

All-or-None Type Photochemical Switching of Cation Binding with Malachite Green Carrying a Bis(monoazacrown ether) Moiety

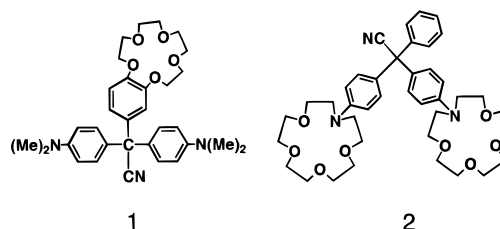
Keiichi Kimura,*[†] Ryoko Mizutani,[†] Masaaki Yokoyama,[†] Ryuichi Arakawa,[‡] Gen-etsu Matsubayashi,[‡] Masanori Okamoto,[§] and Hidekazu Doe[§]

Chemical Process Engineering, Faculty of Engineering
Osaka University, Yamada-oka 2-1
Suita, Osaka 565, Japan
Department of Applied Chemistry
Faculty of Engineering, Osaka University
Machikaneyama-cho 1-16, Toyonaka 560, Japan
Department of Chemistry, Faculty of Science
Osaka City University, Sugimoto-cho 3-3
Sumiyoshi-ku, Osaka 558, Japan

Received September 30, 1996

Crown ether derivatives incorporating a photochromic moiety, what we call photochromic crown ethers, are attractive tools for photochemical control of metal ion binding.^{1–5} For instance, the azobenzene moiety, which isomerizes photochemically between its trans and cis forms, can be used for changing the bis(crown ether) configuration⁶ and the cryptand⁷ cavity sizes upon photoisomerization. In a crowned spirobenzopyran which undergoes photoisomerization between its electrically neutral spiroopyran form and zwitterionic merocyanine one, its cation-binding ability can be controlled photochemically by intramolecular interaction between a metal ion complexed by its crown ether moiety and the phenolate anion in the merocyanine form.^{8,9} In the photocontrol systems of cation binding by photochromic crown ethers, which take advantage of photoinduced changes in the topology of crown ethers, only modest changes between the moderately high and low cation-binding abilities can be realized; any state for cation complexation constants of 0 or nearly 0 can hardly be attained. These modest photoinduced changes in the cation binding is inconvenient for application of the photochromic crown ethers to switching devices that require clear-cut switching between 1 and 0 digits, that is, between “all” and “none” states.

We have already designed a benzocrown ether (**1**) carrying a malachite green leuconitrile moiety that ionizes intermolecularly upon UV-light irradiation, aiming at photoinduced cation release based on electrostatic repulsion.^{10,11} In the crowned malachite green, efficient cation release was expected due to the electrostatic repulsion between the resulting quinoid cation and metal ion complexed by its crown ether moiety. Potentiometric measurements, however, suggested that the photoion-



ized crowned malachite green does not necessarily reject a metal ion. Also, the benzocrown ether itself does not have very high cation-binding ability, even in the non-ionized state of **1** under dark conditions.

This prompted us to design a malachite green derivative incorporating a bis(monoazacrown ether) structure (**2**). Not only high cation-binding ability of the bis(crown ether) moiety^{12,13} under dark conditions but also efficient cation release by electrostatic repulsion with positively charged nitrogen atom in the crown ether ring^{14,15} under photoirradiated conditions can be expected in the biscrowned malachite green. Here, we report all-or-none type switching of cation binding by the biscrowned malachite green upon photoionization of the photochromic moiety, which is evidenced by electrospray ionization mass spectrometry (ESI-MS).

The biscrowned malachite green derivative **2** was synthesized by the reaction of 4'-lithiated *N*-phenylmonoaza-15-crown-5 ether with methyl benzoate, followed by cyanization of the resulting malachite green leucohydroxide. When irradiated with UV-light (240–400 nm), an acetonitrile solution containing an equimolar amount of **2** and an alkali metal perchlorate (K⁺ or Na⁺) turned green, showing a strong absorption peak around 620 nm. This indicates that the biscrowned malachite green ionizes to its corresponding quinoid cation upon photoirradiation, as is the case for the corresponding system **1**. The ¹H NMR spectrum for a CD₃OD solution of **2** and KClO₄ has new peaks between 3.5 and 3.7 ppm, which can be assigned to the protons -NCH₂CH₂O(CH₂CH₂O)₂- in the crown ether ring complexing a metal ion, under dark conditions, suggesting the powerful complexation of K⁺ by the bis(crown ether) moiety (Figure 1a). Similar new peaks did not appear in the corresponding system **1** containing Na⁺ or K⁺. The difference in the ¹H NMR spectrum between systems **1** and **2** may suggest the powerful cation binding of **2** on basis of the bis(crown ether) effect. UV-light irradiation allowed the new peaks to disappear, as seen in Figure 1b, and the NMR spectrum after photoirradiation was almost the same as that for system **2** without any metal salt. The UV-light-induced ¹H NMR spectral change is very suggestive of the efficient cation release of **2** upon photoirradiation. Figure 2 shows typical spectra for ESI-MS of an acetonitrile solution of **2** and KClO₄ under dark and UV-light-irradiated conditions, affording more dramatic results about the photochromic switching in the cation-binding ability. A base peak for K⁺ complexes of **2** was found at *m/z* = 742 under dark conditions (Figure 2a). UV-light irradiation (for 30 s) afforded a single, significant peak at *m/z* = 677, assigned to the corresponding quinoid cation of **2** (Figure 2b). It should be noted that the peak assigned to the metal ion complexes of **2** cannot be seen after UV-light irradiation. This indicates clearly that almost all metal ions complexed by the crown ether moiety of **2** were released upon photoionization of the malachite green moiety. Very interestingly, the photoionization of **2** realizes a

* Author to whom correspondence should be addressed.

