

Membrane Potential Photoresponse of Crowned Malachite Green Derivatives Affording Perfect Photoswitching of Metal Ion Complexation

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(Received: 1 April 2004; in final form: 24 September 2004)

Key words: alkali metal ion complexation, Malachite Green, membrane potential response, monoazacrown ether, photochemical switching

Abstract

Photoirradiation effect on potential response to metal ion concentrations and photoinduced potential change were investigated with poly(vinyl chloride) membranes based on a Malachite Green derivative carrying a bis(monoaza-15-crown-5) moiety, by comparing other Malachite Green derivatives. The Malachite Green carrying a bis(crown ether) moiety caused a potential response to potassium ion concentration changes under dark condition. In the membrane potential response, a clear-cut photoinduced switching of potential response was realized by the membrane of Malachite Green carrying a bis(crown ether) moiety, which exhibited no potential response to potassium ion concentrations (0 mV/decade) on UV irradiation. On the other hand, a Malachite Green carrying a monocyclic benzocrown ether moiety showed a considerable dependence of the membrane potential on the metal ion concentrations under both dark and UV irradiation conditions.

Introduction

Malachite Green leuconitrile undergoes photoionization to a conjugate triphenylmethyl cation and a cyanide ion with high quantum efficiency [1, 2], providing a molecular system sensitive to UV light. We have already proposed the photochemical control of cation complexation by crowned Malachite Green derivatives [3–5]. In particular, Malachite Green derivative carrying a bis(monoaza-15-crown-5) moiety **1** realized so-called all-or-none type photochemical control of cation complexation by complete release of a complexed metal ion after UV irradiation (Scheme 1). When the monoaza-15-crown-5 moiety possesses a positive charge on its nitrogen atom, electrostatic repulsion between the positive charge on the crown ether ring and a crown-complexed metal ion results in an effective release of the metal ion. On the other hand, Malachite Green derivative carrying a monocyclic benzocrown ether moiety **2** does not release a crown-complexed metal ion completely by the ionization of its photochromic moiety after UV irradiation [3, 4]. It is probably because the crown ether ring of Malachite Green carrying a monocyclic crown ether moiety **2** is fused to a benzene

ring, which does not participate significantly in the delocalization of a positive charge in the conjugated ionized system (Scheme 2).

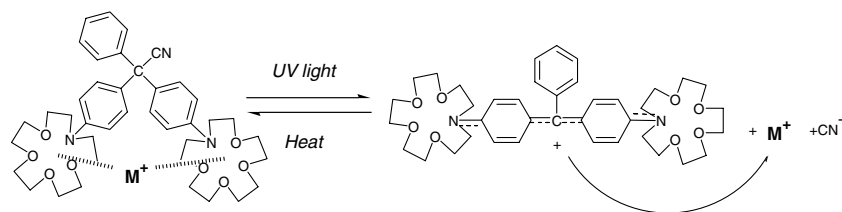
It is very interesting to see how the drastic change in the cation-complexing ability by Malachite Green carrying a bis(crown ether) moiety **1** is reflected in potential response of membranes incorporating the photosensitive compound and if photochemical switching in the ion selectivity for the membrane ion sensors is feasible. Here we report photoinduced switching of potential response for poly(vinyl chloride) (PVC) membranes containing Malachite Green **1** to metal-ion concentration changes. A comparison with membranes of Malachite Green carrying a monocyclic crown ether moiety **2** is also mentioned. Furthermore, the potential photoresponse is discussed by comparing Malachite Green **1** with Malachite Green carrying no crown ether moiety **3**.

Experimental

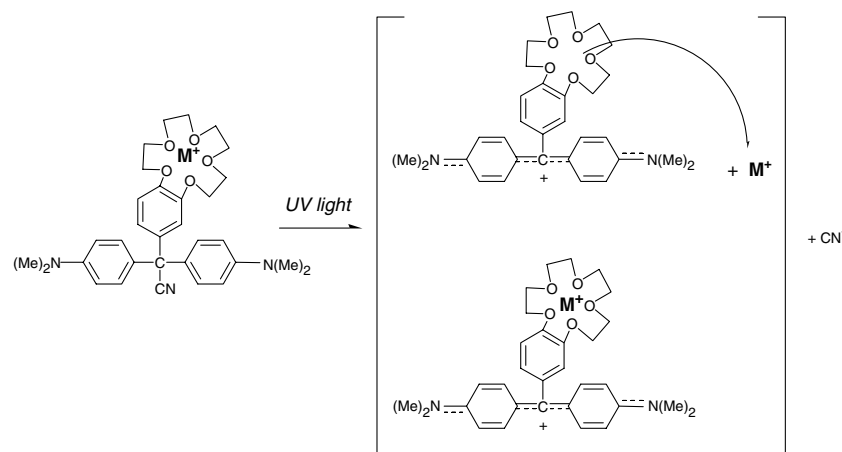
Materials

The synthesis of crowned Malachite Green derivatives **1** and **2**, and reference compound **3** is described elsewhere

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Scheme 1.



