

Cation Complexation, Photochromism, and Photoresponsive Ion-Conducting Behavior of Crowned Malachite Green Leuconitrile

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Cation complexation of a 2,2-bis(*N,N*-dimethylamino)phenyl-2-phenylmethanenitrile (Malachite Green leuconitrile) derivative carrying a 15-crown-5 moiety affects its photochromic ionization remarkably. The crowned Malachite Green leuconitrile can afford photochemical cation-complexing control of its crown moiety; photoionization of the crowned Malachite Green to its triphenyl or quinoid cation suppresses cation complexation of the crown moiety mainly due to the intramolecular electrostatic repulsion. Applications of the crowned Malachite Green to ion-conducting materials indicate that the photochemical control of cation-complexing ability is reflected in the ionic-conductivity switching of composite films containing the photochromic crown compound and a sodium salt.

Introduction

Photochromic crown compounds, in which crown ether derivatives are provided with photochemical functions, are interesting key materials that may carry out molecular control of cation-complexing properties of their crown moieties photochemically. A way for molecular control of cation-complexing properties by photochromic crown ethers is to alter the shape of their crown moieties by photochemical reaction of their photochromic moieties. For instance, intramolecular photodimerization of anthracenophane-type crown ethers can change the cavity size of their crown moieties and thereby modify the cation-complexing ability.¹ Also, photochemical cation-complexing control by azobenzene-containing crown ethers has been successfully made, which is based on the difference in ease of complex formation between the *cis* and *trans* isomers.² Furthermore, photoisomerization of thioindigo crown ethers can change their cation-complexing ability by twisting their crown rings.³

Another way for modification of cation-complexing properties by photochromic crown ethers is to employ intramolecular additional interaction of their crown-complexed metal cations, especially with anionic sites, induced by photoisomerization of their photochromic moieties. In a crown-ether styryl dye carrying a sulfonate anion, photoisomerization of its styrene moiety from *trans* to *cis* forms allows intramolecular interaction of its sulfonate anion and crown-complexed metal ion, thus enhancing the cation-complexing ability.⁴ We have already designed two types of photochromic crown compounds, i.e., crown ethers bearing a spirobenzopyran

or spironaphthoxazine moiety for molecular control of cation complexation by their crown moieties. In the crowned spirobenzopyrans, UV-light-induced isomerization of the spirobenzopyran moiety to its merocyanine form causes powerful intramolecular interaction between the phenolate anion and metal ion complexed by the crown moiety, in turn promoting the cation-complexing ability. The backward isomerization to the initial spirobenzopyran form by visible-light irradiation or heating alleviates the cation complexation. This reversible photochromism of the crowned spirobenzopyrans has thus realized photochemical control of cation complexation and the photochromic crown compounds have proved to be useful key materials for photoinduced ionic-conductivity switching.⁵ The crowned spironaphthoxazine can undergo similar photochemical cation-complexation control and was found to be a more photoresistant material for the ionic-conductivity switching.⁵ A crowned merocyanine can also perform photoejection of metal ions.⁶

Well-known photochromic compounds undergoing intermolecular photoionization are Malachite Green dyes, which dissociate to a triphenyl cation and an anion on UV-light irradiation.⁷ This photochromism of Malachite Green dyes has been receiving attention as an attractive tool for photocontrol of ionic environments.⁸ By providing Malachite Green dyes with a crown moiety, a unique type of photochemical control system of cation complexation can be designed. We recently communicated that in a Malachite Green leuconitrile

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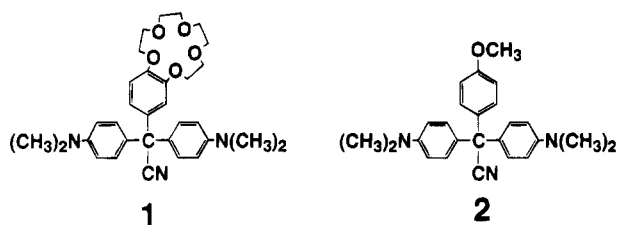
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carrying a crown moiety, crowned Malachite Green 1,



the cation complexation of its crown moiety can be controlled photochemically, based on electrostatic repulsion between the triphenyl cation and a metal ion complexed by its crown moiety.⁹ Here we wish to report the details for the photochemical cation-complexation control of the crowned Malachite Green 1, a comparison with an uncrowned derivative 2, and its application to photoresponsive ion-conducting materials.