[†] Chemical Process Engineering, Osaka University.

[‡] Department of Applied Chemistry, Osaka University.

[§] Osaka City University.

(1) Shinkai, S. New Developments in “Switched-on” Crown Ethers. In *Studies in Organic Chemistry 45: Crown Ethers and Analogous Compounds*; Hiraoka, M., Ed.; Elsevier: Amsterdam, 1992; pp 335–380.

(2) Desvergne, J.-P.; Fages, F.; Bouas-Laurent, H.; Marsau, P. *Pure Appl. Chem.* **1994**, *64*, 1231–1238.

(3) de Silva, A. P.; McCoy, C. P. *Chem. Ind. (London)* **1994**, 992–996.

(4) Yamashita, I.; Fujii, M.; Kaneda, T.; Misumi, S.; Otsubo, T. *Tetrahedron Lett.* **1980**, *21*, 541–544.

(5) Kimura, K. *Coord. Chem. Rev.* **1996**, *148*, 41–61.

(6) Shinkai, S.; Nakaji, T.; Ogawa, T.; Shigematsu, K.; Manabe, O. *J. Am. Chem. Soc.* **1981**, *103*, 111–115.

(7) Shinkai, S.; Nakaji, T.; Nishida, Y.; Ogawa, T.; Manabe, O. *J. Am. Chem. Soc.* **1980**, *102*, 5860–5865.

(8) Kimura, K.; Yamashita, T.; Yokoyama, M. *J. Chem. Soc., Perkin Trans. 2* **1992**, 613–619.

(9) Kimura, K.; Yamashita, T.; Yokoyama, M. *J. Phys. Chem.* **1992**, *96*, 5614–5617.

(10) Kimura, K.; Kaneshige, M.; Yokoyama, M. *J. Chem. Soc., Chem. Commun.* **1994**, 1103–1104.

(11) Kimura, K.; Kaneshige, M.; Yokoyama, M. *Chem. Mater.* **1995**, *7*, 945–950.

(12) Bourgoin, M.; Wong, K. H.; Hui, J. Y.; Smid, J. *J. Am. Chem. Soc.* **1975**, *97*, 3462–3467.

(13) Kimura, K.; Maeda, T.; Tamura, H.; Shono, T. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *95*, 91–101.

(14) Létard, J. F.; Delmond, S.; Lapouyade, R.; Braun, D.; Rettig, W.; Kleissler, M. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 517–527.

(15) Martin, M. M.; Plaza, P.; Meyer, Y. H.; Badaoni, F.; Bourson, J.; Lefebvre, J. P.; Valeur, B. *J. Phys. Chem.* **1996**, *100*, 6879–6888.

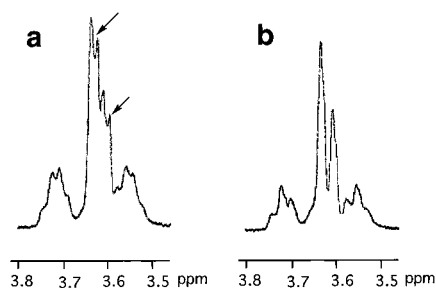


Figure 1. ^1H NMR spectra of crown ether ring protons for system containing equimolar amounts of the biscrowned malachite green leuconitrile **2** and KClO_4 before (a) and after (b) UV-light irradiation ($[\mathbf{2}]$ and $[\text{KClO}_4]$ are $1 \times 10^{-3} \text{ mol dm}^{-3}$ in CD_3OD). The peaks shown by arrows cannot be found in the absence of KClO_4 .

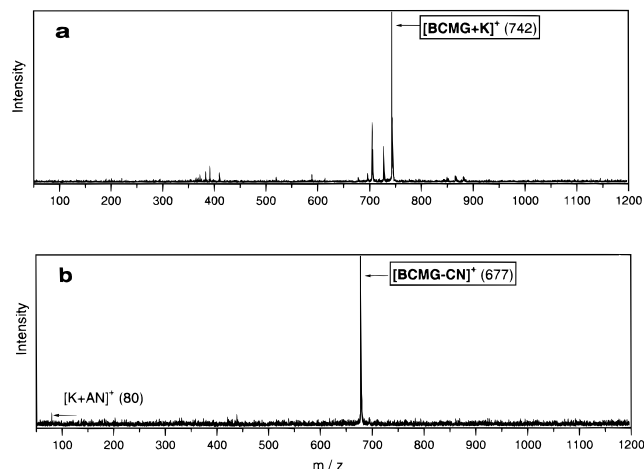


Figure 2. ESI-MS for acetonitrile (AN) solution of biscrowned malachite green leuconitrile (BCMG) **2** and KClO_4 under dark (a) and photoirradiated (b) conditions ($[\mathbf{2}]$ and $[\text{KClO}_4]$ are $2 \times 10^{-4} \text{ mol dm}^{-3}$; UV-light of 240–400 nm for 30 s).

