



Photochemical Ionic-Conductivity Switching Systems of Photochromic Crown Ethers for Information Technology

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Abstract. Design of two types of ion-conducting systems using photochromic crown ethers as the photocontrol agents is described; one type is based on the phase transition of azobenzene derivatives induced by their photoisomerization and the other based on the molecular control of metal ion complexation by crowned spirobenzopyrans. The photoresponsive ion-conducting systems are applicable to electrostatic imaging and photorefractive materials.

Key words: crown ethers, photochromism, photocontrol of ionic conduction, electrostatic imaging, photorefractivity.

1. Introduction

Electric conduction can be performed by migration of electron (or hole) or ions. Considerable attention has been focused on the design of electric conducting materials. Especially, organic materials for electric conduction are attractive for device applications due to the high processibility and diversity. The design of electron-conducting organic materials and their applications to information technology is being investigated intensively, probably because the devices by electronic conduction often show a high speed response. In biological systems, on the other hand, the information networks are primarily based on ionic conduction which enables parallel information delivery unlike electronic conduction. Ion-conducting organic materials, therefore, have high potentiality for their applications to information technology.

Crown ethers, which form complexes with various cations, can be utilized for ion-conducting materials. Addition of crown ethers to polymer electrolytes often promotes metal salt solubilization, ion separation, and carrier migration, thus enhancing ionic conductivities of polymer electrolytes. Ion-conducting organic materials, the ionic conductivity of which can be switched by external stimuli

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such as light and heat, are useful for applications to material chemistry such as device fabrication for imaging, memory, and printing. Photochromic compounds [1], which isomerize reversibly by photoirradiation, are convenient tools for controlling physical properties, and can be also applied to photochemical control systems of ionic conductivity [2]. That is to say, the combination of a crown ether with a photochromic compound enables us to control ionic conductivity by photoirradiation. Our recent studies on photochemical ionic-conductivity switching systems of photochromic crown ethers for information technology are described here. Emphasis is placed on their applications to information technology.

2. Photoinduced Ionic-Conductivity Switching by Photochromic Crown Ethers

2.1. AZOBENZENE DERIVATIVES

Azobenzene derivatives isomerize from their trans to cis forms by UV-light irradiation and vice versa by visible-light irradiation or heating. The two azobenzene isomers often experience different thermal phase transitions and often show different phases at the same temperature [3]. In that case, the photoisomerization of azobenzene derivatives should cause their distinct phase transition at the temperature. When the azobenzene phase contains appropriate ion-conducting carriers, the ionic conduction should be affected by the photoinduced phase transition of the azobenzene derivative which in turn brings about mobility changes of the ion-conducting carriers.

Thus, the combination of azobenzene derivative **1** and a crown ether can regulate ionic conduction photochemically [4–6]. For instance, composite films consisting of poly(vinyl chloride) (PVC), azobenzene **1**, LiClO₄, and 12-crown-4 undergo photochemical ionic-conductivity switching as demonstrated in Figure 1. Under dark conditions, the azobenzene derivative **1** is in the trans form and in the crystal state at room temperature. UV-light irradiation allows trans-**1** to isomerize to its corresponding cis isomer, which is in the isotropic liquid state at room temperature. The UV-light-induced phase transition of the azobenzene derivative from the crystal to isotropic liquid states increases the mobility of the ion-conducting carriers, Li⁺ or ClO₄⁻, thereby increasing the ionic conductivity. Turning off the UV light causes gradual isomerization of cis-**1** back to its trans form and the isomerization proceeds very quickly by visible-light irradiation. The back isomerization of the azobenzene derivative again diminishes the ionic conductivity to the initial value. The photochemical ionic-conductivity changes in the composite films are quite reversible. Azobenzene derivatives carrying a crown ether moiety, i.e., crowned azobenzenes such as **2**, are also useful reagents for photochemical ionic-conductivity switching systems based on a similar photoinduced phase transition [7]. The ion-conducting carriers are almost always in the domain participating in the photoinduced ionic-conductivity change for the ion-conducting system containing the crowned azobenzene, where its crown moiety is connected