Scheme 2.

[4–6] See Chart 1. PVC with an average polymerization degree of 1100 was purified by reprecipitation from tetrahydrofuran (THF) solution with methanol. Bis(2-ethylhexyl)sebacate (DOS) was purified by vacuum

distillation. THF was distilled over Na metal. Alkali metal chlorides were analytical reagent grade. Water was deionized. Picric acid and alkali metal hydroxides were analytical grade and 1,2-dichloroethane was spectroscopy grade for extraction measurement.

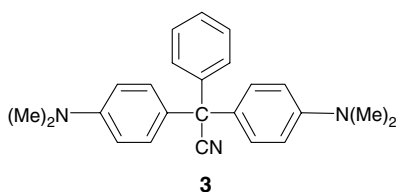
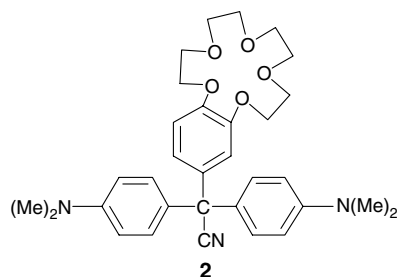
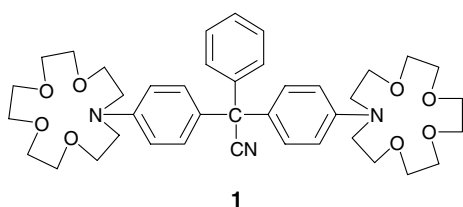


Chart 1.

Measurements

Preparation of membrane

PVC membranes were prepared by pouring the mixture of PVC (50 mg), DOS (200 mg), a Malachite Green derivative (5 mg), and THF (2 cm³) onto a flat Petri dish of 3 cm inner diameter. After allowing the solution to evaporate for three days, the membrane disk was cut off from the dish and conditioned by soaking in alkali metal chloride solution (1 × 10⁻⁶ mol dm⁻³) overnight.

Membrane potential measurement

Electromotive force (e.m.f) measurements were done by using a cell described elsewhere [7]. A U-type cell equipped with a quartz window was used for photoirradiation at 25 °C. In a measurement cell, a membrane with an effective area of 0.785 cm² separated two aqueous phases. The electrochemical cell was Ag | AgCl | 1 × 10⁻³ mol dm⁻³ alkali metal chloride | membrane | measuring solution || 0.1 mol dm⁻³ NH₄NO₃ || 3 mol dm⁻³ KCl | AgCl | Ag. The measuring solution contained various concentrations of sodium chloride or potassium chloride. The alkali metal chloride solution at the opposite side of the measuring solutions

contained the same salt as the measuring solution with a concentration of $1 \times 10^{-3} \text{ mol dm}^{-3}$. The pH of measuring solution was adjusted by CsOH or HCl solution. The complexation of cesium ion with Malachite Green derivatives was considered negligible as our previously reported extraction data had indicated [8]. Photoirradiation of the membrane was achieved from the measuring solution through a quartz window. UV light source ($< 330 \text{ nm}$) was a xenon lamp (500 W) equipped with a photoguide tube and a Toshiba UV-D33S filter.

Absorption Spectra

Membranes for absorption-spectral measurements were prepared in a similar way to those for the e.m.f. measurements with some difference in the membrane thickness, i.e. twice as thin as that for e.m.f. measurement. After conditioning with alkali metal chloride solution ($1 \times 10^{-6} \text{ mol dm}^{-3}$) overnight, the membrane was attached to inner wall of a quartz cell for absorption measurements. The cell was filled with 3 cm^3 of potassium chloride solution ($1 \times 10^{-3} \text{ mol dm}^{-3}$) at various pH. Photoirradiation was carried out for three minutes.

