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Metal-Ion Complexation and Photochromism of Triphenylmethane Dye Derivatives Incorporating Monoaza-15-crown-5 Moieties

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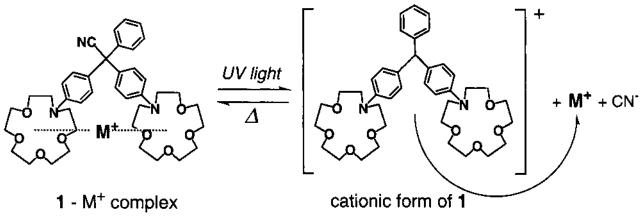
Abstract: Three types of triphenylmethane leuconitrile derivatives incorporating one, two, and three monoaza-15-crown-5 moieties have been designed to attain photocontrol of metal-ion complexation primarily by intramolecular electrostatic repulsion. Photochromism of the crowned triphenylmethane leuconitriles is influenced by the cation complexation of their crown ether moiety to a considerable extent. Molecular orbital calculations allowed some prediction regarding the possibility of photochemical control of metal-ion complexation by the photochromic crown ethers. High efficiency in the photocontrol has been evidenced by electrospray-ionization mass spectrometry, NMR spectroscopy, and thermal reaction kinetics.

Triphenylmethane dyes, such as Malachite Green and Crystal Violet, often show photochromism. For instance, Malachite Green leuconitrile in solution ionizes to a triphenylmethyl cation (or quinoid cation) and cyanide anion on UV-light irradiation, thus turning green.[1] Crystal Violet derivatives seem to undergo similar photoionization with a color change to blue.[2] This type of photochromism, bringing about remarkable environmental changes from electrically neutral to ionic (cationic) states, can be used for photocontrol of physical properties.[3−5]

We have already designed a Malachite Green leuconitrile derivative carrying a benzo-15-crown-5 moiety, to control metal-ion complexation of its crown ether moiety by the photoionization of its photochromic moiety.[6] The benzocrown ether moiety of the electrically neutral Malachite Green derivative can bind a metal ion under dark conditions. Photoinduced ionization of the Malachite Green moiety to its corresponding triphenylmethyl (quinoid) cation decreases the metal-ion complexing ability of the crown ether moiety, because the resulting organic cation is likely to repel the metal ion in the crown ether ring due to the intramolecular electrostatic repulsion. However, the photochemical changes in the metal-ion complexing ability of the crowned Malachite Green was not very remarkable, since the positive charge formed by photoionization of the Malachite Green moiety is a little too far from the crown-ether-complexed metal cation to repel the metal ion efficiently.

Scheme 1



This prompted us to incorporate monoazacrown ether moieties to a Malachite Green skeleton at its dimethylamino groups and synthesize a Malachite Green leuconitrile possessing a bis-(monoaza-15-crown-5) structure **1**. In general, the photoionization of Malachite Green leuconitriles forms a positive-charge delocalized triphenylmethyl cation, which is the origin of the green color (Scheme 1). In the cationic form of **1**, some positive charge is located at the nitrogen atom of its dimethylamino groups. Since the nitrogen atoms are included in the monoazacrown ether rings of **1**, efficient electrostatic repulsion can be expected on photoionization of its Malachite Green moiety owing to the proximity of a crown-ether complexed metal ion to the resulting positive charge. We recently communicated highly efficient, all-or-none type switching in the photocontrol of metal-ion complexation of **1**.[7] We have furthermore designed triphenymethane dye derivatives **2** and **3**, in which one and three monoaza-15-crown-5 rings are incorporated into a triphenylmethane skeleton, respectively. Here we describe in detail the syntheses of crowned triphenylmethane derivatives **1**−**3** and their behavior in the metal-ion complexation, photochromism, and complexation photocontrol.

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Experimental Section

Synthesis. Bis[4-(1,4,7,10-tetraoxa-13-aza-cyclopentadec-13-yl)-phenyl]phenylmethanenitrile or Biscrowned Malachite Green Leuconitrile 1. *N*-(4-Bromophenyl)-monoaza-15-crown-5 (4.3 mmol), which was prepared by the reaction of *N*-phenyl-monoaza-15-crown-5 and *N*-bromosuccinimide (NBS) in refluxing CCl_4 for 3 h, was dissolved in anhydrous tetrahydrofuran (THF) (8 cm^3) and the solution was kept at −78 °C in a liquid nitrogen bath under an argon atmosphere. A hexane solution of butyllithium (BuLi) (4.9 mmol) was injected gradually into the THF solution with stirring. To the mixture was added dropwise a THF (3 cm^3) solution of methyl benzoate (1.9 mmol). The reaction mixture was allowed to warm slowly to room temperature and then stirred for an additional hour. After the reaction, the THF was evaporated off under vacuum and water (about 25 cm^3) was added to the residue. The aqueous phase was then neutralized by 0.1 mol dm^{-3} hydrochloric acid. Extraction with dichloromethane, followed by vacuum evaporation of the solvent, afforded a dark-green oily product of biscrowned Malachite Green hydroxide, which was used for the subsequent cyanization without further purification. The biscrowned Malachite Green leucohydroxide (2.3 mmol) was dissolved in dimethyl sulfoxide (DMSO) (about 5 cm^3) and heated at 60 °C in a hood. Hydrochloric acid (3.4 mmol) and then KCN (12.6 mmol) were added to the solution and the mixture was stirred for 10 min. For complete dissolution of the KCN, an appropriate amount (up to 20 cm^3) of water was added. The reaction mixture turned light yellow and then a crude product of biscrowned Malachite Green leuconitrile **1** precipitated. Recrystallization of the filtered sticky precipitate from hexane yielded a pale-green solid of **1** (30%): mp 112 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 3.5−3.8 (m, 40H, CH_2O), 6.5−6.58 (d, $J = 9$ Hz, 4H, *o*-H of NPh), 7.01 (d, $J = 9$ Hz, 4H, *m*-H of NPh), 7.2−7.4 (m, 5H, PhC); MS, *m/e* 678 (55%), 703 (M^+, 100%). Anal. Calcd for $C_{40}H_{53}N_3O_8$: C, 68.25; H, 7.59; N, 5.96. Found: C, 68.27; H, 7.74; N, 5.82.