Experimental Section

Synthesis of Malachite Green Leuconitrile Derivatives. 4'-[Bis((*N,N*-dimethylamino)phenyl)cyanomethyl]benzo-(15-crown-5), or crowned Malachite Green 1, was synthesized by the reaction of 4'-lithiated benzo-15-crown-5 with 4,4'-bis((*N,N*-dimethylamino))benzophenone (Michler's ketone). 4'-Bromobenzo-15-crown-5 was prepared according to a procedure described in the literature.¹⁰ An anhydrous tetrahydrofuran (THF) solution (15 cm³) containing 4'-bromobenzo-15-crown-5 (7.3 mmol) was placed into a reaction flask and was cooled to -78 °C in a dry ice/acetone bath under an argon atmosphere. A hexane solution of butyl lithium (7.8 mmol) was added to the flask through a septum while stirring. After 15 min, a THF solution (50 cm³) of Michler's ketone (5.1 mmol) was added dropwise. The reaction mixture was warmed gradually to room temperature in half an hour and then refluxed for 3 h. After the reaction, water (30 cm³) was added to the mixture, which was then extracted by chloroform (3 × 100 cm³). Vacuum evaporation of the chloroform extract afforded a crude product of 4'-[bis((*N,N*-dimethylamino)phenyl)hydroxymethyl]benzo-(15-crown-5) (crowned Malachite Green leucohydroxide), which was subjected to the following cyanization reaction without further purification. Crude crowned Malachite Green leucohydroxide (about 2.7 mmol) was dissolved in dimethyl sulfoxide (40 cm³), to which concentrated HCl (9 mmol) was added. To the mixture was added sodium cyanide (110 mmol) while heating at about 80 °C in a hood. The reaction mixture was then stirred for 10 min and was then filtered. Addition of a large amount of water afforded a sticky precipitate, which was then extracted by chloroform/water. The solvent removal from the chloroform extract yielded a crude product of crowned Malachite Green leuconitrile, which was then purified by silica gel chromatography by gradient elution (from 30/70 to 10/90 of chloroform/hexane) to yield a colorless crystal of pure 1 (total yield 35%): mp 146–147 °C; ¹H NMR (270 MHz, CDCl₃) δ 2.95(s, 12H), 3.8–4.1 (m, 16H), 6.6–7.1 (m, 11H); MS, *m/e* 278 (60%), 545 (M⁺, 100%). Anal. Calcd for C₃₂H₃₉N₃O₅: C, 70.43 H, 7.20; N, 7.70. Found: C, 70.29; H, 7.27; N, 7.59. In a similar way, uncrowned model compound 2 was obtained as a colorless crystal (total yield 30%): mp 245–246 °C; ¹H NMR (100 MHz, CDCl₃) δ 2.95 (s, 12H), 3.85 (s, 3H), 6.7–7.4 (m, 12H); MS, *m/e* 278 (96%), 385 (M⁺, 100%). Anal. Calcd for

C₂₅H₂₇N₃O: C, 77.89 H, 7.06; N, 10.90. Found: C, 77.93; H, 7.13; N, 10.91.

Other Materials. Unless otherwise specified, all the reagents were the best grade. The solvents for the spectroscopy were spectrograde from Dojindo. Water was deionized. Polyester elastomer, poly(butylene terephthalate) (Pelprene 40-H, Toyobo) containing an oligooxybutylene moiety with an average molecular weight of 1000 as a soft segment (*T*_g = -80 °C) was purified by repeated reprecipitation from chloroform in methanol. Poly(perfluorosulfonic acid) (PPFS, Nafion) was purchased as a 5 wt % alcohol solution from Aldrich and its Na⁺ salt (PPFS-Na⁺) was obtained by neutralizing the polymer acid with a sodium methoxide methanol solution. Oligooxyethylene diacetate (OOEAc) was prepared by treating oligooxyethylene (average molecular weight of about 400) with excess acetic anhydride (70 °C, 1 day) and then purified by alumina chromatography. THF and *N,N*-dimethylformamide (DMF) for the preparation of composite films were distilled over LiAlH₄ and CaH₂, respectively.