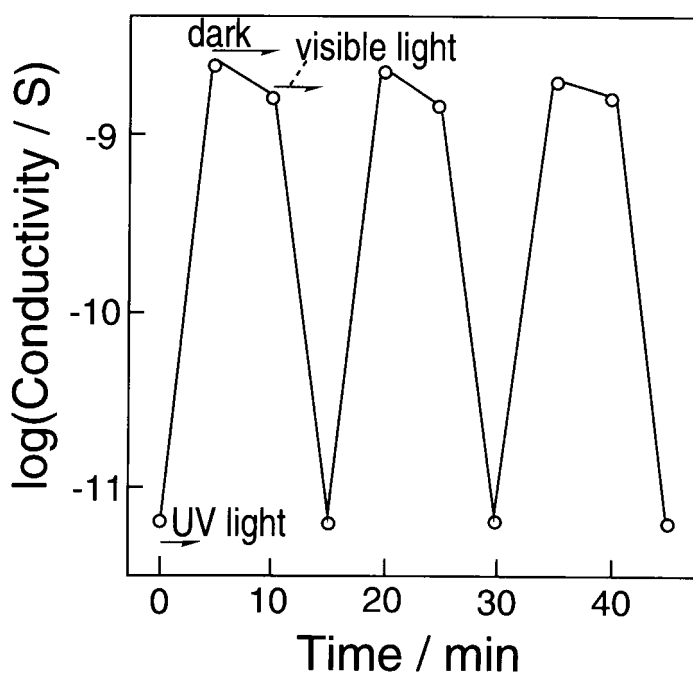
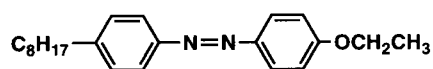
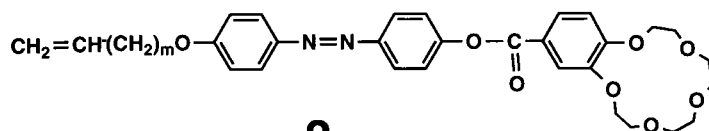
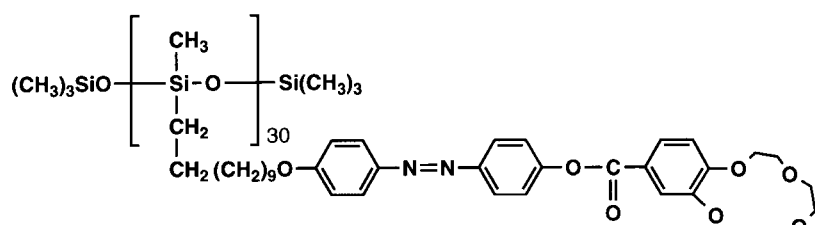
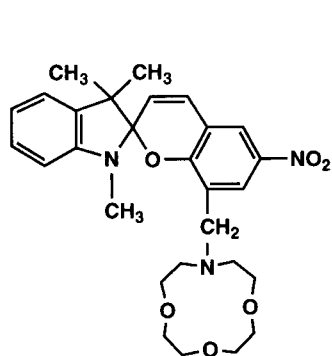
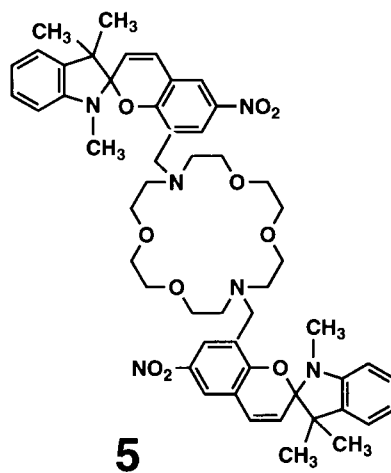


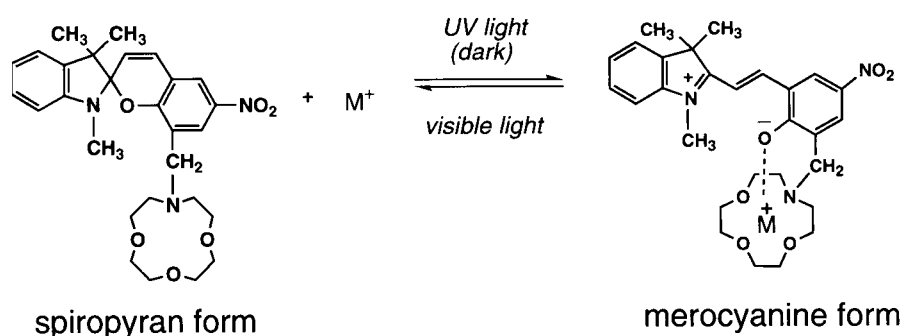
Figure 1. Photoinduced ionic-conductivity switching of composite film of PVC/1/LiClO₄/12-crown-4.

with the azobenzene moiety forming a domain for the photoinduced phase transition. Significant ionic-conductivity switching is, therefore, expected to occur in the crowned azobenzene system. However, in crowned azobenzene polymers such as **3**, which can be a polymeric liquid crystal, a different type of phase transition is observed by photoisomerization of their azobenzene moiety. Crowned azobenzene polymer **3** easily forms a smectic liquid crystal under dark conditions [8]. In the liquid crystal state, the adjacent crown ether rings get close to each other due to the highly-ordered arrangement of its crowned azobenzene side chains. In such a highly-ordered liquid crystal state, therefore, metal cations or their counteranions can migrate effectively among the adjacent crown ether rings. This in turn allows high ionic-conductivity states. UV-light-induced isomerization of the azobenzene moiety to its *cis*-form, on the other hand, disturbs the ordered arrangement of the crown ether rings, that is, the ion-hopping sites, thus suppressing the ionic conduction.

2.2. SPIROBENZOPYRAN DERIVATIVES

Spirobenzopyran derivatives are another type of photochromic compounds, which exhibit photochromism between the electrically neutral spiroopyran form and the zwitterionic one. Spirobenzopyran derivatives incorporating a crown ether moiety,

**1****2****3****4****5***Formulas 1-5.*



Scheme 1.

spiropyrans, such as **4**, exhibit interesting photochromism in the presence of crown ether-complexing metal ions [9–10]. In the opposite sense, crowned spiropyrans **4** can realize molecular control of metal ion complexation by the photoisomerization of its photochromic moiety, as illustrated in Scheme 1 [11]. On UV-light irradiation, the intramolecular interaction with a phenolate anion in the crowned merocyanine promotes the metal ion binding due to the additional-binding-site effect. On the contrary, visible-light irradiation induces the isomerization to the spiropyran isomer and thereby attenuates the additional-binding-site effect, thus decreasing the cation-binding ability. Crowned spiropyrans, when incorporated into composite films containing a monovalent metal salt, can control the ionic conductivity photochemically. In ion-conducting composite films containing lithium poly(perfluorosulfonate) (PPFS- Li^+) and crowned spiropyrans **4**, photochemical switching of ionic conductivity is observed by turning on and off visible light (Figure 2). A crown ether carrying two spiropyrans moieties, crowned bis(spiropyrans) **5**, is a promising candidate as a photocontrol reagent for ion-conducting systems using divalent metal ions as the carrier [12].

