

# Electrospray Ionization Mass Spectrometry for Mechanism Analysis of Metal Ion Complexation and Photoionization of Malachite Green Derivatives Incorporating a Crown Ether Moiety

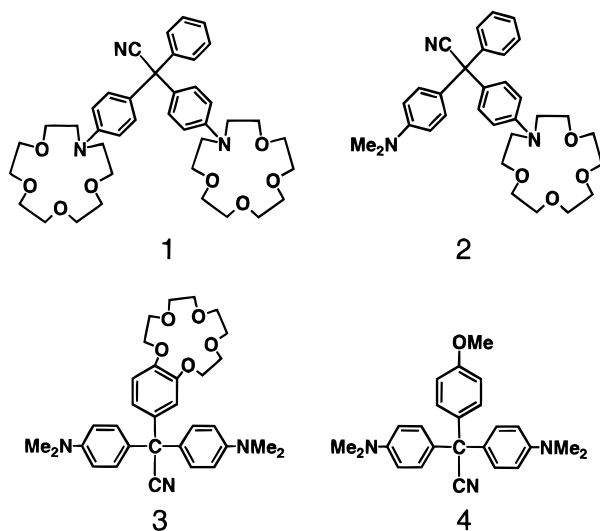
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**Electrospray-ionization mass spectrometry using a photoirradiation interface has been successfully applied to the investigation of metal-ion complexation and photoionization of crowned Malachite Green leuconitrile derivatives in solution. The mass spectrometry clearly showed that the Malachite Green derivatives in their electrically neutral forms can complex metal ions with their crown ether moiety. Ionization of the Malachite Green derivatives to their corresponding cationic forms, accompanied by metal-ion repelling from their crown ether moiety, was detected upon UV-light irradiation. A remarkably different photoionization behavior in various solvents, which is difficult to detect by other analytical techniques, was also found by the mass spectrometry.**

Mass spectrometry (MS) is an attractive technique for determining molecular weight and molecular fragmentation. Recently, considerable attention has been focused on very soft ionization for MS. One of the very soft techniques is electrospray ionization (ESI) that can form pseudomolecular ions with little or no fragmentation.<sup>1,2</sup> ESI-MS is therefore a powerful technique for analyzing complexed ions and unstable ionic species in solution.<sup>3–8</sup> Mass spectrometry has also been applied to metal-ion complex-

Chart 1



ation studies of macrocyclic ligands such as crown ether derivatives.<sup>9–14</sup>

Malachite Green leuconitrile, a kind of triphenylmethane dye, is a typical photochromic compound in which the chemical bond is cleaved heterolytically to form a colored cation and a cyanide anion on photoirradiation,<sup>15</sup> but the details of its photochromism is not well-understood. We have already designed Malachite Green dyes incorporating a crown ether moiety, such as **1** and **3** (Chart 1), for photochemical control of metal-ion complexation based on electrostatic repulsion.<sup>16,17</sup> Under dark conditions, the crowned

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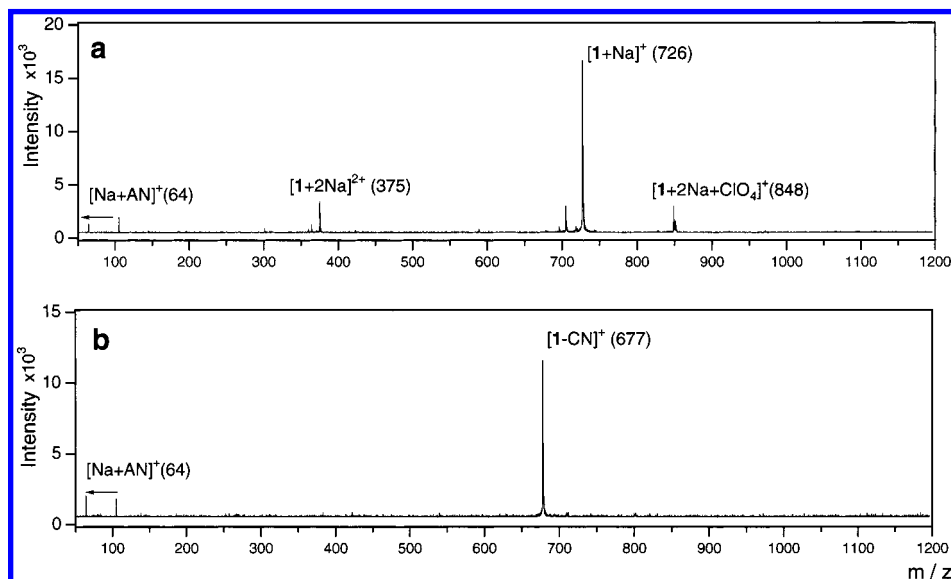


Figure 1. Mass spectra for acetonitrile (AN) solution of biscrowned Malachite Green leuconitrile **1** and  $\text{NaClO}_4$  under (a) dark and (b) photoirradiated conditions.  $[\mathbf{1}]$  and  $[\text{NaClO}_4]$ :  $2 \times 10^{-4} \text{ mol dm}^{-3}$ . UV light: 240–400 nm for 30 s.