Spectrophotometric Measurements. Acetonitrile or methanol solutions containing a Malachite Green derivative (1 × 10⁻⁵ mol dm⁻³) and an appropriate concentration of an alkali metal perchlorate were prepared, and their absorption spectra were then taken. Photoirradiation was made by using UV light (240–400 nm), which was obtained by passing a light from a 500-W Xe lamp through a color filter of Toshiba UV-D33S. For determination of thermal decoloration rates, Malachite Green derivative acetonitrile (or methanol) solutions with and without an alkali metal perchlorate were irradiated by UV light for 10 min. Immediately after the photoirradiation, the absorbance for the corresponding colored quinoid ion form at 605–615 nm was followed with time at 40 °C. The first-order rate constants of thermal decoloration (*k*) were determined from the slope in the plots of log(*A*_{*t*}/*A*₀) vs time (*T*), where *A*_{*t*} and *A*₀ are the absorbance at *T* = *t* and *T* = 0, respectively.

Potentiometric Measurements. A MeOH/H₂O (95/5) solution (20 cm³) containing an equimolar amount of 1 and NaClO₄ (1 × 10⁻⁴ mol dm⁻³) was placed in a measurement cell equipped with a quartz window for UV-light irradiation. Emf measurements were made at 23 °C, using a Na⁺-selective glass electrode (TOKO, type 1100) and a double-junction-type reference electrode whose inner and outer barrels contain a saturated KCl and a 0.1 mol dm⁻³ NH₄NO₃ aqueous solutions, respectively. When the system was heated to enhance the thermal back reaction, the emf reading was made after the system was at constant temperature (23 °C).

Molecular Orbital Calculation. Calculation by the MN-DO-PM3 method¹¹ was performed with the MOPAC program (ver. 6) using an Iris Indigo R4000 computer. The structural output was recorded by using the MOL-GRAPH program (ver. 2.8) by Daikin Industries Ltd.

Composite Film Fabrication. Polyester-based composite films for ionic-conductivity measurements were prepared on indium tin oxide coated (ITO) glasses (2 × 2.5 cm) by casting from chloroform solutions and then dried at 40 °C under a nitrogen stream. In general, 0.2 cm³ of a chloroform solution (0.9 cm³) containing polyester elastomer (50 mg, 60.8 wt %), OOEAc (30 mg, 36.4 wt %), and a Malachite Green derivative (2.2 mg, 2.7 wt %) was used for each casting on an ITO glass, affording a composite film with 30 μm thickness. Composite films based on PPFS-Na⁺ were obtained on ITO glasses by casting 0.2 cm³ of a DMF solution (0.5 cm³) containing PPFS-Na⁺ (25 mg, 43.1 wt %), OOEAc (10 mg, 17.2 wt %), and a Malachite Green derivative (23 mg, 39.7 wt %). The DMF was evaporated in about 2 h under a pressure of 2.7 kPa at 40 °C. The films were dried at 60 °C for 1 day under the reduced pressure to yield films of about 25 μm thickness. On the composite films for ionic-conductivity measurements, gold was evaporated as an electrode (4.7 mm diameter, about 10 nm thickness).

Ionic Conductivity Measurements. Ac impedance of composite films was measured under an argon stream, as

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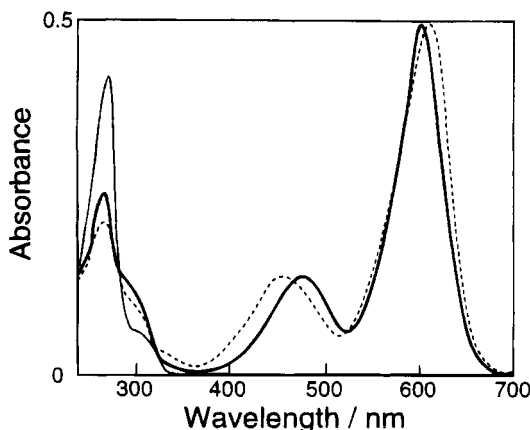