[4-(Dimethylamino)phenyl][4-(1,4,7,10-tetraoxa-13-azacyclopentadec-13-yl)phenyl]phenylmethanenitrile or Monocrowned Malachite Green Leuconitrile 2. A similar reaction of the crowned phenyllithium with 4-(*N*,*N*-dimethylamino)benzophenone (3.7 mmol) afforded monocrowned Malachite Green leucohydroxide, which was reacted with KCN to yield a crude product of the corresponding leuconitrile. Recrystallization from hexane afford a pale-green solid of **2** (20%): mp 125 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 2.98 (s, 6H, NCH_3), 3.5−3.8 (m, 20H, CH_2O), 6.5−6.8 (m, 4H, *o*-H of NPh), 6.9−7.1 (m, 4H, *m*-H of NPh), 7.2−7.4 (m, 5H, PhC); MS, *m/e* 289 (42%), 530 ($(M + 1)^+$, 100%). Anal. Calcd for $C_{32}H_{39}N_3O_4$: C, 72.60; H, 7.37; N, 7.93. Found: C, 72.34; H, 7.53; N,7.70.

Tris[4-(1,4,7,10-tetraoxa-13-aza-cyclopentadec-13-yl)phenyl]-methanenitrile or Triscrowned Crystal Violet Leuconitrile 3. 4-Carboxylphenyl-monoaza-15-crown-5 was obtained by bubbling dry CO_2 gas into the crowned phenyllithium THF solution over 1 h, followed by neutralization by HCl. Dimethyl sulfate (2.8 mmol) and 4-carboxylphenyl-monoaza-15-crown-5 (2.5 mmol) were added to a mixture of dry acetone (90 cm^3) and K_2CO_3 (2.8 mmol). After the reaction mixture was refluxed for 3 h, the acetone was evaporated off under vacuum. The residue was extracted with water and diethyl ether and the solvent evaporation of the organic phase afforded 4-methoxycarbonylphenyl-monoaza-15-crown-5. The reaction of crowned phenyllithium with 4-methoxycarbonylphenyl-monoaza-15-crown-5 (1.9 mmol) afforded triscrowned Crystal Violet leucohydroxide, which was reacted with KCN to yield a crude product of the corresponding leuconitrile. Recrystallization from benzene/hexane afforded a pale-green solid of **3** (30%): mp 279 °C; ^1H NMR (270 MHz, $CDCl_3$) δ 3.5−3.8(m, 60H, CH_2O), 6.57 (d, $J = 9$ Hz, 2H, *o*-H of NPh), 7.03 (d, $J = 9$ Hz, 2H, *m*-H of NPh); MS, *m/e* 626 (25%), 921 ($(M + 1)^+$, 100%). Anal. Calcd for $C_{50}H_{72}N_4O_{12}$: C, 65.20; H, 7.83; N, 6.09. Found: C, 64.73; H, 7.70; N, 5.98.

Other Materials. Alkali metal salts were of analytical grade. The solvents for the measurements were spectro-grade from Dojindo. Water was deionized.

Metal-Ion Extraction. Equal volumes (3 cm^3) of 2.1×10^{-3} mol dm^{-3} crowned triphenylmethane 1,2-dichloroethane solution and an aqueous solution containing a mixture of 0.1 mol dm^{-3} alkali metal hydroxide and 7.5×10^{-5} mol dm^{-3} picric acid were introduced into a stoppered vial and shaken vigorously by a reciprocating shaker under dark conditions for 15 min.[8] After phase separation, the aqueous phase was subjected to absorption-spectral measurements. The percent of extraction was calculated as $100 \times (A_0 - A)/A_0$, where A_0 and A denote absorbances of picrate ion (355 nm) for the aqueous phase before and after the extraction, respectively.

Spectrophotometric Measurements. Acetonitrile 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 under dark conditions. 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. UV-light-induced coloration rates for triphenylmethane derivative acetonitrile solutions with and without an alkali metal perchlorate were determined at room temperature, by using a laboratory-made setup consisting of a 500-W Xe lamp, a 1-cm quartz cell containing a measuring solution, a monochromator with 0.5-mm slit (Shimadzu SPG-100ST), and a silicon photodiode (Hamamatsu Photonics, S2387-33R). The wavelengths for detection were 625, 620, and 590 nm for the systems of **1**, **2**, and **3**, respectively. The first-order rate constant of coloration (k) was calculated, which is defined by the following equation: $\log(A_t - A_\infty)/(A_0 - A_\infty) = kt$, where A_t, A_0, and A_∞ are the absorbance at T(measured time) $= t$, $T = 0$, and $T = \infty$, respectively.

Similarly, thermal reverse reaction rates of **1** were measured at 30, 40,and 50 °C after UV-light irradiation for 5 min. Arrhenius plots of the reverse reaction rates afforded straight lines, from the slopes of which the values of activation energy for the reverse reaction were calculated. The concentrations of **1** and solvent were the same as those for the photoinduced coloration reaction.