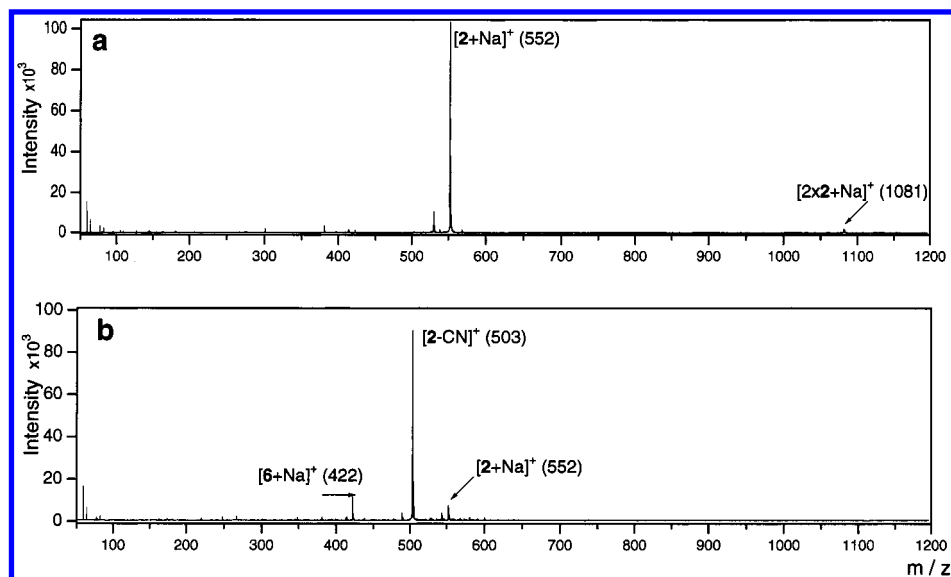


Figure 2. Mass spectra for acetonitrile solution of monocrowned Malachite Green leuconitrile **2** and  $\text{NaClO}_4$  under (a) dark and (b) photoirradiated conditions.  $[\mathbf{2}]$  and  $[\text{NaClO}_4]$ :  $2 \times 10^{-4} \text{ mol dm}^{-3}$ . UV light: 240–400 nm for 30 s.

Malachite Green derivatives can form metal complexes with their crown ether moiety. On UV-light irradiation, on the other hand, their photochromic moiety can ionize to a triphenylmethyl or its isomeric cation. That is to say, the crowned Malachite Green derivatives assume different ionic species under dark versus photoirradiated conditions and thereby undergo photochemical switching of metal-ion complexation. This induced us to apply ESI-MS using a photoirradiation interface for investigation of the photoionization of crowned Malachite Green derivatives in the presence of metal ions. This paper focuses on the excellent applicability of ESI-MS, with a photoirradiation interface, for the study of photoionization and photochemical switching of metal-ion complexation for photochromic crown ether derivatives.

## EXPERIMENTAL SECTION

**Materials.** Malachite Green derivative carrying bis(crown ether) structure **1** was synthesized by 4'-lithiated *N*-phenyl-monoaza-15-crown-5 with methyl benzoate, followed by cyanization of the resulting Malachite Green hydroxide. Similarly, Malachite Green carrying a monoazacrown ether ring, **2**, is accessible from 4'-lithiated *N*-phenyl-monoaza-15-crown-5 and 4-(*N,N*-dimethylamino)benzophenone. Their synthetic procedures will be reported in detail elsewhere. Malachite Green derivatives with a benzo-15-crown-5 moiety and without any crown ether moiety, **3** and **4**, were prepared according to the procedure reported previously.<sup>16</sup> The metal salts are of analytical-grade and the solvents were of spectro-grade (Wako Pure Chemical Industries, Ltd., Osaka, Japan).

**Measurements.** A sector-type mass spectrometer (JEOL-D300) connected with a laboratory-made ESI interface for photoirradiation, which has already been described elsewhere,<sup>7,8</sup> was

