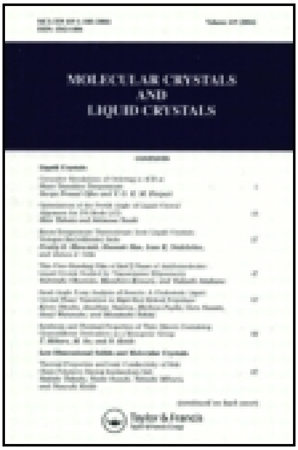

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DESIGN OF PHOTOCHROMIC CROWN COMPOUNDS AND THEIR APPLICATIONS TO PHOTOSWITCHABLE ION-CONDUCTING MATERIALS

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Abstract Crowned spirobenzopyran and spironaphthoxazine have been designed which are capable of modulating their cation-binding ability by photoisomerization. They have been successfully applied as a key compound for photoswitchable ion-conducting composite films.

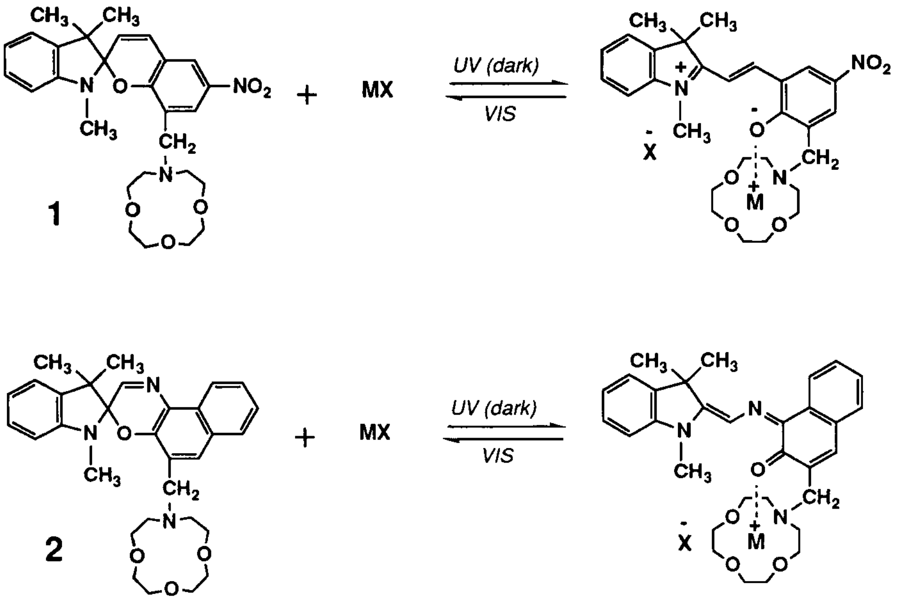
INTRODUCTION

Ion-conducting materials whose ionic conductivities can be switched photochemically are useful for devices for memory and printing. Very few organic ionic conductors, which possess high processibility, however, can undergo photochemical switching of ionic conductivity. We have already reported significant photoinduced change of ionic conductivity in ion-conducting composite films containing an azobenzene derivative, which is based on the photoinduced phase transition of the photochromic compound between its crystal (or liquid crystal) and isotropic liquid phases.[1] The photoswitchable ion-conducting system has realized photoinduced electrostatic imaging.[2] One can expect photochemical control of ionic conductivity, using photochromic compounds which carry out ionization on their photoisomerization. Here we describe the design of spirobenzopyran and spironaphthoxazine derivatives carrying a crown ether moiety for fabrication of photoinduced ionic-conductivity switching system based on cation-binding ability changes of the photochromic crown compounds.

DESIGN AND CATION COMPLEXATION OF PHOTOCHROMIC COMPOUNDS

Designing of crowned spirobenzopyrans is very important for attaining effective photochemical control of their cation-binding ability. We decided to incorporate a crown ether moiety at the 8-position of a spirobenzopyran skeleton, aiming at such photocontrol of cation-binding ability by its photoisomerization as shown in SCHEME I. When crowned spirobenzopyran **1** is isomerized to the corresponding merocyanine by photoirradiation, its phenolate anion as well as its crown moiety is most likely to participate in the cation

SCHEME I



binding due to the formation of a stable six-member-ring chelate by the anion and crown-ring nitrogen atom.[3] Results for cation extraction and absorption spectroscopy of **1** implied that the interaction between the phenolate anion and crown-complexed cation promotes its binding of high-charge-density metal ions such as Li^+.[4] ^7Li-NMR spectroscopy of an acetonitrile solution containing equimolar **1** and $LiClO_4$ under dark conditions strongly supports the intramolecular interaction (FIGURE 1). A significant peak, which can be assigned to the Li^+ complex of the merocyanine form of **1**, was found at the higher frequency besides the peak for Li^+ solvated by acetonitrile or complexed simply by the crown moiety. This was, however, not the case with the NMR spectra of any mixtures of an uncrowned spirobenzopyran and a conventional crown ether. On visible-light irradiation, the higher-frequency peak decreased, while the lower-frequency one increased. This means that visible light enhances the isomerization from the merocyanine to spiropyran forms, thus resulting in disappearance of the additional interaction of the phenolate anion with the crown-complexed Li^+. UV-light irradiation can recover the interaction by isomerization to the merocyanine form. In crowned spironaphthoxazine **2**, a similar complexation equilibrium change can be also attained by its photoisomerization, with a slight difference in that instead of a phenolate anion, an oxo group interacts intramolecularly with a crown-complexed Li^+ in the open form of **2** (SCHEME I).[5]

