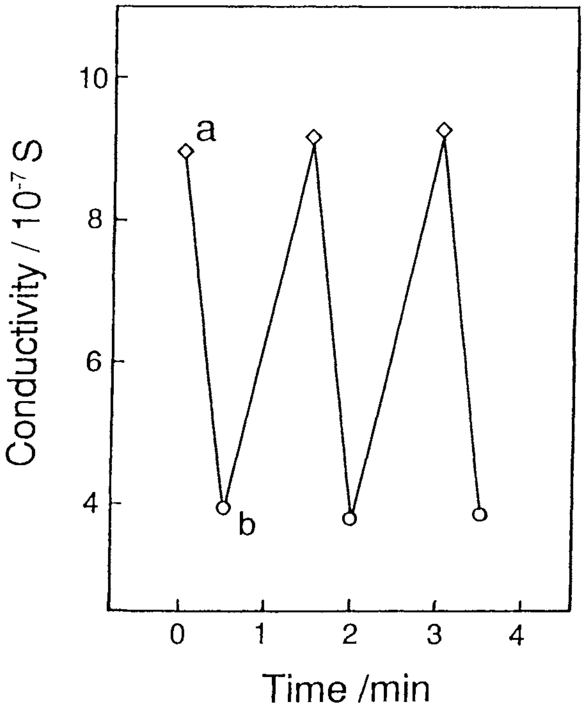


Fig. 1. Photo-induced ionic conductivity changes in composite film containing crowned spirobenzopyran.
a: UV light turned on , **b**: visible light turned on.

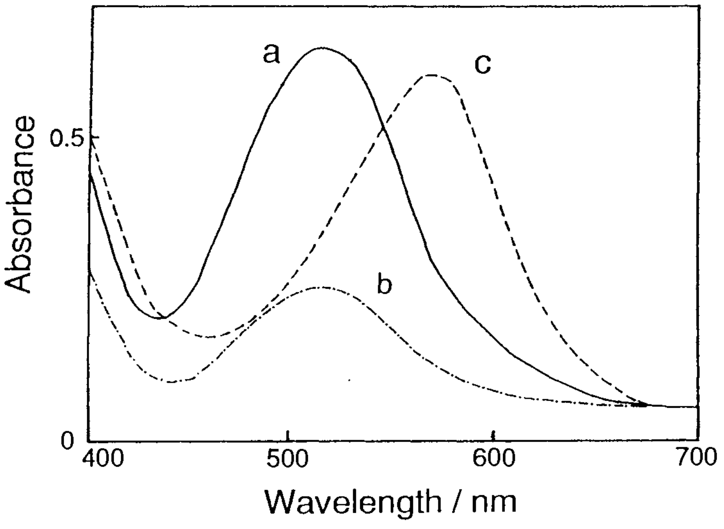


Fig. 2. Spectral changes of composite films containing crowned spirobenzopyran on photo-irradiation.
a: on UV light irradiation, **b**: on visible light irradiation after the UV light irradiation, **c**: for composite film without $LiClO_4$ on UV light irradiation.

the film by the enhanced Li+ binding to its merocyanine isomer. In the film incorporating **1**, on the other hand, any distinct change in the Li+ transference number (0.82) was not found on the photo-irradiation. This is possibly because the interaction of Li+ with the merocyanine isomer of **1**, which does not possess any powerful binding site such as crown moiety, is quite small.

In summary, the photo-isomerization of the crowned spirobenzopyran is capable of modulating the Li+ conduction in the composite film by its variable cation-binding ability, thus bringing about the ionic conductivity change. Further studies are currently under way to design singly-ionic conductors incorporating the crowned spirobenzopyran in order to realize more remarkable ionic-conductivity switching.

References

1) R. C. Bertelson, "Photochromic Process Involving Heterocyclic Cleavage," in "Photochromism," ed by G. H. Brown, Wiley-Interscience, New York (1971), Chap. 3.
2) J. Sunamoto, K. Iwamoto, Y. Mohri, and T. Kominato, *J. Am. Chem. Soc.,* , **104**, 5502 (1982).
3) J. D. Winkler, K. Deshayes, and B. Shao, *J. Am. Chem. Soc.*, **111**, 769 (1989).
4) S. Kato, M. Aizawa, and S. Suzuki, *J. Membr. Sci.*, **1**, 289(1976); M. Irie, A, Menju, and K. Hayashi, *Nippon Kagaku Kaishi*, **1984**, 227 ; H. Sasaki, A. Ueno, J. Anzai, and T. Osa, *Bull. Chem. Soc. Jpn.*, **59**, 1953 (1986); O. Ryba and J. Petranek, *Makromol. Chem., Rapid Commun.*, **9**, 125 (1988).
5) M. Irie, T. Iwayanagi, and Y. Taniguchi, Y. *Macromolecules*, **18,** 2418 (1985); F. Ciardelli, D. Fabbri, O. Pieroni, and A. Fissi, *J. Am. Chem. Soc.*, **111**, 3470 (1989).
6) M. Inouye, M, Ueno, T, Kitao, and K. Tsuchiya, *J. Am. Chem. Soc.*, 1990, **112**, 8977; S. Akabori and Y. Fujimine, 59th National Meeting of the Chemical Society of Japan, 1990, Abstr., No. 1E315.
7) K. Kimura, T. Yamashita, and M. Yokoyama, *J. Chem. Soc., Chem. Commun.*, **1991**, 147.
8) K. Kimura, T. Suzuki, and M. Yokoyama, *J. Phys. Chem.*, **94**, 6090 (1990).
9) Before the ionic conductivity measurements, most of the merocyanine isomers formed by the cation-induced isomerization were reverted to the corresponding spiropyran isomers by visible light irradiation, in order to attain as great ionic conductivity changes as possible.
10) A. Kaifer, D. A. Gustowski, L. Echegoyen, V. J. Gatto, R. A. Schultz, T. P. Cleary, C. R. Morgan, D. M. Goli, A. M. Rios, and G. W. Gokel, *J. Am. Chem. Soc.*, **107**, 1958 (1985); L. Echegoyen, D. A. Gustowski, V. J. Gatto, and G. W. Gokel, *J. Chem. Soc., Chem. Commun.*, **1986**, 220.
11) Y. Katayama, K. Nita, M. Ueda, and H. Nakamura, K. Ueno, *Anal. Chim. Acta,* **173**, 193 (1985).
12) G. Greeuw and B. J. Hoenders, *J. Appl. Phys.*, **55**, 3371 (1984); M. Watanabe, K. Rikukawa, and K. Sanui, N. Ogata, *ibid.*, **58**, 736 (1985).

(Received March 18, 1991)