Electrospray Ionization Mass Spectrometry (ESI-MS). A sector-type mass spectrometer (JEOL-D300) connected with a laboratory-made ESI interface was used to obtain ESI-MS spectra. A sample solution was sprayed with a flow rate of 0.15 cm^3 h^{-1} at the tip of a needle applied by a voltage 3.5 kV higher than that of a counter electrode. A heated nitrogen gas flowing between the needle and counter electrode was used to enhance desolvation of charged droplets sprayed. The resulting ions were then introduced into the vacuum system through the first and the second skimmers of a mass analyzer. The pressures of differential pumping stages were about 1 and 1×10^{-3} Torr, respectively. A rotary pump and a mechanical booster pump in their region were floating electrically to suppress a discharge. The voltage of the first skimmer was the same as that of the counter electrode and was 50 V higher than that of the second skimmer in the present case. The solutions for mass spectrometry contained an equimolar amount (1×10^{-4} mol dm^{-3}) of a triphenylmethane derivative and a metal salt, but no additive for promoting the ionization. Photoirradiation was made by using UV light (240−400 nm), which was obtained by passing a light from a 500 W Xe lamp equipped with a quartz waveguide through a color filter of Toshiba UV-D33S.

Molecular Orbital Calculation. The calculation by the MNDO-PM3 method[9] was performed with the MOPAC program (version 6) using a Macintosh computer. The structural output was recorded by using the CAChe program by Sony Tektronix.

Results and Discussion

Design of Triphenylmethane Leuconitriles Carrying Crown Ether Moieties. The syntheses of crowned triphenylmethane leuconitriles **1**−**3** are based on the reaction of a benzophenone derivative with a phenyllithium derivative, followed by cyanization with KCN, as outlined in Scheme 2. A phenyllithium derivative carrying a monoaza-15-crown-5 moiety can be obtained by treating its corresponding phenyl bromide derivative with butyllithium. The nucleophilic addition of the crowned phenyl anion to an appropriate benzoate or benzophenone derivative in THF can afford the corresponding crowned

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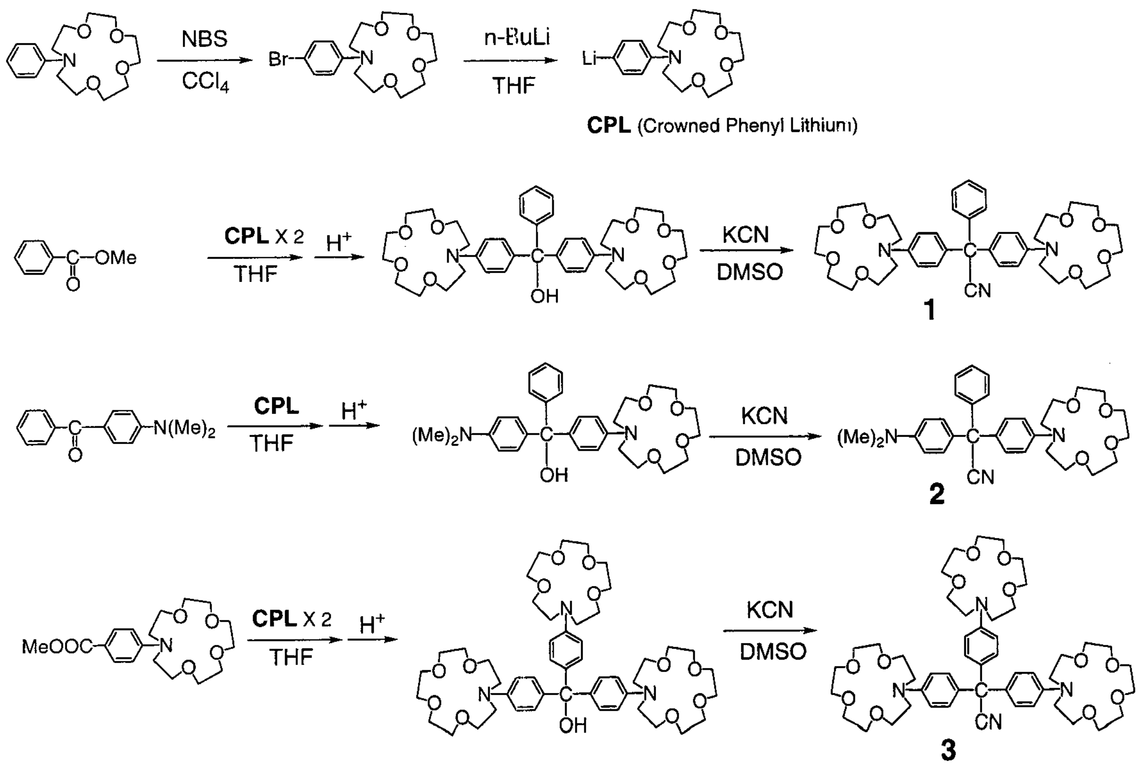
Scheme 2



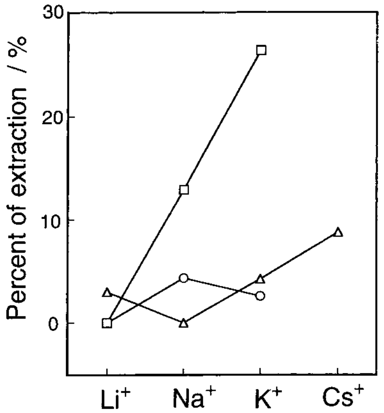


Figure 1. Alkali metal-ion extraction with crowned triphenylmethane leuconitrile derivatives under dark conditions: (□) **1**, (○) **2**, and (△) **3**.

triphenylmethane leucohydroxides, which can be converted into their leuconitrile derivatives **1**− **3** by treatment with KCN. Grignard reactions using a phenylmagnesium bromide possessing the monoazacrown ether moiety instead of the crowned phenyllithium were also attempted, but they failed probably due to the Mg^{2+} complexation of the crown ether moiety.