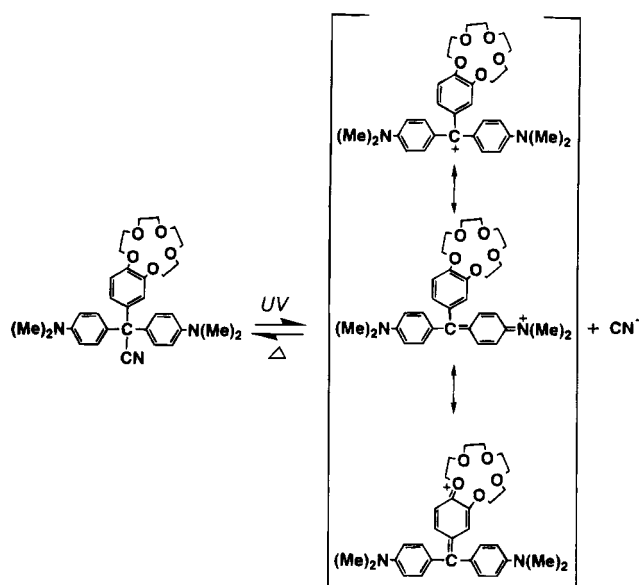
Figure 1. Absorption spectra of methanol solution of crowned Malachite Green 1. Concentration of **1**: 1×10^{-5} mol dm $^{-3}$; solid line, under dark conditions; bold solid line, on UV-light irradiation; dotted line, in the presence of 0.1 mol dm $^{-3}$ NaClO $_4$ on UV-light irradiation.

reported previously.¹² Ionic-conductivity calculation was made by the Cole–Cole plot method. Isothermal transient ionic currents were measured in a manner similar to a procedure in the literature,^{13,14} using a cell setup for the ionic-conductivity measurements. After applying an appropriate dc voltage across a composite film for 3 h, its polarity was rapidly switched and the resulting transient currents were then monitored every second.

Results and Discussion

Photochromism in the Presence of Alkali Metal Ions. Malachite Green leuconitrile bearing a crown ether moiety **1** exhibits a distinct photochromism as shown in Figure 1. A methanol solution of crowned Malachite Green **1** is colorless under dark conditions, but the solution turns green on UV-light irradiation. This indicates that crowned Malachite Green **1** ionizes to a triphenyl or quinoid cation and a cyanide anion, as seen in Scheme 1. Similar spectral changes were observed in methanol and acetonitrile solutions of **1** in the presence of NaClO $_4$ which forms stable complexes with the benzo-15-crown-5 moiety of crowned Malachite Green. The UV-light-induced absorption peaks based on the colored cation of **1**, however, shifted remarkably with increasing Na $^+$ concentrations, as demonstrated in Figures 1 and 2. It should be noted that such spectral shifts cannot be seen in the corresponding model compound containing no crown moiety **2**, even in the presence of high concentrations of Na $^+$. Also, in acetonitrile where crown ethers can complex metal ions powerfully, the spectral shift for crowned Malachite Green **1** by Na $^+$ addition started at lower Na $^+$ concentrations than in methanol. This means that the crown moiety of crowned Malachite Green **1** is able to bind Na $^+$ quite strongly even during its photochromic ionization. Figure 3 depicts a comparison in the photoionization degree between crowned and uncrowned Malachite Greens, **1** and **2**, in the absence and presence of Na $^+$. In the crowned Malachite Green, the presence of Na $^+$ suppressed the photoionization, whereas Na $^+$ enhanced

Scheme 1



photoionization in the uncrowned derivative. This explains qualitatively that the uncrowned derivative is promoted to photoionize by the increase in solvent polarity induced by the Na $^+$ addition. The crowned derivative, on the other hand, can undergo Na $^+$ complexation with its crown moiety, which in turn prevents the formation of its triphenyl or quinoid cation due to the intramolecular electrostatic repulsion.

Thermal decoloration of the Malachite Green derivatives was followed after UV-light-induced ionization (coloration), in order to obtain more information about the effect of metal ion complexation of crowned Malachite Green on its ionization equilibrium. Dependences of Na $^+$ concentration on thermal decoloration rates for crowned Malachite Green in both methanol and acetonitrile are summarized in Figure 4, together with that for the uncrowned derivative for comparison. In the uncrowned derivative, the thermal decoloration rate decreased simply with increasing Na $^+$ concentrations in both methanol and acetonitrile. On the contrary, anomalous dependence of Na $^+$ concentration on the decoloration rate was found in the crowned Malachite Green. Specifically in methanol, a maximal rate for the decoloration appeared in the Na $^+$ concentration of 1×10^{-2} mol dm $^{-3}$. Obviously, this is a result from the counterbalance between the cation-complexation-induced suppression and solvent polarity-induced enhancement in the ionization of crowned Malachite Green. The anomalous photochromism for crowned Malachite Green is very different in the presence of Na $^+$ from that in the presence of Li $^+$, probably due to the difference in the cation-complexing ability of the benzo-15-crown-5 moiety toward Na $^+$ and Li $^+$. Thus the cation complexation of crowned Malachite Green **1** affects its photochromic ionization to a great extent, resulting in the anomalous photochromism.