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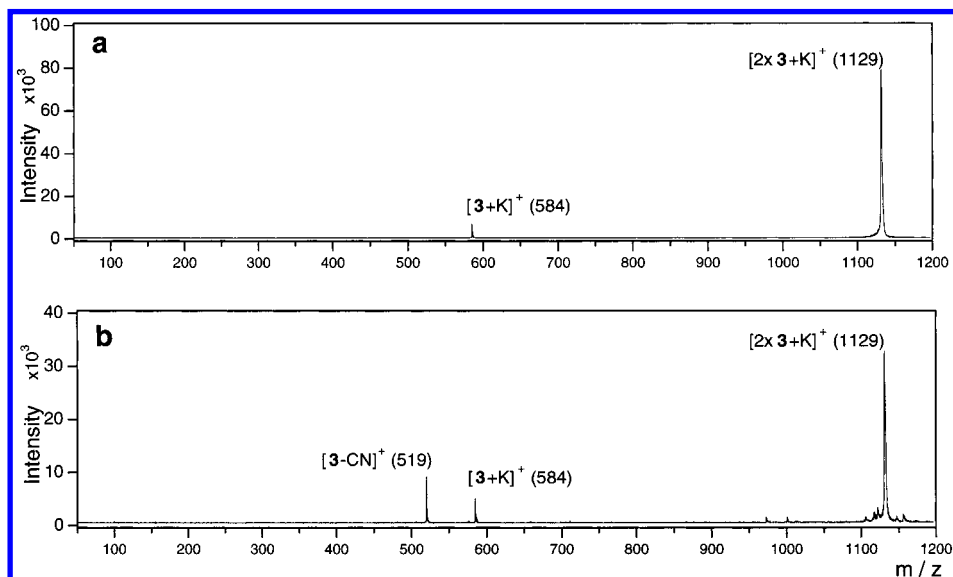


Figure 3. Mass spectra for acetonitrile solution of Malachite Green leuconitrile of benzocrown ether **3** and  $\text{KClO}_4$  under (a) dark and (b) photoirradiated conditions.  $[\mathbf{3}]$  and  $[\text{KClO}_4]$ :  $2 \times 10^{-4} \text{ mol dm}^{-3}$ . UV light: 240–400 nm for 5 min.

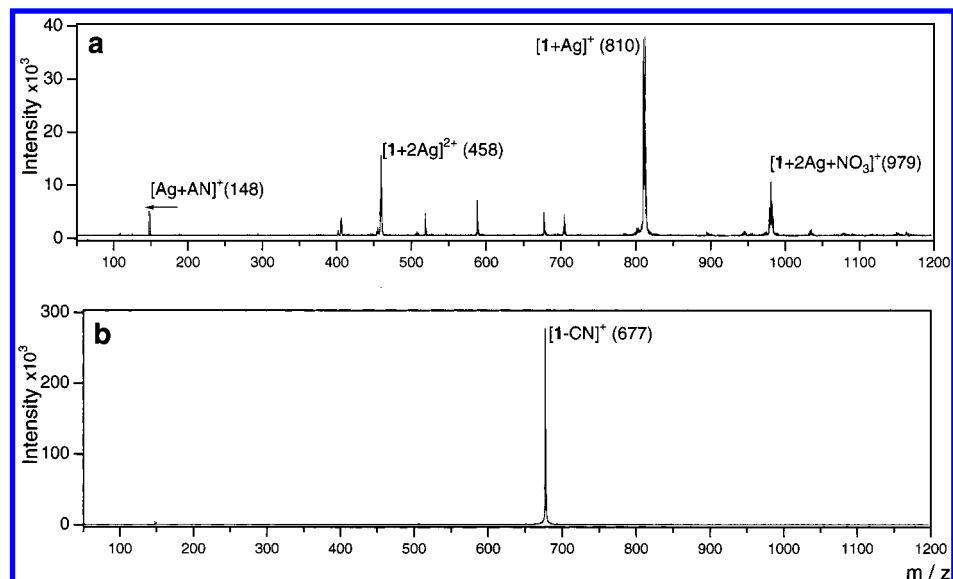


Figure 4. Mass spectra for acetonitrile solution of biscrowned Malachite Green leuconitrile **1** and  $\text{AgNO}_3$  under (a) dark and (b) photoirradiated conditions.  $[\mathbf{1}]$  and  $[\text{AgNO}_3]$ :  $2 \times 10^{-4} \text{ mol dm}^{-3}$ . UV light: 240–400 nm for 30 s.

used to obtain ESI-MS spectra. A sample solution was sprayed with a flow rate of  $0.15 \text{ mL h}^{-1}$  at the tip of a needle applied by a voltage 3.5 kV higher than that of a counter electrode. A heated nitrogen gas flow was applied between the needle and the counter electrode to promote desolvation of the charged droplets sprayed. The resulting ions were then introduced into the vacuum system through the first and second skimmers of a mass analyzer. The pressures of differential pumping stages were about 1 and  $1 \times 10^{-3}$  Torr, respectively. A rotary pump and a mechanical booster pump in their region were floating electrically to depress 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 equimolar amounts ( $1 \times 10^{-4} \text{ mol dm}^{-3}$ ) of a Malachite Green derivative and a metal salt in a solvent without any additive for promoting the ionization. Photoirradiation

on the ESI interface was made by using UV light (240–400 nm), which was obtained by passing a light from a Xe lamp equipped with a quartz waveguide through a Toshiba UV-D33S color filter. Absorption spectra were taken with an acetonitrile solution containing a Malachite Green derivative ( $1 \times 10^{-5} \text{ mol dm}^{-3}$ ).