3. Applications to Information Technology

3.1. ELECTROSTATIC IMAGING SYSTEM

In recent electrostatic imaging systems, electron (or hole)-conducting materials are generally employed [13]. Ion-conducting materials are also applicable to electrostatic imaging [14]. For instance, ion-conducting composite films containing azobenzene derivative **1** have successfully been applied to electrostatic imaging process. The basic concept is shown schematically in Scheme 2. The device was fabricated by casting a composite film of poly(vinyl chloride)(PVC)/**1**/ LiClO_4 (about $12\ \mu\text{m}$) on an indium-tin-oxide-coated glass substrate, followed by an insulating film of poly(ethyleneterephthalate) ($2\ \mu\text{m}$ thickness). When the composite film containing **1** is irradiated by UV light through an exposure image, its photoirradiated region is highly ion-conducting due to the photochromic phase transition of the azobenzene derivative from the crystal to the isotropic liquid states,

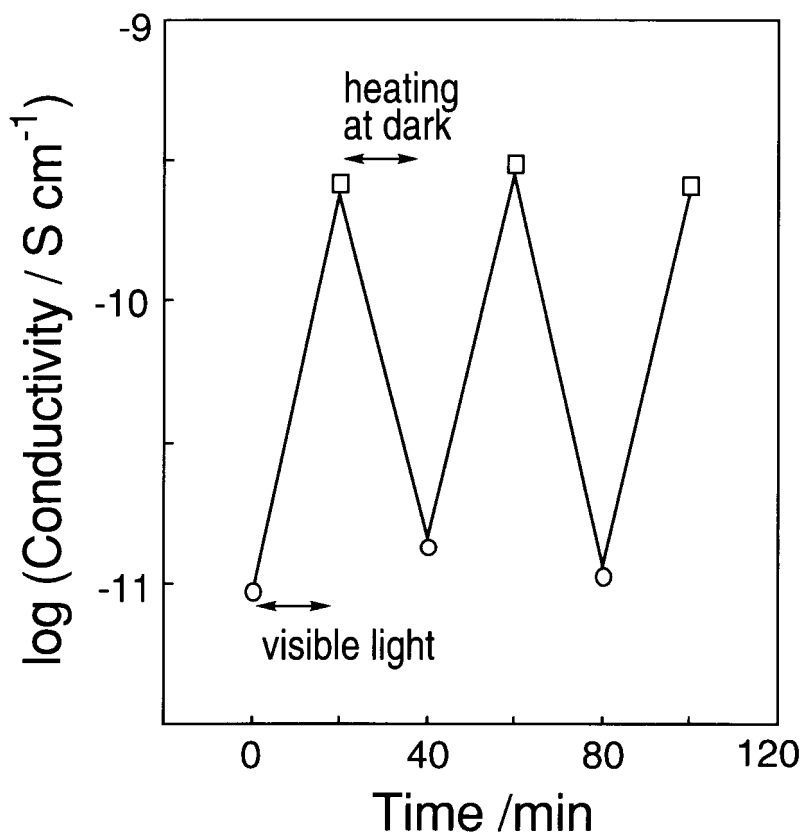
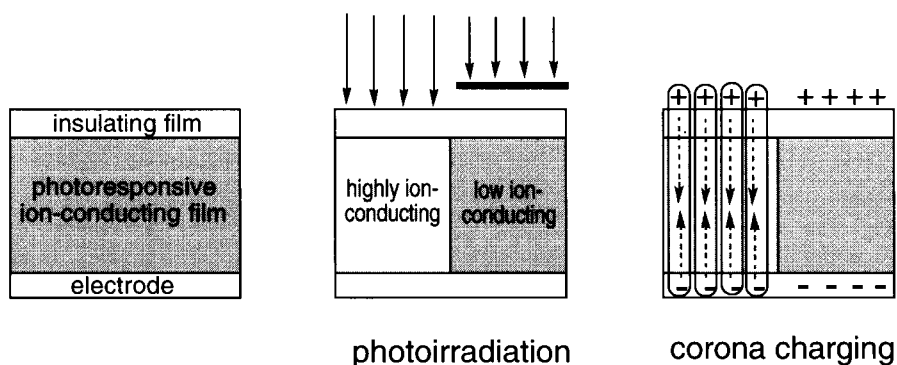


Figure 2. Photoinduced ionic-conductivity switching in a composite film of PPFS-Li⁺/oligo(oxyethylene) diacetate/4 on turning visible light on and off while being heated at 70 °C under dark conditions.

while the unirradiated region is still low ion-conducting. The ionic-conductivity difference between the photoirradiated and unirradiated regions of the composite films can afford image storage, which can be read easily by corona charging. The surface charges induced by corona charging are easily canceled out on the highly ion-conducting photoirradiated region by its internal polarization, while the low ion-conducting unirradiated region still possesses stable surface charges. Figure 3 demonstrates a typical surface-potential difference of a composite film induced by corona charging before and after UV-light irradiation. The initial surface potential is much lower in the dark than that after photoirradiation, with a difference of 200 V. The latent image can be readily duplicated by a conventional xerographic method, i.e., a photoirradiated composite film is positively-charged, developed by negatively charged toners, and then transferred to a white paper. The surface potential decreased by photoirradiation was gradually changed with time, unless the composite film was irradiated subsequently by visible light (Figure 4). A surface potential difference higher than 100 V was kept between the photoirradiated and



Scheme 2.