Complex Formation with Alkali Metal Ions. For rapid screening of metal-ion complexing ability of crowned triphenylmethane leuconitriles, **1**−**3**, under dark conditions, extraction was carried out with a 1,2-dichloroethane solution of a crown ether derivative from an aqueous solution containing an alkali metal picrate. The results for metal-ion extraction were summarized in Figure 1. Biscrowned Malachite Green **1** extracts alkali metal ions in the order $K^+ > Na^+ \gg Li^+$, preferring K^+ to Na^+. Monoaza-15-crown-5 itself can complex Na^+ more strongly than K^+ on the basis of the size-fit concept.[10] This is supported by the fact that the metal-ion extractability for monocrowned Malachite Green **2** is in the order $Na^+ > K^+ > Li^+$. Therefore, the K^+ selectivity over Na^+ for biscrowned Malachite Green **1** suggests that K^+ can be sandwiched intramolecularly by two adjacent crown ether rings, as was the case with previously reported bis(crown ether) derivatives.[11,12] Thus, the intramolecular formation of sandwich-type 2:1 (crown ether ring/metal ion) complexes resulted in high complexing ability and extractability of **1** for K^+. In the triscrowned Crystal Violet leuconitrile **3**, a selectivity for the larger alkali metal ions such as Cs^+ might be expected by cooperative metal-ion complexation with the three crown ether rings. The extractability of **3** with respect to alkali metal ions is in the order $Cs^+ > K^+ > Li^+ > Na^+$, as expected.

Mass spectrometry also gives some information about the selectivities of crowned triphenylmethane leuconitriles **1**−**3** on cation complexation. ESI-MS was taken with acetonitrile solutions containing a crowned triphenylmethane and a mixture of Li^+, Na^+, and K^+ (and Cs^+). In ESI-MS for the system of biscrowned Malachite Green **1** (Figure 2), strong peaks assigned to 1:1 (**1**/metal ion) complexes of K^+ and Na^+ were observed as well as a tiny peak for the corresponding Li^+ complex, suggesting that the metal-ion complexing ability of **1** is in the order $K^+ > Na^+ \gg Li^+$. In the mass spectrum for the **2** system (Figure 3), the peak intensity for 1:1 (**2**/metal ion) complexes is in the order $Na^+ > K^+ \gg Li^+$. In the monocrowned Malachite Green, some formation of sandwich-type 2:1 (**2**/metal ion) complexes was also found. The mass spectrum for the system containing triscrowned Crystal Violet **3** and a mixture of Li^+, Na^+, K^+, and Cs^+ showed that the peak intensity for 1:1 (**3**/metal ion) complexes is in the order $Na^+ \sim K^+ > Cs^+$ (Figure 4). Peaks assigned to 1:2 (**3**/metal ion) complexes with the Na^+ and K^+, especially with the former metal ion, were also seen in the mass spectrum, indicating that triscrowned Crystal Violet

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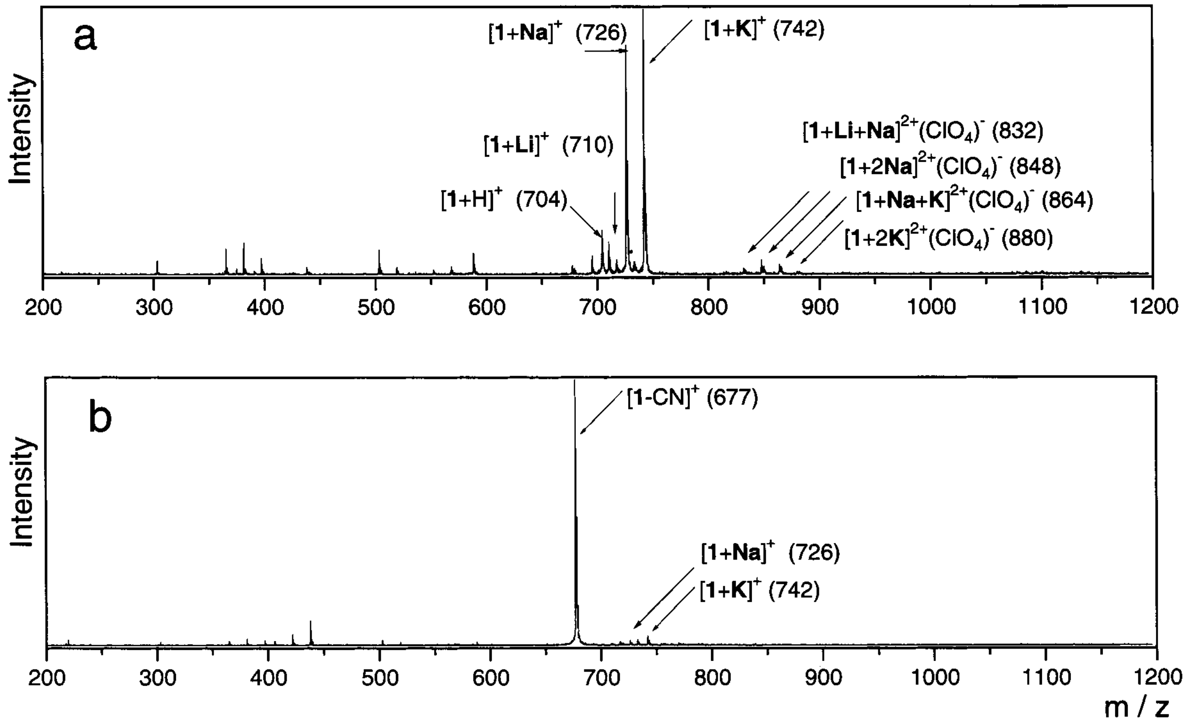

Figure 2. ESI-MS for acetonitrile solution of biscrowned Malachite Green leuconitrile **1** and alkali metal (Li^+, Na^+, and K^+) perchlorates under dark (a) and photoirradiated (b) conditions. [**1**] and [$MClO_4$]: 2×10^{-4} mol dm^{-3} each. UV light: 240−400 nm for 30 s.