Photochemical Control of Cation-Complexing Ability. Taking advantage of the cation-complexation-dependent photoionization of crowned Malachite Green **1**, one can expect photochemical control of its cation-complexing abilities, as illustrated in Scheme 2. That is to say, electrically neutral crowned Malachite Green can complex Na $^+$ easily. When UV light forces the

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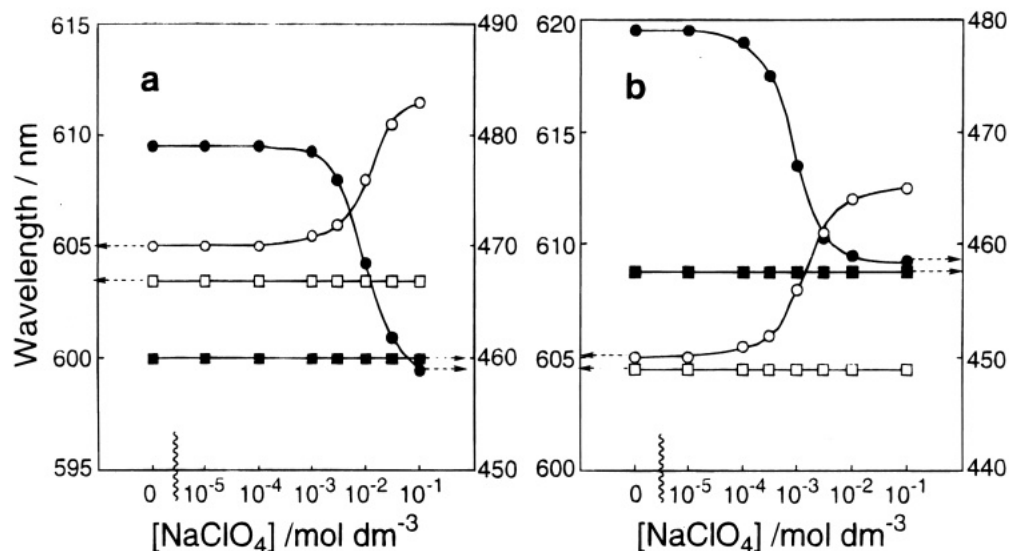


Figure 2. Dependence of metal salt concentration on λ_{\max} value for absorption spectra of crowned Malachite Green **1** (○, ●) and uncrowned derivative **2** (□, ■) in methanol (a) and acetonitrile (b) after UV-light irradiation. Concentration of **1**: 1×10^{-5} mol dm^{-3} .

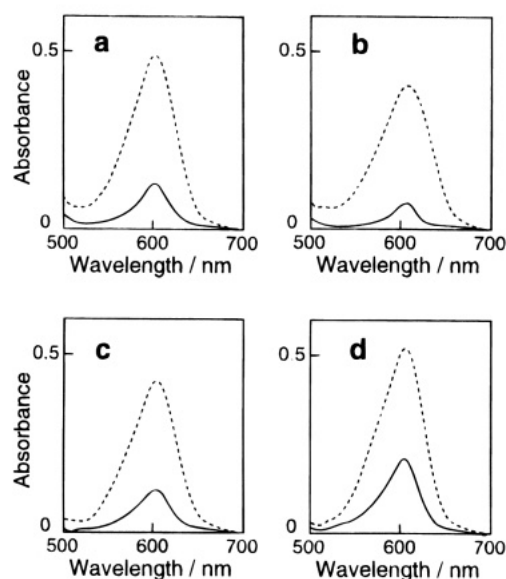
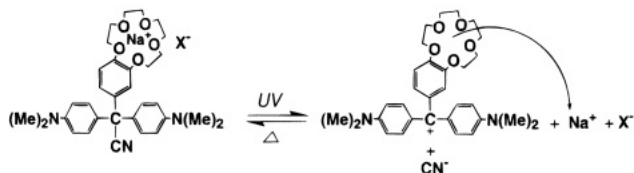


Figure 3. Comparison of absorption spectra of crowned Malachite Green **1** and uncrowned derivative **2** in methanol in the absence and presence of NaClO_4 . a: 1×10^{-5} mol dm^{-3} **1** without Na^+ . b: **1** with 1×10^{-2} mol dm^{-3} Na^+ . c: 1×10^{-5} mol dm^{-3} **2** without Na^+ . d: **2** with 1×10^{-2} mol dm^{-3} Na^+ . Dotted line: on UV-light irradiation; solid line: on heating at 50°C after the photoirradiation.