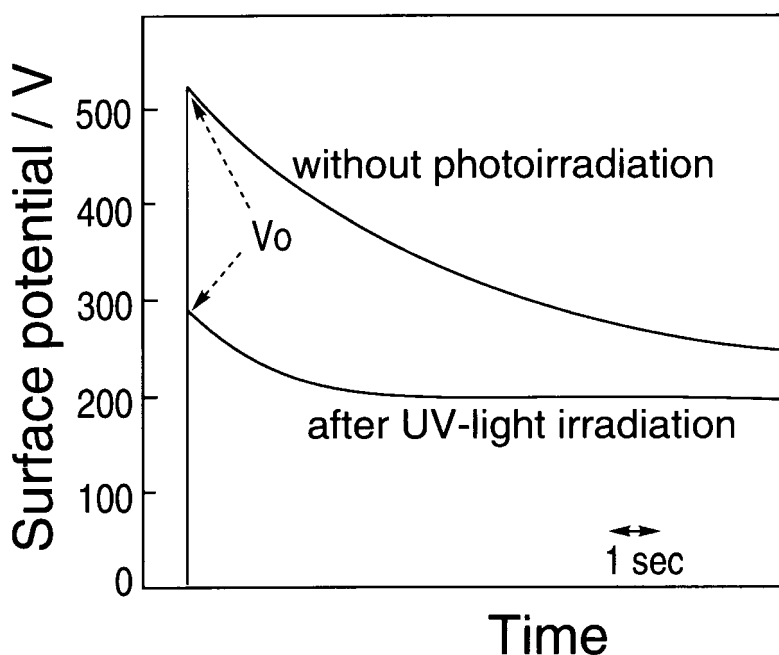


Figure 3. Surface potential induced by corona charging in a layered ion-conducting film containing 1.

unirradiated regions even after 2 days. That is to say, the latent image can last for a while, being memorized after turning off the light. This indicates a possibility for one-time exposure and multi-time printing by the electrostatic imaging systems using the photoresponsive ion-conducting composite films. Of course, the latent image can be erased immediately by visible-light irradiation. Also, the write-in and erasing of the electrostatic image are quite reversible as demonstrated in Figure 5.

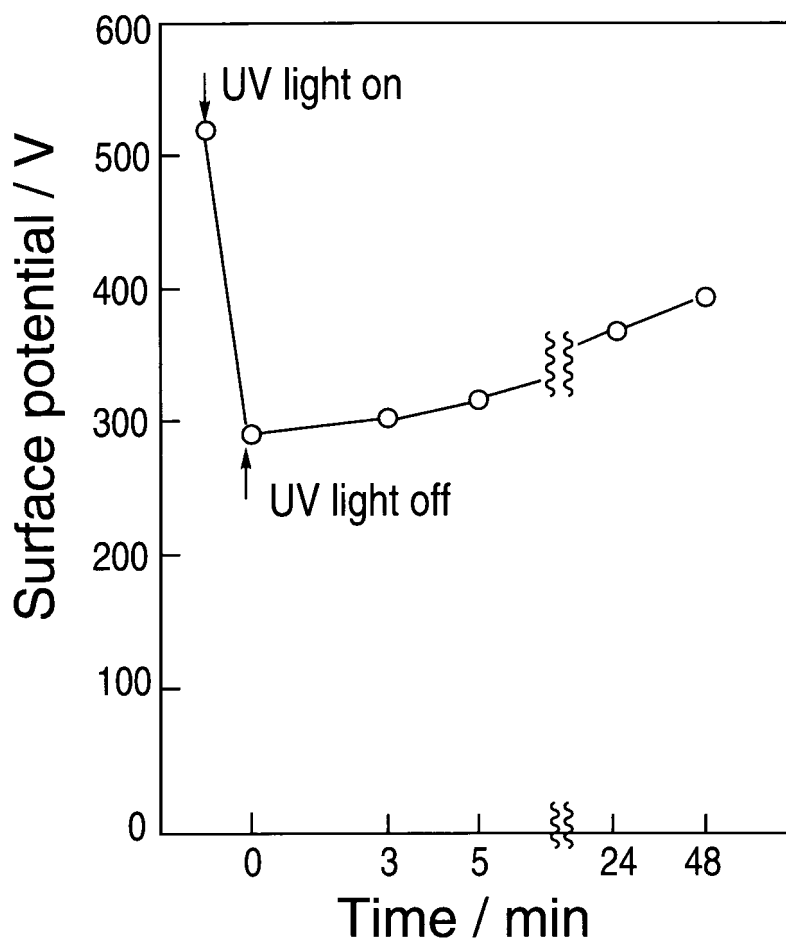


Figure 4. Time-course change of surface potential in a layered ion-conducting film containing 1.

3.2. PHOTOREFRACTIVE SYSTEM

The photorefractive effect can be applied to various optical information processing, such as real-time image processing, optical switching and holographic memory. A main issue in this effect involves the design of photorefractive materials. The photorefractive effect was first observed in inorganic crystals [15] and organic photorefractive materials are also being studied [16, 17]. In order to manifest photorefractivity, the organic material must possess both photoconductivity and the electro-optic effect. Therefore, photorefractive materials should contain a photoinduced carrier (electric charge) generator, a carrier-transporting medium, a carrier-trapping site, and a nonlinear-optical moiety whose refractive index is changed by a space-charge field. In most cases, electronic carriers, i.e., electron and hole, are responsible for the space-charge field formation. In photorefractive