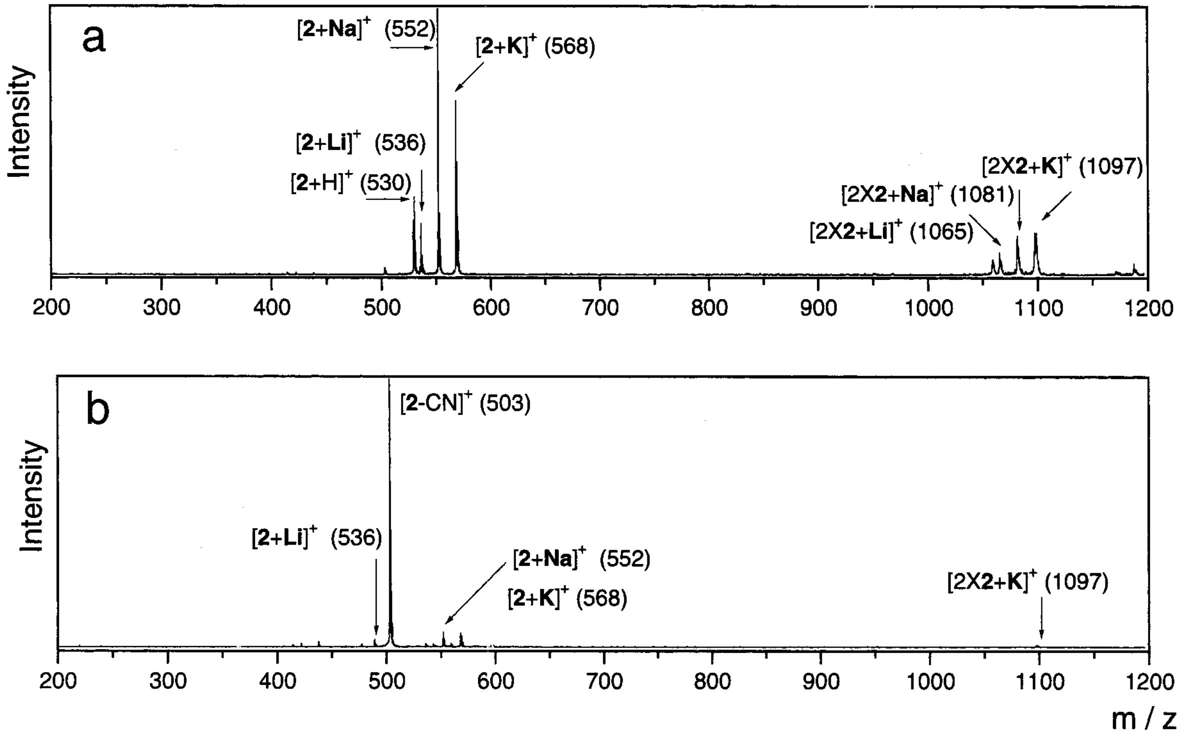

Figure 3. ESI-MS for acetonitrile solution of monocrowned Malachite Green leuconitrile **2** and alkali metal (Li^+, Na^+, and K^+) perchlorates under dark (a) and photoirradiated (b) conditions. [**2**] and [$MClO_4$]: 2×10^{-4} mol dm^{-3} each. UV light: 240−400 nm for 30 s.

3 quite easily form multinuclear metal-ion complexes with the metal ions. However, the metal-ion order in the MS peak intensity for **3** is different from that in the extractability. This is probably because Cs^+ forming 1:1 (**3**/metal ion) complexes is easier to extract to an organic phase than Na^+ and K^+ capable of forming multinuclear metal-ion complexes. Despite the relatively large cation size, Cs^+ can be complexed by the tris(crown ether) derivative, but there is no significant peak for the multinuclear complexes with Cs^+. This implies some cooperative effect of three adjacent crown ether rings on the Cs^+ complexation, although the effect is not so remarkable as that for the biscrowned Malachite Green **1**.

Photoionization in the Presence of Metal Ions. UV-light irradiation on acetonitrile solutions of crowned triphenylmethane leuconitriles **1**−**3** changed their absorption spectra remarkably (Figure 5). Under dark conditions, the solutions of crowned