## RESULTS AND DISCUSSION

**Complex Formation of Crowned Malachite Green with Alkali Metal Ions.** Since the Malachite Green derivatives, **1–3**, carry crown ether moieties, they can form complexes with appropriate metal ions. Attempts were made to detect metal-ion complexes of the crowned Malachite Green derivatives by ESI-MS. Typical mass spectra for acetonitrile solutions of crowned Malachite Green derivatives **1–3** in the presence of an equimolar amount of a metal salt are shown in Figures 1a through 4a. For the solution containing biscrowned Malachite Green **1** and  $\text{Na}^+$ , the base peak is at  $m/z$  726, which can be assigned to 1:1

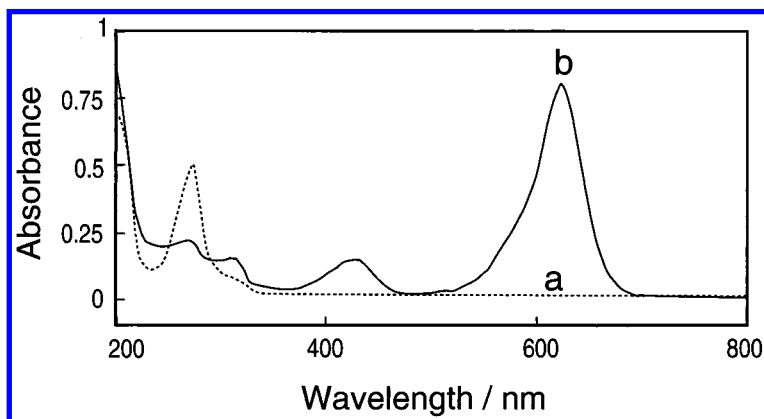
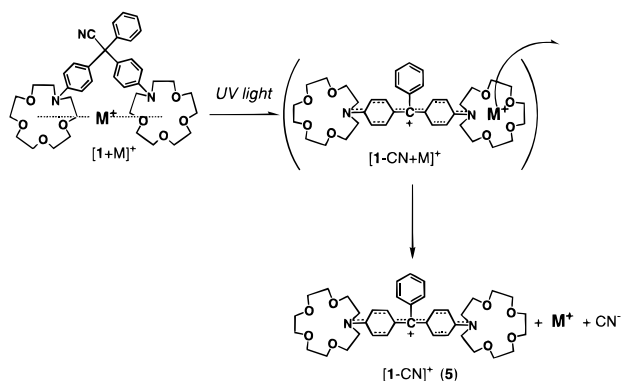


Figure 5. Absorption spectra of crowned Malachite Green **1** (a) before and (b) after UV-light irradiation. [**1**]:  $1 \times 10^{-5}$  mol dm<sup>-3</sup> in acetonitrile. Photoirradiation: 5 min.