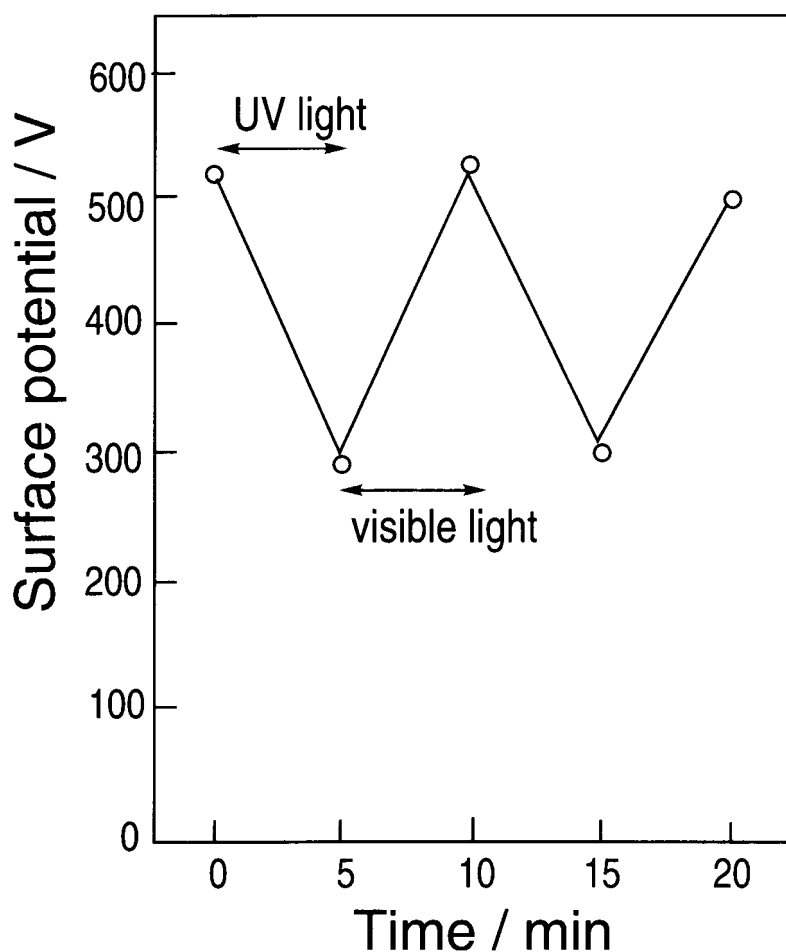
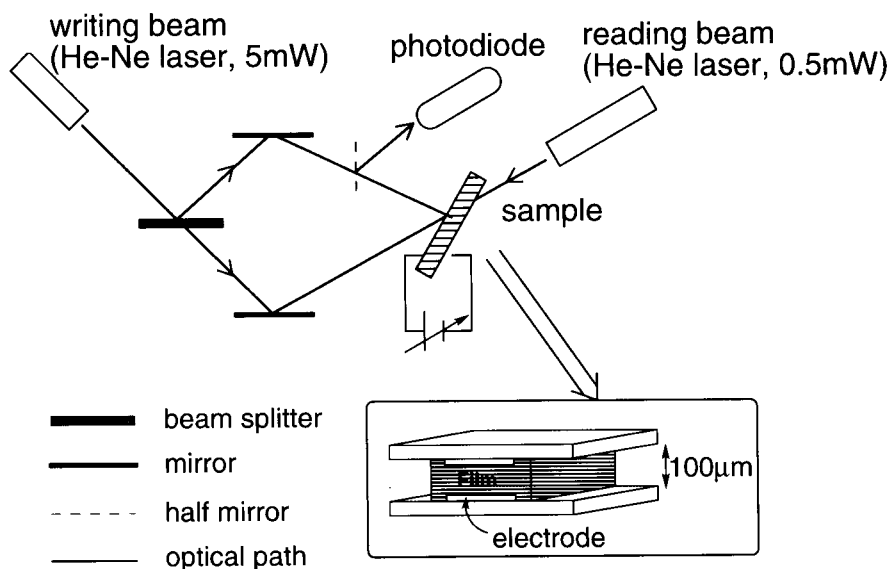


Figure 5. Surface potential changes in a layered composite film containing **1** on alternating photoirradiation.

organic materials, space-charge formation, which brings about ordered orientation of the nonlinear-optical moiety, is performed by photoinduced redistribution (charge generation followed by electric-field-induced drift) of electronic carriers, i.e., electron or hole. Ionic carriers, i.e., cation and anion, can also produce space-charge fields by ionic conduction. Ionic conduction is also expected to provide photorefractive systems with memory effect, since ions migrate slowly in the composite films due to their masses. As mentioned above, the photochemical control of the metal-ion-complexing ability by **4** can afford photoinduced ionic-conductivity changes, when the photochromic crown compound is contained in ion-conducting composite polymers [18]. The ionic-conductivity switching system of crowned spirobenzopyran **4** in turn leads to the photorefractive effect by redistribution of ionic species.



Scheme 3.

Composite films consisting of 4'-(*N,N*-dimethylamino)-benzylidene-2-methyl-4-nitroaniline (DBMNA) as the nonlinear optical compound, crowned spirobenzopyran **4** as the photocontrol agent of ionic conductivity, a lithium salt as the ion-conducting species, and poly(methyl methacrylate) (PMMA) as the binder polymer, were hot-pressed between two indium-tin-oxide-coated glasses with a polyamide-made spacer. Diffraction efficiencies of the composite films were measured by a four-wave mixing system with writing (5 mW) and reading (0.5 mW) beams of He-Ne lasers (Scheme 3). The typical response of the diffraction signal is shown in Figure 6. When an electric field is applied while irradiating the writing and reading beams, the signal is increased. Turning off the electric voltage immediately restores almost to the initial signal. The diffraction efficiency was increased with a rise in the applied electric field (Figure 7). Little diffraction was observed without the applied electric field or without any lithium salt or/and the nonlinear-optical compound in the composite film. Also, when a 1 : 1 mixture of a spirobenzopyran without a crown ether moiety (SP) and monoaza-12-crown-4 (A12C4), which cannot control the ionic conduction photochemically, is employed instead of crowned spirobenzopyran **4**, the light diffraction is much less significant than that for the crowned spirobenzopyran system (Figure 7). Definitely, some refractive-index change derived from the photoisomerization between spiroopyran and merocyanine forms of the spirobenzopyran derivatives is not the primary reason for such significant light diffraction. The photoinduced diffraction is therefore ascribable to the photorefractive effect based on space-charge formation caused by the photoinduced metal-ion-complexing ability change of crowned spirobenzopyran **4**.