Scheme 2



cation-complexed **1** to ionize to its triphenyl or quinoid cation and a cyanide anion, the Na^+ in the crown moiety is presumably repelled by the intramolecular electrostatic repulsion between the Na^+ and the resulting organic cation. An attempt was made to detect the photoinduced changes of cation-complexing ability of **1** in aqueous methanol potentiometrically by using a Na^+ -selective glass electrode. Definitely, UV-light irradiation raised the emf of solutions containing an equimolar

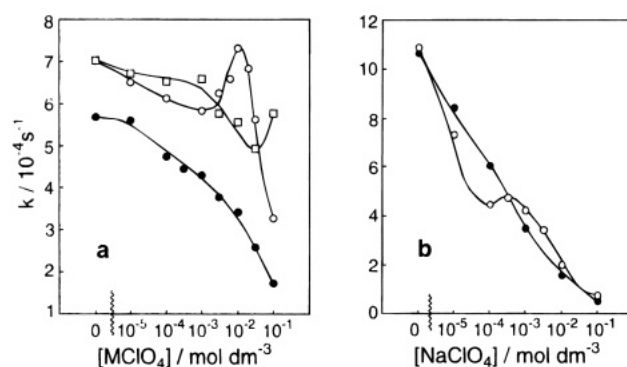


Figure 4. Dependence of metal salt concentration on first-order rate constant of thermal decoloration for methanol (a) and acetonitrile (b) solutions of crowned Malachite Green **1** and uncrowned derivative **2**. (○) **1** + Na^+ ; (●) **2** + Na^+ ; (□): **1** + Li^+ . Concentration of **1**: 1×10^{-5} mol dm^{-3} .

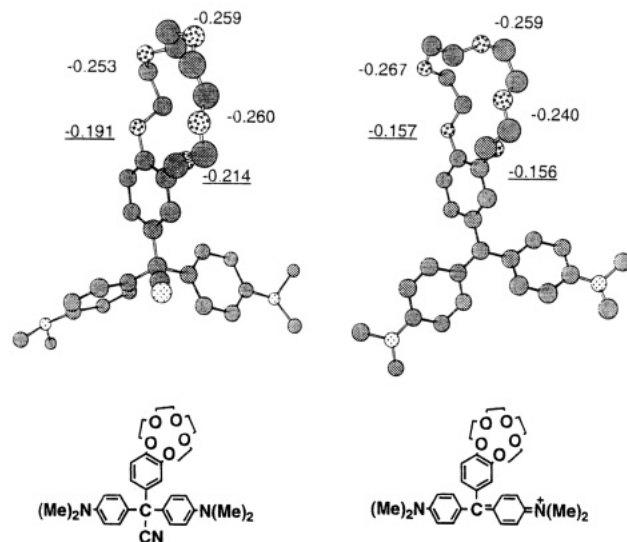


Figure 5. Molecular models and negative point charges of crown ring oxygen atoms for crowned Malachite Green **1** and its quinoid cation.

amount of **1** and NaClO_4 (1×10^{-4} mol cm^{-3}) by more than 1 mV. The following dark reaction, which was enhanced by heating, then restored the emf almost to

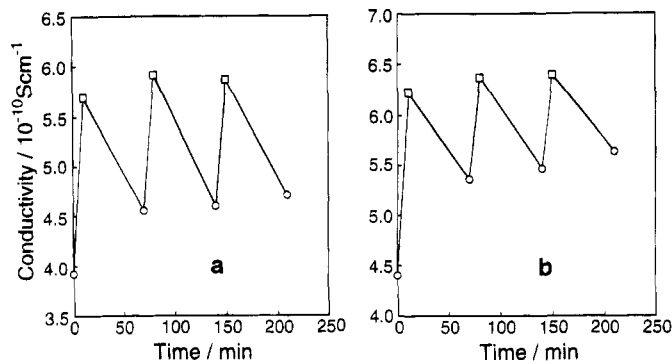


Figure 6. Photoinduced ionic-conductivity changes for composite films containing crowned Malachite Green 1 (a) and uncrowned derivative 2 (b). UV-light irradiation started at each point of (○) and then finished at the point of (□), and vice versa for heating at 50 °C.

the initial value. This potentiometry clearly indicates that releasing and binding of Na^+ by the crown moiety of crowned Malachite Green occur on the photoionization and recombination of its Malachite Green moiety, respectively.