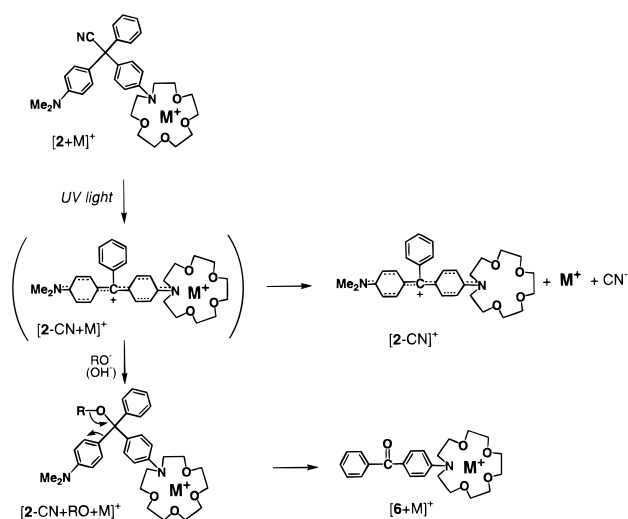
Scheme 1



complexes of **1** and Na<sup>+</sup> ( $[1 + \text{Na}]^+$ ). The biscrowned Malachite Green can also form 1:2 complexes of **1** and Na<sup>+</sup>, the idea of which is supported by small peaks of  $[1 + 2\text{Na}]^{2+}$  and  $[1 + 2\text{Na} + \text{ClO}_4]^+$ . Of course, in the Na<sup>+</sup> system of monocrowned Malachite Green **2**, a 1:1 complex of **2** and Na<sup>+</sup> was observed as a main complex at  $m/z$  552. A tiny peak at  $m/z$  1081 also indicates some formation of a sandwich-type 2:1 complex of **2** and Na<sup>+</sup>. The tendency for the formation of sandwich-type 2:1 (crown ether ring/metal ion) complexes is more remarkable in the system of Malachite Green incorporating a benzo-15-crown-5 moiety **3** and K<sup>+</sup>, as shown in Figure 3a. Surprisingly enough, the benzocrown ether derivative **3** predominantly forms sandwich-type 2:1 (crown ether/K<sup>+</sup>) complexes despite the equimolar concentration of the crown ether and metal ion. It is generally believed that crown ethers can complex metal ions with 2:1 (crown ether/metal ion) stoichiometry only in excess of the crown ether, but the present ESI-MS data clearly shows that this is not always true.<sup>11</sup> Figure 4a demonstrates that biscrowned Malachite Green **1** can also bind Ag<sup>+</sup> in addition to alkali metal ions. For an acetonitrile solution containing a control compound without crown ether moiety **4** and a metal ion, a peak assigned to metal-ion complexes of **4** was not observed as anticipated.

**Photoionization of Crowned Malachite Green.** On UV-light irradiation, the acetonitrile solutions containing a Malachite Green derivative and a metal salt turned green-colored, as indicated in a typical absorption spectral change of **1** (Figure 5). ESI-MS afforded dramatic results about the photoisomerization of crowned Malachite Green derivatives in the presence of a metal ion. UV-light irradiation on an acetonitrile solution containing biscrowned

Scheme 2



Malachite Green **1** and NaClO<sub>4</sub> decreased the peak for  $[1 + \text{Na}]^+$ , while increasing a new peak for  $[1-\text{CN}]^+$  at  $m/z$  677. The ion of  $[1-\text{CN}]^+$  is a triphenyl or quinoid cation (**5**) formed by the photoionization of **1**. The absorption spectrum of **1** after UV-light irradiation suggests that the resulting ion,  $[1-\text{CN}]^+$ , is a charge-delocalized or conjugated cation. The peak for  $[1-\text{CN}]^+$  can, therefore, be attributed to a quinoid cation such as that shown in Scheme 1. It is worth noting that any peak assigned to the Na<sup>+</sup> complexes of **1** cannot be found at all after photoirradiation for only 30 s (Figure 1b). This indicates that the Na<sup>+</sup> complexes of **1** release their Na<sup>+</sup> very efficiently on photoirradiation. This is probably due to the electrostatic repulsion between the metal ion and the resulting quinoid ion in the metal complexes of quinoid form (Scheme 1). Thus, biscrowned Malachite Green **1** has realized all-or-none-type photochemical switching of cation complexation.<sup>17</sup>

In the system of a Malachite Green derivative carrying a monoazacrown ether ring (monocrowned Malachite Green), **2**, a similar tendency was observed on UV-light irradiation (Scheme 2). The difference between the photoionization behavior of the **1** and **2** systems is that the photoionization accompanied by metal-ion ejection is a little slower in the system of **2** as compared with that in that of **1**. A small peak for  $[2 + \text{Na}]^+$  as well as a base peak of its quinoid ion ( $[2-\text{CN}]^+$  at  $m/z$  552) were still found on