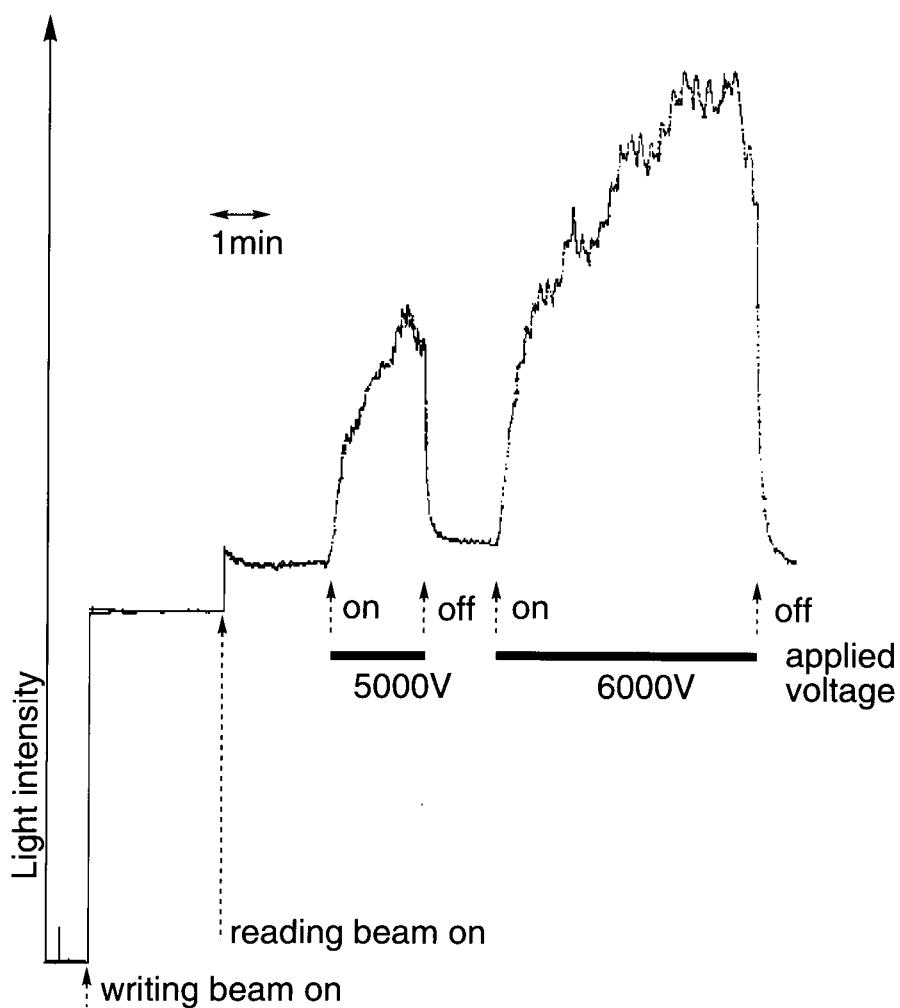


Figure 6. Response profile for four-wave-mixing measurement in a composite film of PMMA/DBMNA/4/LiClO₄.

The composite films as cast were dark red with an absorption at 633 nm. This means that the crowned spirobenzopyran is considerably isomerized to its corresponding merocyanine form even under dark conditions and that the crowned merocyanine can bind Li⁺ strongly in composite films. Visible-light (>500 nm) irradiation on the composite film decreases the absorbance at 633 nm remarkably (Figure 8), causing the isomerization of the crowned merocyanine back to its spiropyran form. This allows Li⁺ release from the crown ether moiety. In a control composite film containing an equimolar mixture of SP and A12C4 instead of **4**, there is little photoinduced change of absorbance at 633 nm. It is thus considered that the photoinduced change in the metal-ion-complexing abil-