Molecular orbital calculation of crowned Malachite Green 1 and its quinoid cation was made by the MNDO-PM3 method¹¹ to compare the electrical charges of their crown ether oxygen atoms (Figure 5). It is worth noting that the crown ether oxygen atoms for the electrically neutral derivative 1 generally have the higher negative point charges than those for the corresponding quinoid cation do. Specifically in the aromatic oxygen atoms, the point charge difference is very remarkable. The higher negative charges on the crown ether oxygen atoms for the electrically neutral crowned Malachite Green than for its quinoid cation imply that the former possesses the higher metal ion-complexing ability than does the latter. The photochemical control of cation-complexing ability in crowned Malachite Green 1 is therefore derived not only from the intramolecular electrostatic repulsion but also from the differences in the electric charges of crown ether oxygen atoms between the electrically neutral species and its cationic species.

Photoinduced Switching of Ionic Conductivity.

A great application of the photochemical control system of metal ion complexation by crowned Malachite Green is in photoresponsive ion-conducting materials. Photoinduced switching of ionic conductivity was attempted in composite films containing crowned Malachite Green 1 and NaClO_4 . The photoionization of the Malachite Green leuconitrile moiety of 1 causes generation of two ion-conducting carriers, i.e., a cyanide anion and a triphenyl or quinoid cation, which themselves in turn raise the ionic conductivity of the composite films, as also observed in uncrowned Malachite Green derivatives such as 2. In the photochromism of crowned Malachite Green in the presence of a crown-complexable metal ion, Na^+ , as shown in Scheme 2, the photoionization brings about release of Na^+ complexed by the crown moiety of 1. The resulting free Na^+ is also able to participate in ionic conduction. In other words, the photoionization of Na^+ -complexed crowned Malachite Green 1 results in synergistic generation of ion-conducting carriers, unlike that of uncrowned Malachite Green 2. The ion-conducting system of the crowned Malachite Green is therefore expected to exhibit more remarkable photoinduced changes in the ionic conductivity than the uncrowned derivative. A typical photoinduced switch-

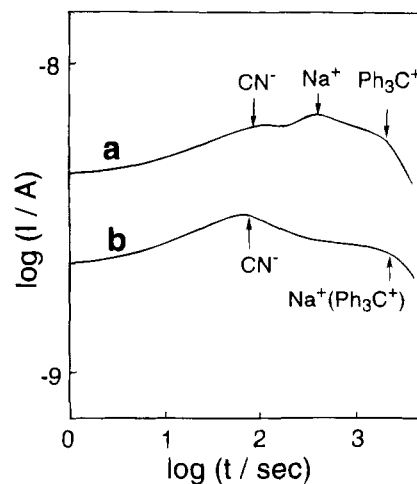


Figure 7. Isothermal transient ionic current curves for composite films containing sodium poly(perfluorosulfonate) and crowned Malachite Green 1 under UV-irradiated (a) and dark (b) conditions, using a pair of Pt electrodes.

ing profile of ionic conductivity for the crowned Malachite Green system is given in Figure 6, together with that for the uncrowned derivative. The magnitude in the photoinduced ionic-conductivity change for the 1 system (1.4-fold) is greater than that for the 2 system (1.2-fold), although the magnitude difference is not so drastic as expected.

To elucidate the mobility of ion-conducting carriers for the ionic conduction in composite films containing 1 and sodium poly(perfluorosulfonate), isothermal transient ionic currents were measured by a polarity-switching procedure (Figure 7). A comparison of the isothermal transient ionic currents shows a significant difference in the Na^+ mobility between dark and UV-irradiated conditions. This means that Na^+ can contribute to the ionic conductivity of the composite film on photoirradiation much more than in the dark. This phenomenon strongly supports the mechanism of Scheme 2 for the photochemical Na^+ -complexing control of crowned Malachite Green 1.

In conclusion, the metal-ion-complexing ability of crowned Malachite Green 1 can be modulated by the photochromism of its Malachite Green moiety, mainly based on the intramolecular electrostatic interaction. The ion-conducting behavior of 1-containing composite films surely reflected the photoinduced cation-complexing control by the photochromic crown compounds.

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