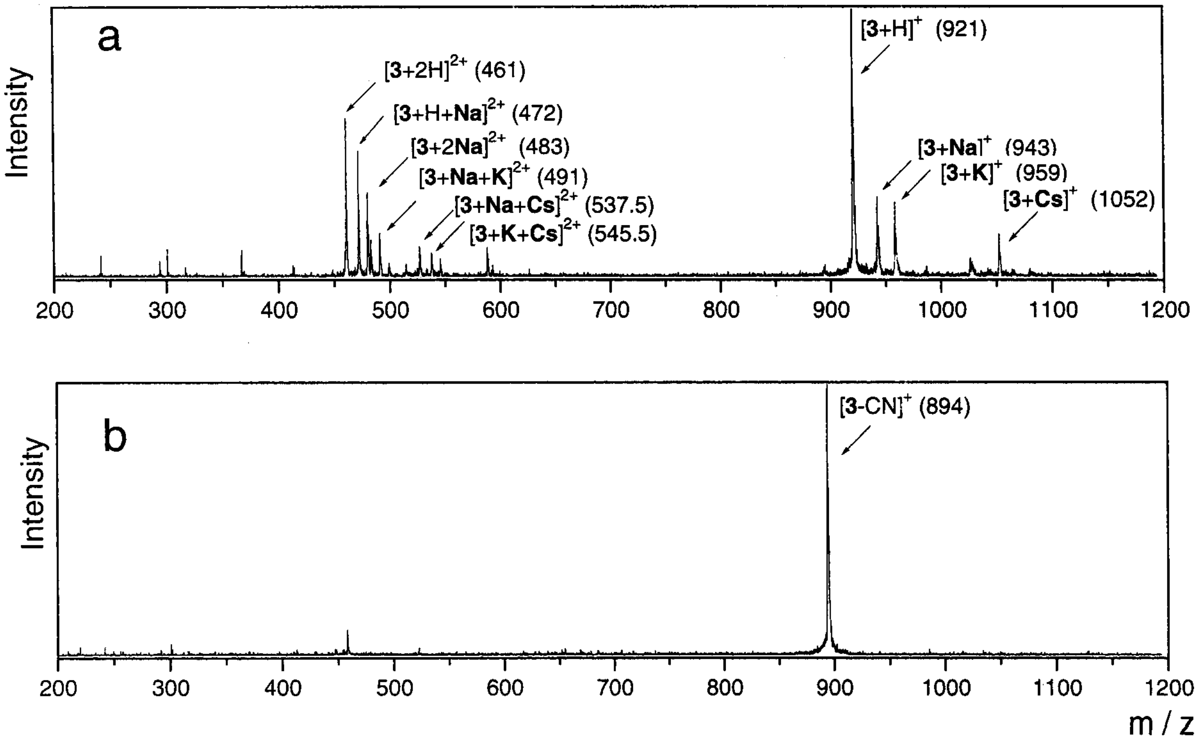

Figure 4. ESI-MS for acetonitrile solution of triscrowned Crystal Violet leuconitrile **3** and alkali metal (Li^+, Na^+, K^+, and Cs^+) perchlorates under dark (a) and photoirradiated (b) conditions. [**3**] and [$MClO_4$]: 2×10^{-4} mol dm^{-3} each. UV light: 240–400 nm for 30 s.

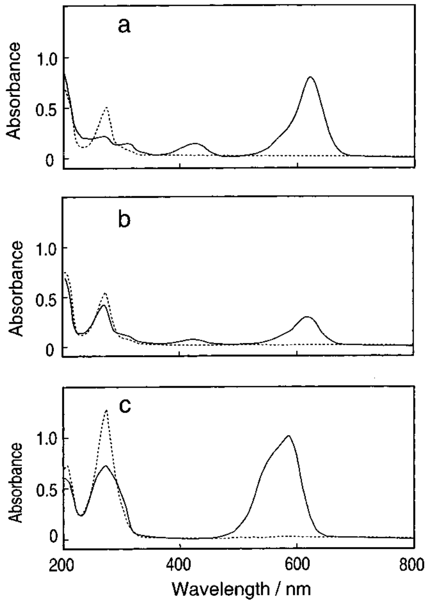

Figure 5. Absorption spectra of acetonitrile solutions of crowned triphenylmethane derivatives with and without photoirradiation: (a) **1** system, (b) **2** system, and (c) **3** system. Broken line: without photoirradiation. Full line: after UV-light irradiation for 5 min. [crowned triphenylmethane]: 1×10^{-5} mol dm^{-3}. UV light: 240–400 nm.

triphenylmethane leuconitriles are essentially colorless and transparent. On photoirradiation, the solutions of Malachite Green derivatives **1** and **2** and Crystal Violet derivative **3** turned green and blue, respectively. The photoinduced coloration of crowned triphenylmethane leuconitriles indicates that the triphenylmethyl cations resulting from the heterolytic C−C bond scission are in highly conjugated forms. For instance, the Malachite Green derivatives produce quinoid-like cations.

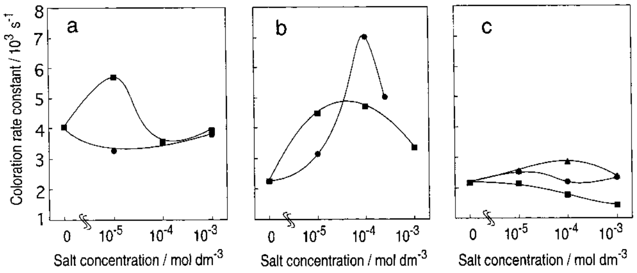

Figure 6. Metal-ion effects on UV-light-induced coloration (ionization) of crowned triphenymethane leuconitriles **1** (a), **2** (b), and **3** (c) in acetonitrile. Salt: $NaClO_4$ (■); $KClO_4$ (●); and $CsClO_4$ (▲). [crowned triphenylmethane]: 1×10^{-5} mol dm^{-3}. UV light: light from a 500-W Xe lamp.