Extraction

An aqueous solution (5 cm^3) containing $7.0 \times 10^{-5} \text{ mol dm}^{-3}$ picric acid and 0.1 mol dm^{-3} alkali metal hydroxide was vigorously shaken with an equal volume of 1,2-dichloroethane solution containing $2.1 \times 10^{-3} \text{ mol dm}^{-3}$ Malachite Green **1** or **2** under dark condition for 15 min by using a reciprocating shaker. After phase separation, the concentration of picric acid in aqueous phase was measured by absorption spectroscopy at 350 nm. The extraction percentage was calculated as $(A_0 - A)/A_0 \times 100$, where A_0 and A denote the absorbance at 350 nm before and after the extraction, respectively.

Results and discussion

Potential response to metal ion under dark condition

Figure 1 shows typical membrane potential responses to potassium ion concentration changes under dark condition. The membrane potential for Malachite Green carrying a bis(crown ether) moiety **1** and Malachite Green carrying a monocyclic crown ether moiety **2** was increased with potassium ion concentration. The slopes for the calibration plots are 29 mV/decade for **1** and 56 mV/decade for **2** at pH 10 in the range of potassium ion concentration higher than $1 \times 10^{-3} \text{ mol dm}^{-3}$. The membranes containing Malachite Green **2** exhibited a higher sensitivity to potassium ion concentration than the membranes containing Malachite Green **1**. We consider that the sensitivity depends on their metal-ion binding property of crowned Malachite Green derivatives. A liquid-liquid extraction process is concerned with the distribution of metal ions between

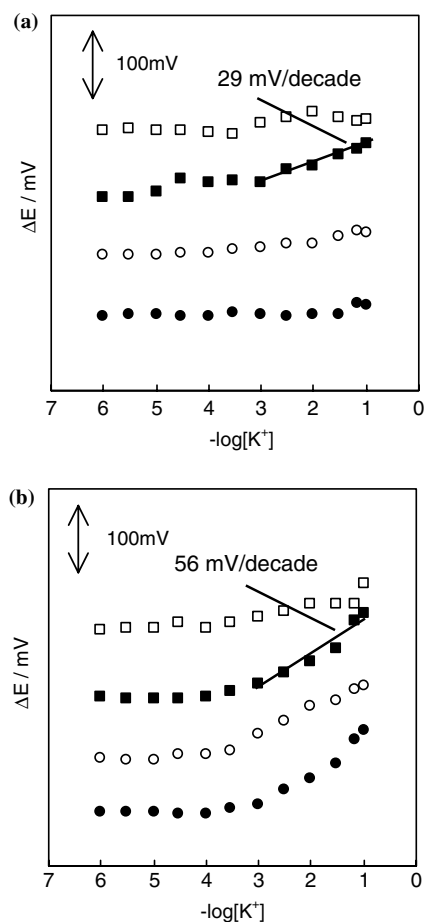


Figure 1. Potential response for membrane containing Malachite Green derivative **1** (a) and **2** (b) under dark condition at pH 6 (●), pH 8 (○), pH 10 (■), and pH 12 (□).

organic and aqueous phases. Thus, the membrane potential response is related to metal-ion complexation equilibrium at the interface of lipophilic membrane and aqueous phase. Figure 2 shows extraction percentages by crowned Malachite Green derivatives, indicating the

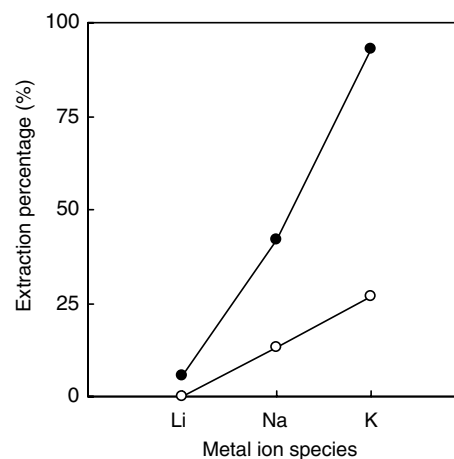


Figure 2. Alkali metal ion extraction by Malachite Green derivative **1** (○) and **2** (●).

high extractability of Malachite Green **2**. A considerably high percentage was obtained especially for potassium ion extraction. A potassium ion is bound intermolecularly by two independent crown ether rings of **2** and then the formation of 1:2 complex of potassium ion and **2** promotes the potassium ion extraction to organic phase. On the other hand, the two adjacent azacrown rings of Malachite Green **1** are responsible for binding a potassium ion. Then, the 1:1 complex of potassium ion and Malachite Green **1** is inferior to the 1:2 complex of potassium ion and Malachite Green **2** in the cation extractability from the viewpoint of the metal-ion complex lipophilicity. Since a crown ether ring of Malachite Green **2** is occupied by one sodium ion, forming 1:1 complex of sodium ion and **2**, the extraction percentage for sodium ion was lower than for potassium ion due to the lower lipophilicity.