switching from the powerful cation binding to the substantially perfect cation ejection, as illustrated in Scheme 1. This is not the case with the previous crowned malachite green **1**, as seen in Figure 3. In the mass spectrum under dark conditions, a strong peak for Na^+ complexes of **1** ($m/z = 568$) can be seen together with a tiny peak for Na^+ solvated by an acetonitrile molecule, which implies poor cation-binding ability as compared with that of system **2**. The UV-light-induced photoirradiation of **1** is quite sluggish as compared with that of **2**; a still strong peak for Na^+ complexes of **1** as well as the corresponding quinoid cation ($m/z = 519$) was observed even after 30 s of photoirradiation. After system **1** was photoirradiated for 5 min, the peak for Na^+ complexes of **1** ($m/z = 568$) almost disappeared. However, the mass spectrum of **1**(Na^+) also exhibits two other significant peaks assigned to the Na^+ complexes of the quinoid form of **1** and its ion pair with ClO_4^- at $m/z = 271$ and 641, respectively (Figure 3b). Definitely, even the quinoid cation of **1** still can bind a metal ion with the crown ether moiety in spite of the intramolecular electrostatic repulsion between the crown-complexed metal ion and the quinoid cation. This is probably because the electrostatic repulsion for system **1** is not so effective as that for system **2** where the nitrogen atoms of the quinoid cation are included in the crown ether ring.

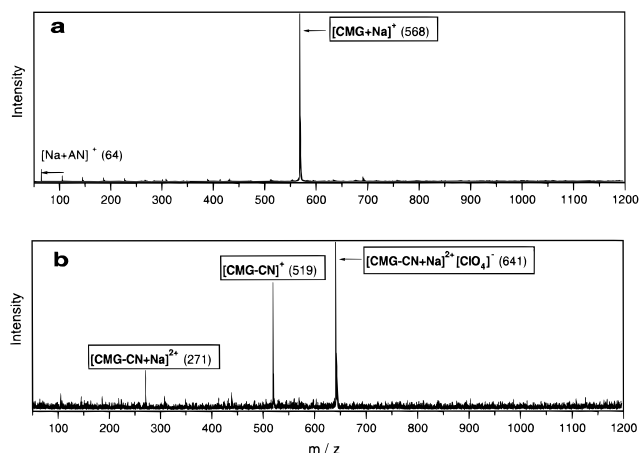
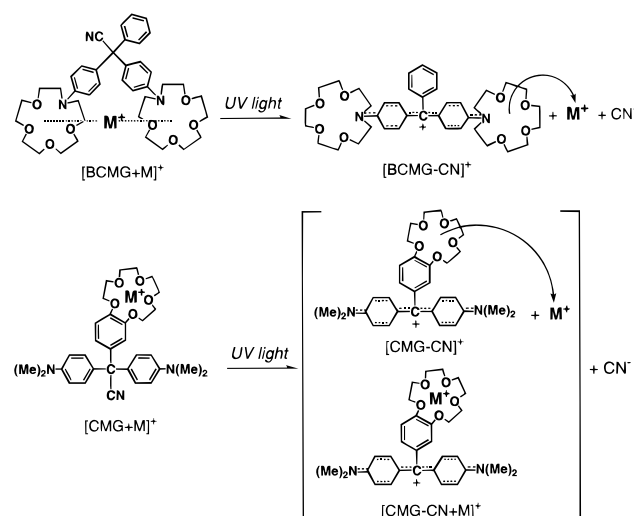


Figure 3. ESI-MS for acetonitrile (AN) solution of crowned malachite green leuconitrile (CMG) **1** and NaClO_4 under dark (a) and photoirradiated (b) conditions ($[\mathbf{1}]$ and $[\text{NaClO}_4]$ are $2 \times 10^{-4} \text{ mol dm}^{-3}$; UV-light of 240–400 nm for 5 min).

Scheme 1



Thus, the biscrowned malachite green leuconitrile **2** can undergo clear-cut switching from the powerful cation binding to the perfect cation release, so-called all-or-none type switching in the cation binding upon photoionization. This photoinduced switching behavior of cation binding is very different from the previous crowned malachite green **1**. This may suggest that similar type malachite green derivatives carrying bis(monoaza-crown ether) moiety with different sizes undergo photochemical control of cation complexation as efficient as that of compound **2**. The clear-cut photoinduced switching system of cation binding with **2** is promising for device applications.

Acknowledgment. The present work was partially supported by a Grand-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture. Financial support from Nagase Science and Technology Foundation and the Japan Securities Scholarship Foundation is also acknowledged.

JA963405L