To elucidate the photochromism of crowned triphenylmethanes **1**−**3** in the presence of crown-ether-complexing metal ions, the coloration reaction was followed spectrophotometrically while irradiating with UV light. In general, addition of a metal salt to an acetonitrile solution of a crowned triphenylmethane leuconitrile increases the polarity of the medium. This accelerates the photoinduced ionization of its triphenylmethane leuconitrile moiety to a conjugated triphenylmethyl cation, unless its crown ether moiety binds metal ions. However, if the crown ether moiety is very likely to bind metal ions powerfully, especially in the case of high stability of the crown ether complexes with a given metal ion, the photoisomerization must be suppressed on account of the intramolecular electrostatic repulsion. Actually, the addition of 1×10^{-5} mol dm^{-3} $NaClO_4$ to an acetonitrile solution of biscrowned Malachite Green **1** enhanced the photoinduced coloration, but the increasing Na^+ concentrations again suppressed it (Figure 6a). In the K^+−**1** system, on the other hand, the addition of only 1×10^{-5} mol dm^{-3} K^+ decreased the coloration rate of **1**. This difference between the two metal ions in the addition effect is reflected in the metal-ion complexing ability of **1**, i.e., the higher complexing

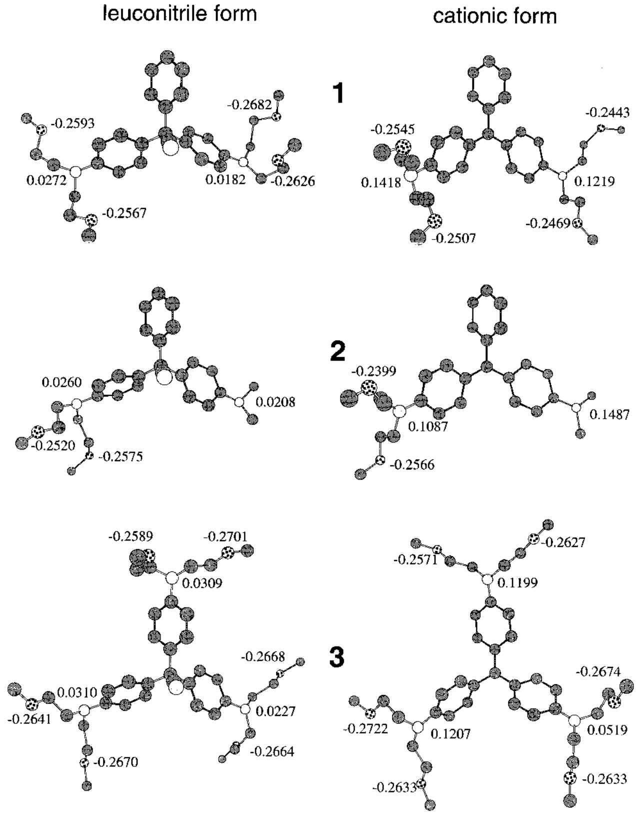

Figure 7. MO calculation for leuconitrile and cationic forms of crowned triphenylmethane derivatives **1**−**3**. The numbers in the vicinity of heteroatoms stand for their point net charges.

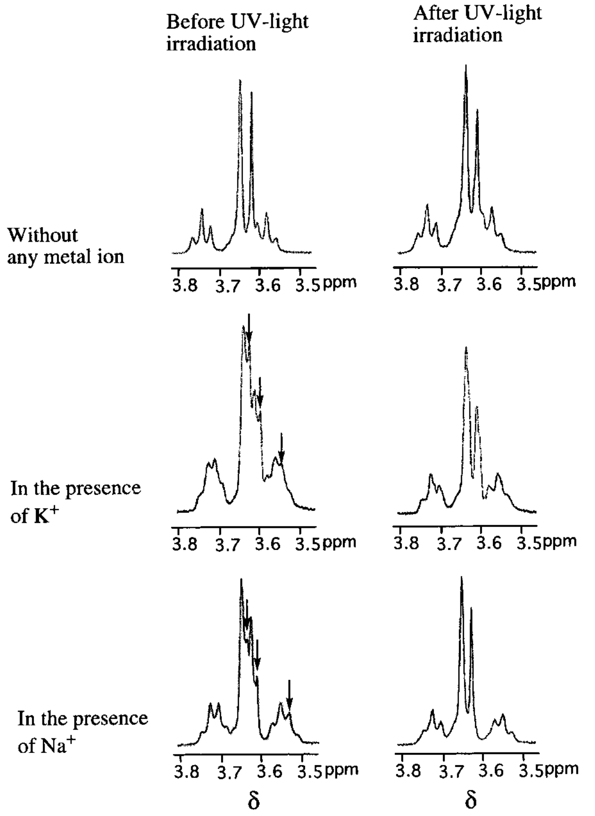

Figure 8. Photoinduced ^{1}H NMR spectral changes of biscrowned Malachite Green **1** in the presence and absence of Na$^+$ or K$^+$. [**1**] and [metal ion]: 1×10^{-4} mol dm^{-3} each in CD$_3$OD, UV-light irradiation for 5 min. The arrows indicate new peaks based on the metal-ion complexation.

ability toward K$^+$ than Na$^+$, which is due to the bis(crown ether) effect of **1**. The Na$^+$ system of monocrowned Malachite Green **2** exhibited a similar tendency to that of the Na$^+$−**1** system in the addition effect on the photoinduced coloration, showing a maximal rate constant at a Na$^+$ concentration between 1×10^{-5} and 1×10^{-4} mol dm^{-3} (Figure 6b). In the K$^+$−**2** system, the maximum in the coloration rate was found at the higher metal-ion concentration. This is derived from the fact that Na$^+$ can fit into the monoaza-15-crown-5 ring better than K$^+$ on the formation of 1:1 (**2**/metal ion) complexes. In the photoinduced coloration for the system of triscrowned Crystal Violet **3**, the suppression effect on addition of an alkali metal salt was decreased in the order Na$^+$ > K$^+$ > Cs$^+$ (Figure 6c). The tris(crown ether) derivative, **3**, can form mulitinuclear complexes, especially with Na$^+$, as demonstrated in the mass spectra (Figure 4), and the resulting plural metal cations in a **3** molecule may be more effective in the electrostatic repulsion with the conjugate triphenylmethyl cation of **3** than a single metal cation. This probably accounts for the metal-ion order in the addition effect on the coloration rate of **3**.