For the membranes containing Malachite Green **1**, the higher sensitivity to potassium ion was obtained under higher pH condition (Figure 1(a)). It is considered that nitrogen atoms of monoaza-15-crown-5 of Malachite Green **1** underwent protonation which resulted in poor cation-complexing ability of **1** at lower pH. On the other hand, no significant pH dependence on the potential response to potassium ion was observed for the membrane containing Malachite Green carrying **2** (Figure 1(b)), because the benzocrown ring of Malachite Green **2** does not have any nitrogen atom for protonation. Despite that the metal ion complexation is hardly disturbed by the protonation at pH 12, the potential response showed a very slight increase with metal ion concentrations for the membranes containing **1** and **2** (Figure 1). Though the reason is not obvious, we speculate that excess hydroxide ion interferes with metal ion complexation of crowned Malachite Green derivatives.

Photoinduced changes of potential response to metal ion

As shown in Figure 1(a), the membrane potential response was increased with potassium ion concentration in the system of Malachite Green carrying a bis(crown ether) moiety **1** under dark condition. However, under UV irradiation (Figure 3(a)), the addition of potassium ion did not cause any potential change in the membrane system of Malachite Green **1**, exhibiting no potential response to potassium ion concentration changes (0 mV/decade) at any pH. In contrast, the potential of membrane containing **2** was increased with potassium ion concentration even on UV irradiation, still maintaining 51 mV/decade at pH 10 (Figure 3(b)). The slope in the calibration plots at pH 10 was as steep as at the other pH for the system of Malachite Green **2**. Thus, so called all-or-none type photoinduced switching of potential response was accomplished by the membrane containing **1** unlike membrane containing **2**. We also followed photoinduced changes in the potential response to sodium ion concentrations for the mem-

branes containing **1** and **2** (data not shown). In sodium chloride solution, drastic photoinduced changes were also attained for the membrane containing Malachite Green **1**. For the membrane containing Malachite Green **2**, the potential response exhibited very little increase with sodium ion concentration under dark condition. For a discussion about the photoinduced change in the potential response to metal ion, it is important to compare the extraction percentage before and after UV irradiation. However, we could not obtain the extraction percentage after photoirradiation, because the photoionized Malachite Green outflowed into the aqueous phase, making difficult assessment of the extraction percentage.

We conclude that the difference in the photoinduced changes of membrane potential for membrane containing **1** and **2** arises from the photoinduced changes of cation binding ability of the ion carriers. In contrast to Malachite Green **2** which still binds metal ion(s) after UV irradiation (Scheme 2), the photogenerated positive charge results in the effective release of a crown-complexed metal ion in the system of Malachite Green **1** (Scheme 1) as our previous work [3] has elucidated by electrospray ionization mass spectroscopy. Thus the

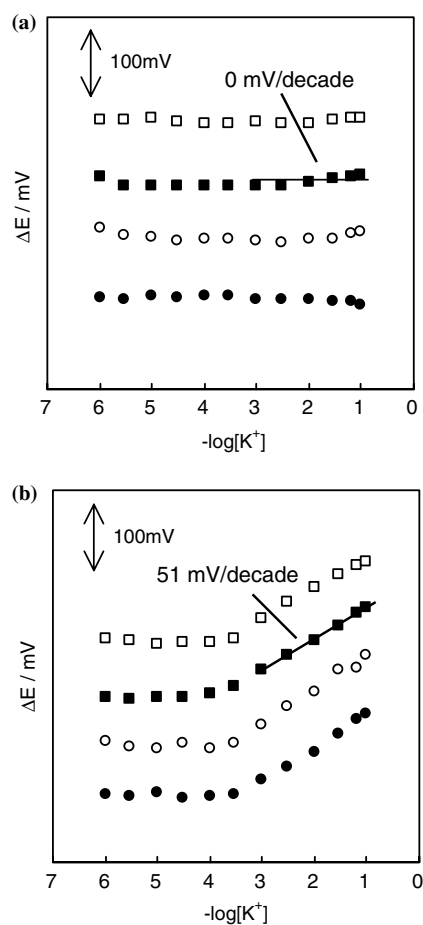


Figure 3. Potential response for membrane containing Malachite Green derivative **1** (a) and **2** (b) under UV irradiation. The symbols used are the same as in Figure 1.

molecular system for photochemical control of metal ion complexation by Malachite Green **1** is superior to that by Malachite Green **2**, which do not induce any significant photoinduced change in the potential response to metal ion concentration changes.