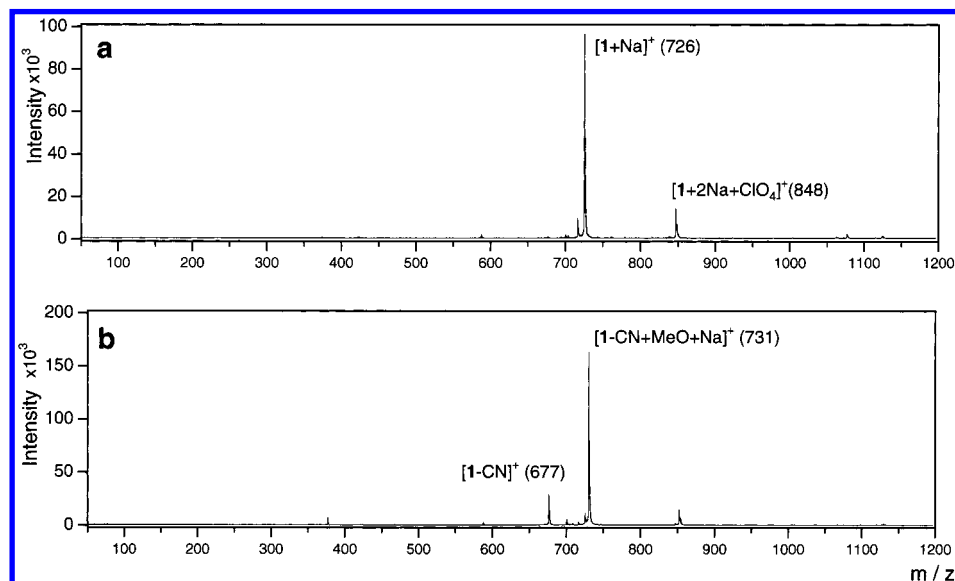
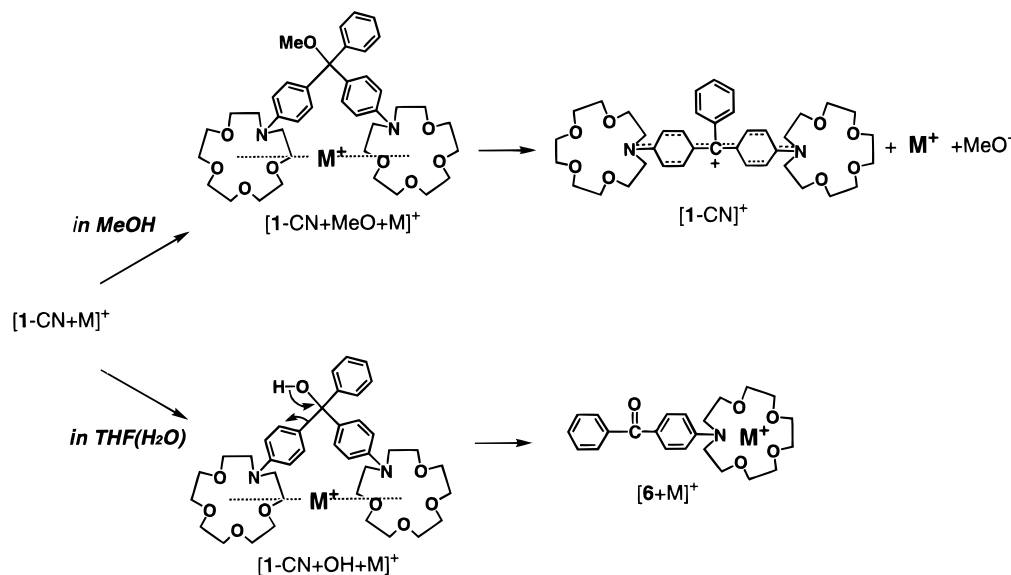


Figure 6. Mass spectra for methanol (MeOH) solution of biscrowned Malachite Green leuconitrile **1** and  $\text{NaClO}_4$  under (a) dark and (b) photoirradiated conditions.  $[\mathbf{1}]$  and  $[\text{NaClO}_4]$ :  $2 \times 10^{-4} \text{ mol dm}^{-3}$ . UV light: 240–400 nm for 30 s.

### Scheme 3



30-s photoirradiation of the solution containing **2** and  $\text{NaClO}_4$  (Figure 2b). After 5-min photoirradiation, the peak for  $[\mathbf{2} + \text{Na}]^+$  finally disappeared. Also, some photodegradation of the mono-crowned Malachite Green **2** seems to occur, because a new peak assigned to a  $\text{Na}^+$  complex of *N*-(4-benzoylphenyl)-monoaza-15-crown-5 **6** ( $[\mathbf{6} + \text{Na}]^+$ ) appeared at  $m/z$  422 after prolonged photoirradiation. That is to say, this peak formation suggests a C–C bond scission on photoionization of the  $\text{Na}^+$  complexes of **2**. Perhaps, the resulting positive charge is somewhat localized on the triphenylmethyl carbon in the quinoid form ( $[\mathbf{2}-\text{CN} + \text{M}]^+$ ) induced by photoionization of metal complexes of the asymmetric Malachite Green **2** to its corresponding quinoid form. This intermediate (asymmetric quinoid cation) is subject to a nucleophilic attack by appropriated anions  $\text{RO}^-$ , such as  $\text{OH}^-$ , followed by a subsequent C–C bond scission (Scheme 2).

A Malachite Green derivative carrying a benzo-15-crown-5 moiety, **3**, is very different from the Malachite Green derivatives

of monoaza-15-crown-5, **1** and **2**, in the behavior of photoionization followed by metal-ion decomplexation (Figure 3b). Of course, UV-light irradiation on the system of **3** and  $\text{KClO}_4$  resulted in the appearance of a new peak based on its quinoid ion ( $[\mathbf{3}-\text{CN}]^+$  at  $m/z$  519). Even after 5-min photoirradiation, however, there were still two significant peaks of 2:1 and 1:1 complexes of **3** and  $\text{K}^+$  left. The photoionization of  $\text{K}^+$  complexes of **3** is very sluggish probably due to the high stability of the sandwich-type 1:2 complexes that suppresses the ionization by intramolecular electrostatic repulsion not only between the resulting quinoid cation and a metal ion in the crown ether ring but also between the two resulting quinoid cations in a complex molecule.