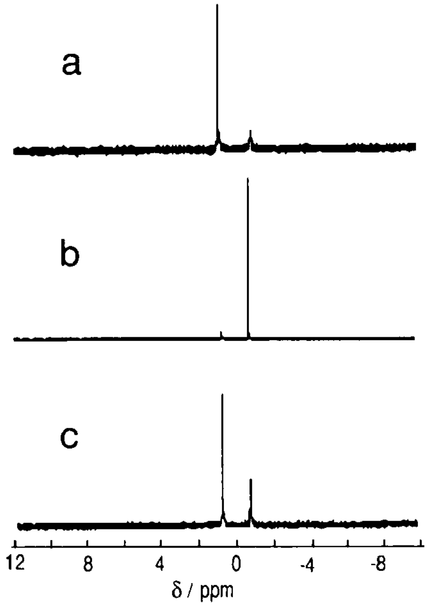


FIGURE 1 ^{7}Li-NMR spectroscopy of **1** -LiClO$_4$ acetonitrile solution. [**1**] and [LiClO$_4$]: 2 X 10^{-2} mol dm^{-3} **a**: under dark conditions, **b**: on visible-light (>490 nm) irradiation; **c**: on UV-light (300-400 nm) irradiation after the visible-light irradiation.

PHOTOCHEMICAL SWITCHING OF IONIC CONDUCTIVITY

Taking advantage of the photoinduced change in the cation-binding ability of the crowned spirobenzopyran and spironaphthoxazine, attempts were made to photochemically control ionic conductivity of composite films containing the photochromic compounds.[6] FIGURE 2 demonstrates typical profiles for photoinduced ionic-conductivity changes in composite films (about 5 μm thickness) consisting of poly(vinyl chloride) (PVC, 49.8 wt%), bis(2-ethylhexyl) sebacate (41.5 wt%), LiClO$_4$ (8.3 wt%), and **1** or **2** (0.4 wt%). In both of the **1** and **2** systems, the ionic conductivity was increased and decreased remarkably by visible- and UV-light irradiation, respectively, as expected from the photoinduced cation-binding ability change. That is to say, visible-light-induced attenuation in the cation binding increases the Li$^+$ mobility in composite films, while the UV-light-induced enhancement decreases it. In single-ionic conducting composite films containing Li$^+$ poly(perfluorosulfonate) instead of LiClO$_4$, where only Li$^+$ can contribute to the ionic conductivity, more remarkable ionic-conductivity switching based on the mechanism of SCHEME I was realized, as compared with the bi-ionic conducting PVC composite films, where not only Li$^+$ but also its counter anion can migrate in films. It is worthy of remark that the photochemical ionic-conductivity switching for the **2** system is highly reversible

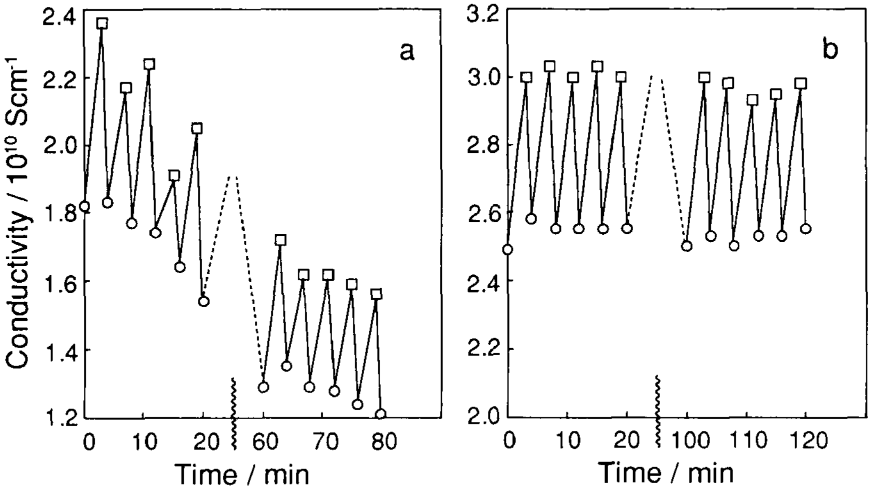


FIGURE 2 Photoinduced ionic-conductivity switching in ion-conducting composite films containing **1** (**a**) or **2** (**b**).

Visible- and UV-light irradiation started at the points of (○) and(□), respectively.

and reproducible, being quite different from that for the **1** system. The reversibility in the ionic-conductivity switching of the **2** system lasted even after 30-time switching, whereas the **1** system declined gradually in the switching magnitude and ionic conductivity. The excellent durability of the **2** system is definitely due to the much better light resistance of the spironaphthoxazine skeleton than that of the spirobenzopyran one.[7,8] Thus, the photochemical switching systems of ionic conductivity using the photochromic crown compounds, particularly **2**, are promising for device applications.

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