Photoresponse of membrane potential change

Photoresponse of membrane potential has been reported for some photochromic compounds undergoing photoinduced charge generation, such as spiropyran derivatives [9–11], and azobenzene derivatives altering cation-binding ability by photoinduced structural change [12–14]. Malachite Green carrying a bis(crown ether) moiety **1** affords generation of a positive charge and thereby photocontrol of cation complexation. Therefore, it is also interesting to investigate photoinduced potential response for the membranes containing Malachite Green **1**, and to compare Malachite Green **3** for investigation of metal–ion complexation effect on the membrane potential photoresponse. UV irradiation increased the potential change for the membrane containing Malachite Green **3**, as shown with ΔE_1 in Figure 4, which is in turn induced by the ionized Malachite Green generated after UV irradiation (Scheme 3). On turning off UV light, the membrane potential decreased and then leveled off, but it did not reach the original level before photoirradiation. After turning off the light, the backward reaction causes isomerization from the ionized Malachite Green to the electrically neutral Malachite Green leuconitrile (Scheme 3). Some ionized Malachite Green molecules still exist under dark condition, resulting in the higher potential level than that before UV irradiation. Thus, by turning on the light again, the less positive charge was induced on the membrane surface, leading to the smaller photoinduced potential change ΔE_2 (Figure 4). The first photoirradiation induced the maximum potential change for each membrane and the further irradiation caused the smaller potential change than the first one

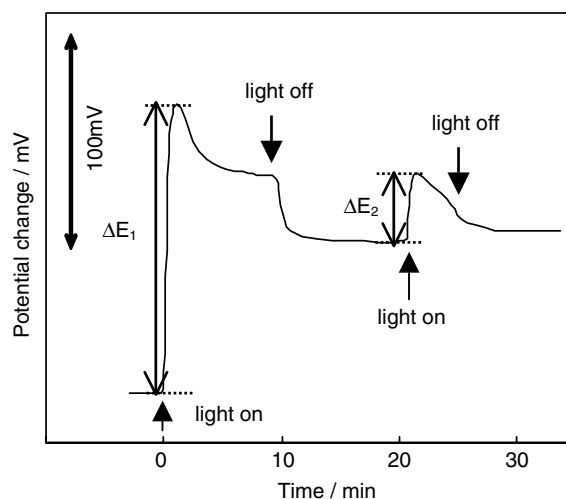
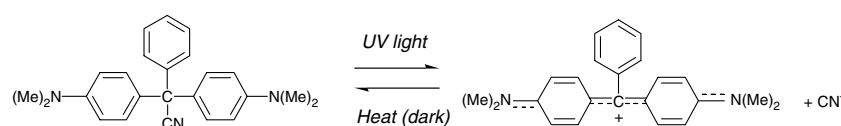


Figure 4. Time-course changes of membrane potentials for the system of Malachite Green derivative **3** on photo-irradiation in 0.1 mol dm^{-3} NaCl aqueous solution at pH 10. ΔE_1 and ΔE_2 are potential change induced by the first and the second irradiation, respectively.

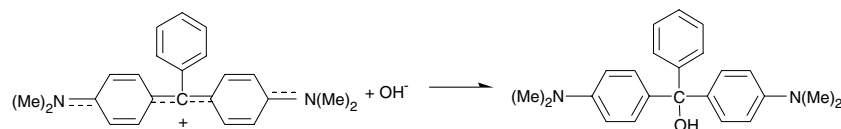
did ($\Delta E_2 < \Delta E_1$). The potential changes upon turning on or off the light are originated from the photoionization of Malachite Green derivatives and not by photoinduced temperature increase, because the membranes not containing any Malachite Green derivative never exhibited potential change by photoirradiation. The values of membrane potential changes induced by the first irradiation (ΔE_1) are summarized in Table 1, showing photoinduced potential changes under various pH conditions. The value of photoinduced potential change for the membrane containing Malachite Green **3** was obviously lowered under the higher pH conditions. The high pH conditions accelerated the backward reaction because electrically neutral Malachite Green (leucohydroxide) was generated by the hydroxylation of ionized Malachite Green as shown in Scheme 4. The similar time-course changes of membrane potentials (Figure 4) were observed in the system of Malachite Green **1** which exhibits the same tendency of pH



Scheme 3.