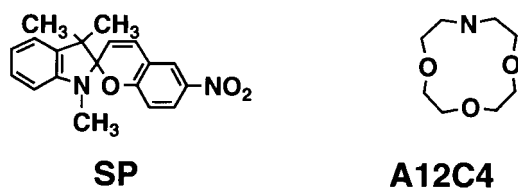
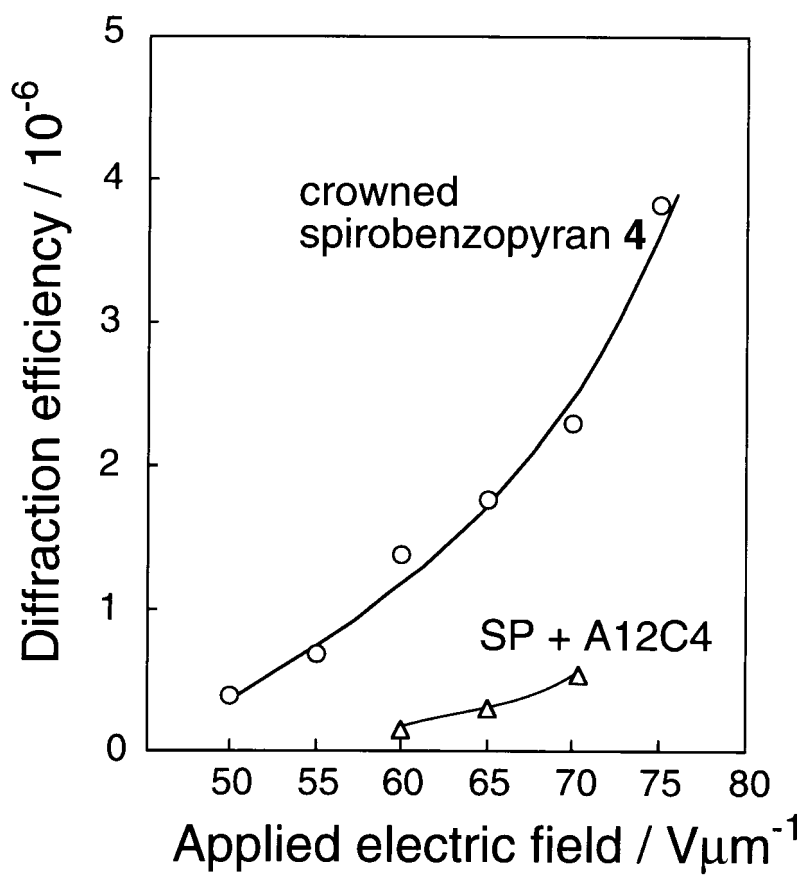


Figure 7. Dependence of diffraction efficiency on applied voltage in four-wave mixing measurement for a photorefractive composite film of **4** and comparison with that containing a mixture of SP and A12C4.

ity of **4** and thereby in the cation mobility leads to the space-charge formation for the photorefractive effect. Since both Li^+ and its counteranion can migrate in composite films containing the ion-conducting carriers (bi-ionic conducting system), the photoisomerization-induced ionic-conductivity change based on the mechanism of Scheme 1 and thereby the light diffraction change are not very

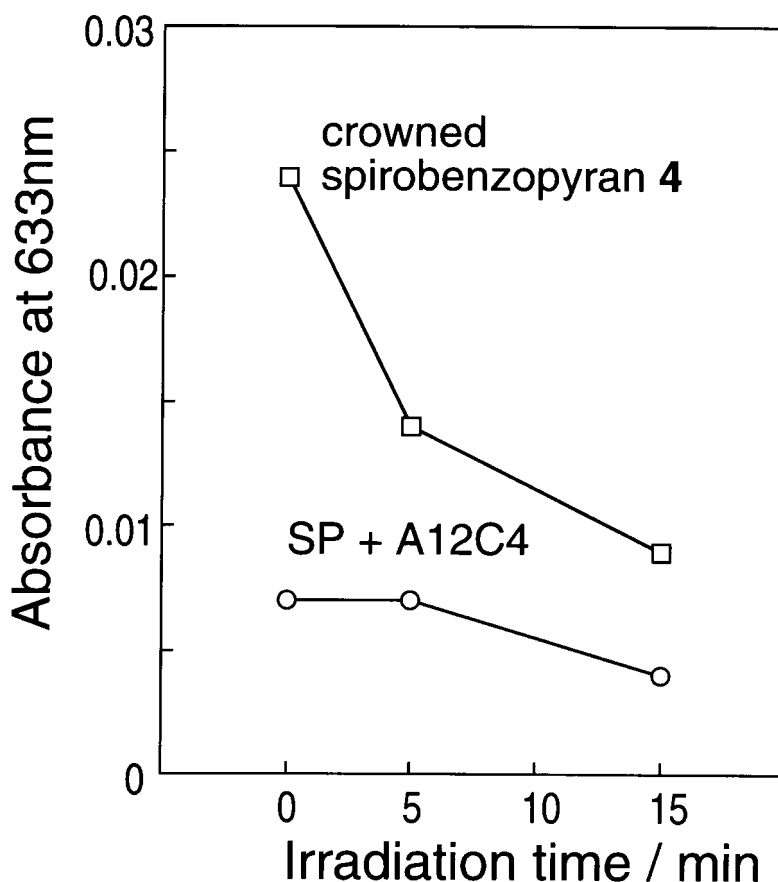


Figure 8. Visible-light-induced isomerization of spirobenzopyran derivatives from their merocyanine to spiropyran forms in photorefractive composite films.

drastic. Suppressed migration of the lithium salt counteranion should increase the contribution of cation-mobility changes to the ionic-conductivity changes. This in turn can enhance the photoinduced space-charge formation and therefore the light diffraction. The use of large counteranions, which have relatively low mobility, increases the diffraction efficiency, as also demonstrated in Figure 9. Specifically, dramatic diffraction enhancement can be attained in the single-ionic conducting systems containing polymer anions as the counteranion, where only the cation participates in the ionic conduction. For instance, this is the case with the ion-conducting system of PMMA-Li which can be prepared by partial hydrolysis of PMMA with lithium methoxide.