A combination of **1** with  $\text{AgNO}_3$  brought about another interesting type of photoionization (Figure 4b). The coexistence of  $\text{AgNO}_3$  accelerates the photoionization of **1** drastically. The efficient photoionization of **1** in the presence of  $\text{AgNO}_3$  can be seen by comparison of the peak intensity for its quinoid cation

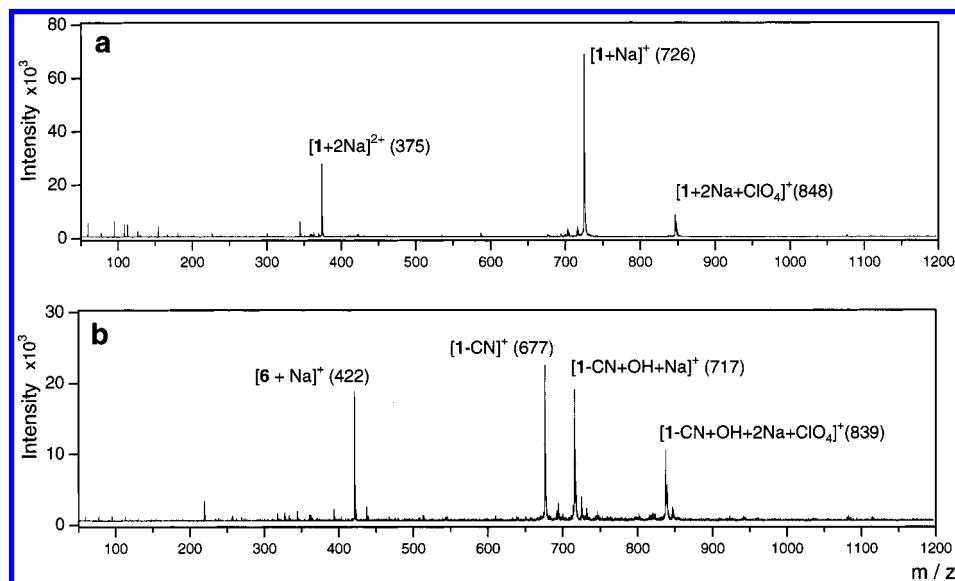


Figure 7. Mass spectra for tetrahydrofuran (THF) solution of biscrowned Malachite Green leuconitrile **1** and  $\text{NaClO}_4$  under (a) dark and (b) photoirradiated conditions.  $[\mathbf{1}]$  and  $[\text{NaClO}_4]$ :  $2 \times 10^{-4} \text{ mol dm}^{-3}$ . UV light: 240–400 nm for 30 s.

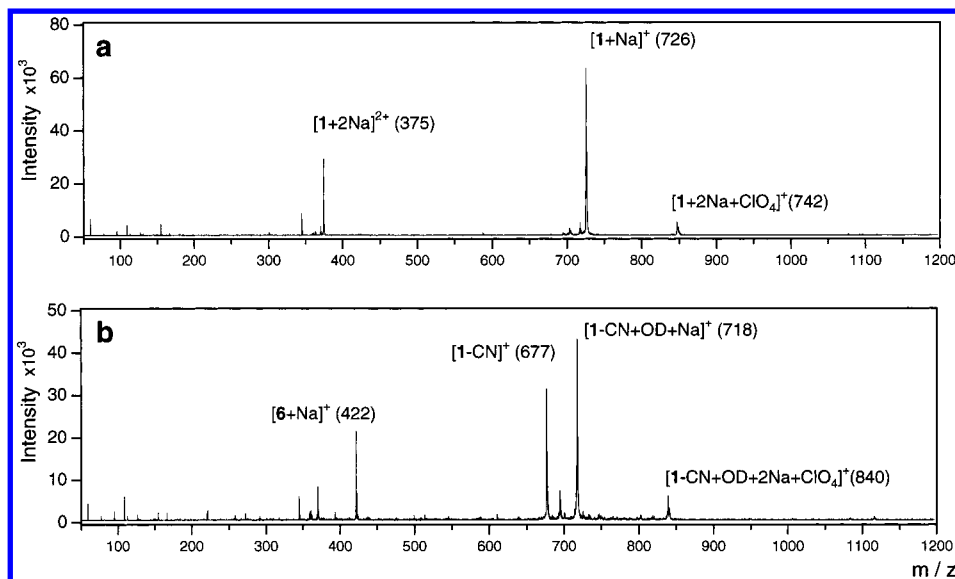


Figure 8. Mass spectra for THF/ $\text{D}_2\text{O}$ (90:10) solution of biscrowned Malachite Green leuconitrile **1** and  $\text{NaClO}_4$  under (a) dark and (b) photoirradiated conditions.  $[\mathbf{1}]$  and  $[\text{NaClO}_4]$ :  $2 \times 10^{-4} \text{ mol dm}^{-3}$ . UV light: 240–400 nm for 30 s.

with those for the other systems (Figure 1b–3b); the intensity is in the order of  $10^5$  for the  $\text{Ag}^+$  system of **1** and  $10^4$  for the other ones. Definitely, the photoionization enhancement in the  $\text{Ag}^+$  system of **1** is attributable to the precipitation of  $\text{AgCN}$  as a result of its low solubility product. The  $\text{AgCN}$  was, in turn, formed by recombination of  $\text{Ag}^+$  and  $\text{CN}^-$  released from its crown ether and Malachite Green leuconitrile moieties, respectively, in the  $\text{Ag}^+$  complex of **1**. Thus, the  $\text{AgCN}$  precipitation can shift the equilibrium in the UV-light-induced ionization of **1** to its quinoid form to a great extent, promoting the photoionization.