Photoinduced Switching of Metal-Ion Complexation. As mentioned above, the UV-light-induced ionization rate of crowned triphenylmethane leuconitriles **1**−**3**, accompanied by coloration, is influenced by the metal-ion complexation of their crown ether moieties to a great extent. It is expected in the opposite sense that the metal-ion complexing ability of the crown ether derivative can be controlled by photoionization of their triphenylmethane leuconitrile moieties, primarily based on the electrostatic repulsion between crown-ether-complexed metal ion(s) and a conjugated triphenylmethyl cation.

To obtain important information about the configurations and point net charges of each atom in the electrically neutral leuconitrile and triphenylmethyl cationic forms, molecular orbital (MO) calculations were carried out by using the corresponding dimethoxyamino derivatives of the crowned triphenylmethane leuconitriles for simplicity (Figure 7). The photoionization of crowned triphenylmethanes causes their appreciable configuration changes. For instance, the triphenylmethyl carbon atom in the leuconitrile form of biscrowned Malachite Green **1** is in sp^3 hybridization. It is therefore likely that two crown ether rings can cooperate in forming intramolecular sandwich-type complexes with a metal ion, especially K$^+$. On the contrary, in the quinoid-like cation of **1** formed by UV-light irradiation, the two crown ether rings are more distant from each other than in the leuconitrile form, so the cooperation is somewhat difficult for the sandwich-type complex formation. The MO calculation data for triscrowned Crystal Violet **3** suggest the formation of a propeller-shaped conjugated triphenylmethyl cation, which makes it more difficult for the three crown ether rings to cooperate on complexing large metal ions such as Cs$^+$ than its corresponding leuconitrile form. Also, there is considerable difference in the point net charges of the crown ether ring heteroatoms (nitrogen and oxygen atoms) between the leuconitrile and triphenylmethyl cationic forms of crowned triphenylmethanes. In any of the crowned triphenylmethane leuconitriles **1**−**3**, the point net charges of the crown ether ring heteroatoms are increased in the triphenylmethyl cationic form. Taking account of the difference in the point net charges as well as of the configuration, one can anticipate diminished metal-ion complexing ability of the crown ether moiety of **1**−**3** in the corresponding conjugated triphenylmethyl cationic form. Thus, photoinduced changes of metal-ion complexing ability in the crowned triphenylmethanes can be expected from the viewpoint not only of the intramolecular electrostatic repulsion but also of the difference in the configuration and point net charges between the two forms.

Photochemical switching of metal-ion complexation in the three crowned triphenylmethane derivatives can be detected by ESI-MS, as shown in Figures 2b−4b. Mass spectra for acetonitrile solutions containing a crowned triphenylmethane leuconitrile and a mixture of Li^+, Na^+, and K^+ (and Cs^+) after UV-light irradiation (30 s) show only a single significant peak, which can be assigned to their corresponding conjugated triphenylmethyl cations, in any systems of the crowned triphenylmethane derivatives. The peaks for the metal complexes of the crowned triphenylmethane leuconitriles almost disappeared on the photoirradiation. These mass-spectral changes have clearly verified the photochemical switching of metal-ion complexation of crowned triphenylmethane leuconitriles **1**−**3**.

To confirm the all-or-none type photochemical switching of metal-ion complexation by the biscrowned Malachite Green, ^1H NMR spectra of **1**−CD_3OD solutions were measured in the presence and absence of metal ions before and after UV-light irradiation. The peaks assigned to crown ether ring protons of **1** as depicted in Figure 8 show significant differences in the presence and absence of a metal ion and before and after photoirradiation. The addition of an equimolar amount of K^+ or Na^+ caused the appearance of new peaks (highlighted by arrows) that can be attributed to the metal-ion complexation by the crown ether moiety. The complex formation constants were determined to be 1.7×10^4 and 8×10^3 $dm^3\ mol^{-1}$ for the K^+ and Na^+ complexes, respectively, assuming the 1:1 stoichiometry of **1** and metal ion. Any the peaks assigned to the metal-ion complexes almost disappeared with UV-light irradiation. The NMR spectra for photoirradiation in the presence of a metal ion are very similar to that in the absence of it. The formation constants for the metal complexes of conjugated quinoid cation of **1** could not be determined due to the disappearance of the peaks for the metal-ion complexes. This NMR observation is in accord with the dramatic photoinduced disappearance of the ESI-MS peaks assigned to the metal complexes of **1** and its quinoid form (Figure 2b). Thus, the photoionization of their triphenylmethane leuconitrile moiety allowed very efficient release of metal ions in their crown ether moiety.

Heating after turning off UV light brings about the thermal reverse reaction from the conjugate triphenylmethyl cations to the corresponding initial triphenylmethane leuconitriles. For instance, such a thermal reverse reaction as shown in Scheme 1 proceeds gradually in the **1**−metal ion systems. The thermal reverse reaction for triphenylmethane lueuconitriles not carrying any crown ether moiety is generally suppressed by adding any metal ion due to the polarity increase, which in turn stabilizes their corresponding triphenylmethyl cation form. To the contrary, the metal-ion complex formation of triphenylmethane leuconitrile **1** may function in a direction to enhance the thermal reverse reaction. Very interestingly, the activation energy for the thermal reverse reaction of **1**−acetonitrile solution (1×10^{-5} mol dm^{-3}) was decreased from 60.0 kJ mol^{-1} successively to 38.8, 25.7, and 23.7 kJ mol^{-1} by K^+ addition at 1×10^{-5}, 1×10^{-4}, and 1×10^{-3} mol dm^{-3}. Obviously, the enhancing effect on the thermal reverse reaction by the complex formation surpasses the suppressing effect, indicating that the difference in the metal-ion complexing ability is very remarkable, all-or-none type, between the triphenylmethane leuconitrile and triphenylmethyl cation forms.

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