A two-beam coupling experiment proves the photorefractivity in the present system is based on photoinduced ionic-conductivity switching by the crowned spirobenzopyran (Figure 10). The composite films of crowned spirobenzopyran **4** were irradiated by two writing beams of equal light intensity (5-mW He-Ne laser)

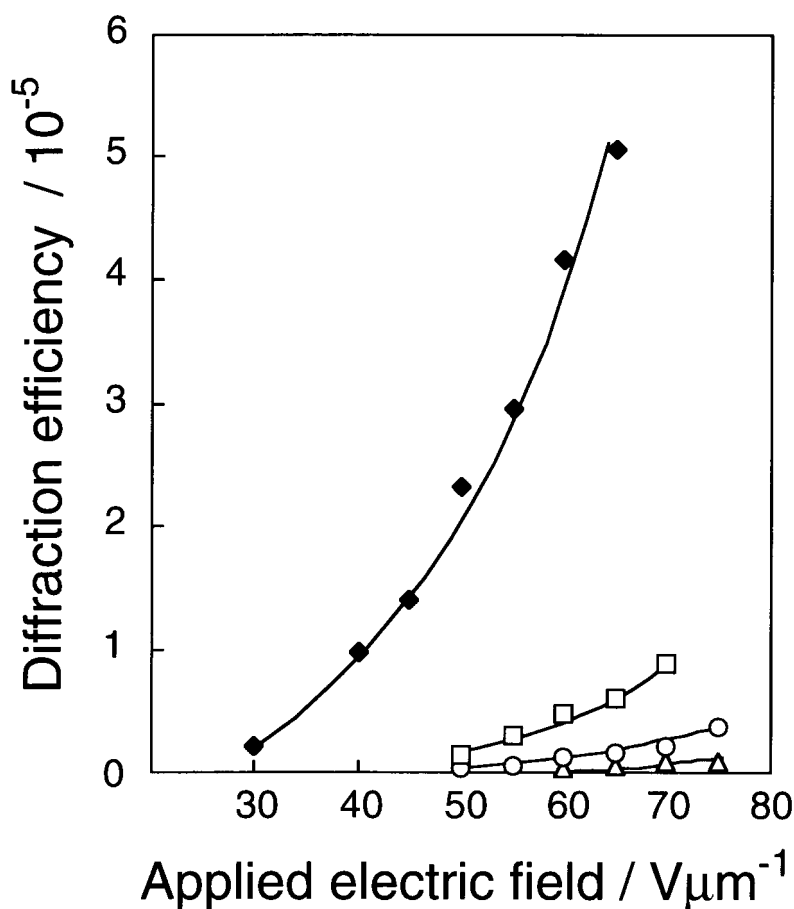


Figure 9. Dependence of diffraction efficiency on the kind of lithium salts in photorefractive composite films. Δ , LiCl; \circ , LiClO₄; \square , CH₃(CH₂)₁₆CO₂Li; \blacklozenge , PMMA-Li⁺.

with an electric field applied. On applying the electric field, one of the writing beam (probe light) was enhanced in intensity, while the other writing beam (pump light) was weakened. This is self diffraction, which is decisive evidence for the photorefractivity.

4. Conclusions

The ion-conducting composite films containing azobenzene derivative **1** is thus useful for electrostatic imaging based on ionic conduction, where some memory effect can be expected. Such electrostatic imaging may be feasible with similar ion-conducting systems containing other crowned azobenzenes as well as crowned spirobenzopyrans. Also, the photoresponsive ion-conducting systems using crowned spirobenzopyran **4** can realize a photorefractive system based on

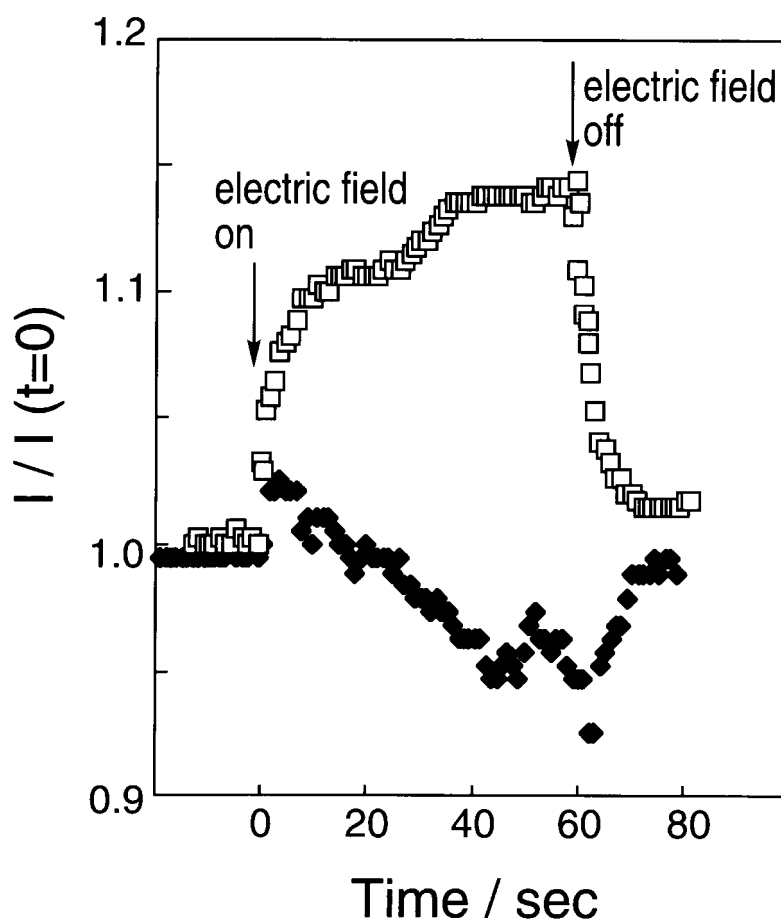


Figure 10. Two-beam coupling measurement for photorefractive composite film of PMMA-Li⁺/DBMNA/4. Electric field: $75 \text{ V } \mu\text{m}^{-1}$. \square , probe light; \blacksquare , pump light.

ionic conduction. The design of photoresponsive ionic conductors containing other photochromic crown ethers may afford high-diffraction-efficiency photorefractive systems. Another possibility for the applications of the photoresponsive ion-conducting systems of photochromic crown ethers may be in photowritable electrochromic display.

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