**Solvent Effects.** In methanol, the photoionization of biscrowned Malachite Green **1** in the presence of a metal ion proceeds not only in the mechanism of Scheme 1 but also in a different way from that in acetonitrile. Naturally, the crown ether moiety of **1** can also complex a metal ion in methanol, as illustrated in Figure 6a. On UV-light irradiation of a methanol solution containing **1** and  $\text{NaClO}_4$  for 30 s, a peak for the quinoid

ion of **1** appeared, as is the case with the corresponding acetonitrile solution (Figure 6b). However, a striking new peak assigned to  $[\mathbf{1} - \text{CN} + \text{MeO} + \text{Na}]^+$ , where a cyano group in the  $\text{Na}^+$  complex of **1** is replaced with a methoxy group (the upper mechanism in Scheme 3), was also found in methanol unlike in acetonitrile. The formation of the Malachite Green methoxide derivative was confirmed by mass spectrometry using  $\text{CD}_3\text{OD}$  instead of  $\text{CH}_3\text{OH}$  as the solvent. This indicates that the photoionization of **1** to its quinoid ion, that is, the release of a cyanide anion, is immediately followed by addition of methoxy anion in methanol. A large amount of methoxy anion in methanol may depress the photoionization of **1** and subsequent metal-ion release. However, prolonged photoirradiation (for 5 min) finally allowed the peaks for the metal-ion complexes to almost disappear, thus forcing the metal-ion release from the crown ether moiety of **1** to completion.



In THF, serious photodegradation of **1** occurred, on UV-light irradiation of the Na<sup>+</sup> system of **1**, in addition to such photoionization-induced metal-ion release as seen in acetonitrile (Scheme 1). UV-light irradiation for only 30 s afforded a variety of new peaks as demonstrated in Figure 7. A peak of [1-CN + OH + Na]<sup>+</sup>, where a cyano group in the Na<sup>+</sup> complex of **1** is replaced with a hydroxy group, as well as a peak of [1-CN + OH + 2Na + ClO<sub>4</sub>]<sup>+</sup> (a binuclear complex accompanying a perchlorate anion) can be seen in addition to a peak for the quinoid cation of **1** ([1-CN]<sup>+</sup>). This suggests that hydroxide ions derived from a trace amount of water in THF led to the formation of these ionic species. This is evidenced by the fact that these peaks can be detected as [1-CN + OD + Na]<sup>+</sup> and [1-CN + OD + 2Na + ClO<sub>4</sub>]<sup>+</sup> in THF containing 10% D<sub>2</sub>O as shown in Figure 8. Another intense peak on the photoirradiation is at *m/z* 422, which can be assigned to Na<sup>+</sup> complexes of **6**. Obviously, the MS data indicate that the photoionization of **1** to its quinoid cation, followed by addition of a hydroxy anion result from water, also proceeds in THF. Subsequently, such photodegradation of **1** to its benzophenone derivative occurs as shown in Scheme 3 (the lower mechanism). That is to say, UV-light irradiation on a THF solution containing **1** and NaClO<sub>4</sub> causes serious hydrolysis of **1** by a trace amount of water that is included as an impurity in the solvent. The photostability difference of **1** in acetonitrile and THF may be attributed to the stability of its corresponding quinoid form itself.

## CONCLUSIONS

The photoionization of Malachite Green leuconitrile derivatives incorporating a crown ether moiety, **1–3**, in the presence of a metal salt, followed by the release of a metal ion from their crown ether moiety, has been successfully investigated in detail by using ESI-MS with a photoirradiation interface. The efficient metal-ion release by photoionization in acetonitrile was found in Malachite Green derivatives of monoazacrown ethers, **1** and **2**. This was not the case in a benzocrown ether derivative, **3**. Drastic enhancement in photoionization of the Ag<sup>+</sup> system of **1** was confirmed by comparison of the peak intensity for the quinoid cation. Mass spectrometry using deuterium solvents has also clarified that the behavior in the photoionization of **1** depends considerably upon the kind of solvent. Furthermore, UV-light-induced hydrolysis in a THF solution containing **1** and a metal ion could be followed by the present ESI-MS technique.

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