Table 1. Photoinduced potential changes of PVC membrane in 0.1 mol dm^{-3} alkali metal chloride solution by the first irradiation

Malachite Green derivative / alkali metal chloride	Membrane potential / mV			
	pH 6	pH 8	pH 10	pH 12
3/NaCl	136 ± 6	131 ± 4	120 ± 22	84 ± 10
1/NaCl	104 ± 3	74 ± 1	66 ± 11	33 ± 7
1/KCl	111 ± 4	93 ± 9	83 ± 16	17 ± 7



Scheme 4.

dependence on the photoinduced potential change with sodium and potassium ions. Table 1 indicates that the hydroxylation also affected the pH dependence on the photoinduced potential change in the system of Malachite Green **1**. Absorption-spectral changes in the membranes containing Malachite Green **1** and Malachite Green **3** support the pH dependence on photoinduced potential change (Figures 5 and 6). Under dark condition, no significant peak at visible region was observed (Figures 5(a) and 6(a)) and an absorption peak around 620 nm, assigned to the ionized Malachite Green, appeared by UV light irradiation (Figure 5(b)–(e) and Figure 6(b)–(e)). By increasing pH, the absorbance at 620 nm was diminished in the systems of Malachite Green **1** and Malachite Green **3**. It indicates that the photoionized Malachite Green was formed under the higher pH conditions while the positive charge disappeared consequently by hydroxylation (Scheme 4). The absorbance at pH 6 in the systems of **1** and **3** was smaller than expected (Figures 5(b) and 6(b)). Under acidic condition at pH 6, the aqueous solution in a sample cell turned green after UV irradiation. Since the hydroxylation is negligible at pH 6, the Malachite Green ionization is promoted. Thus, the ionized Malachite Green was removed from the PVC membrane, resulting in the smaller absorbance at pH 6.

Comparing the photoinduced potential changes between the membranes containing Malachite Green **1**

and Malachite Green **3** at the same pH, the e.m.f. value was smaller in the first system (Table 1). For instance, 66 mV of e.m.f. for the **1** – NaCl system at pH 10 is smaller than that for the **3** – NaCl system by 54 mV. Under any of the pH conditions, a smaller potential change was observed for the **1** – NaCl system by about 50 mV, as compared with the **3** – NaCl system. Therefore, we consider that the metal ion complexation of Malachite Green **1** caused the smaller potential change in its membrane system. A sodium ion is complexed by Malachite Green **1** on the membrane surface under dark condition and the ion is released after UV irradiation (Scheme 1). As a result of the metal ion releasing from the crown ether ring of **1**, the positive charge of crown-complexed metal ion disappears at the membrane surface. The charge loss is subsequently compensated by the photogenerated positive charge of the ionized Malachite Green. Consequently, a photoinduced potential change was observed as the potential gap between the crown-complexed metal ion under dark condition and the ionized Malachite Green after UV irradiation. Since Malachite Green **3** does not bind any metal ion, it induced a greater photoinduced potential change than Malachite Green **1** did. Potassium ion also affected the photoinduced potential change of membrane containing Malachite Green **1** and a smaller value than that for Malachite Green **3** was observed. We suppose that complexation of Malachite Green **1** with

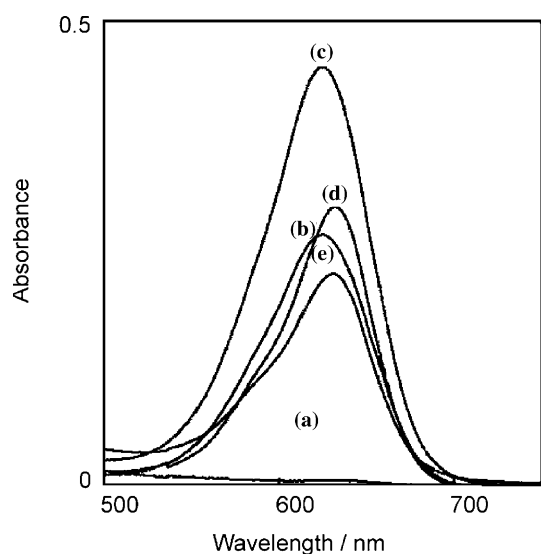


Figure 5. Absorption-spectral change of PVC membrane containing Malachite Green derivative **1** under dark condition (a) and after UV irradiation at pH 6 (b), pH 8 (c), pH 10 (d), and pH 12 (e).

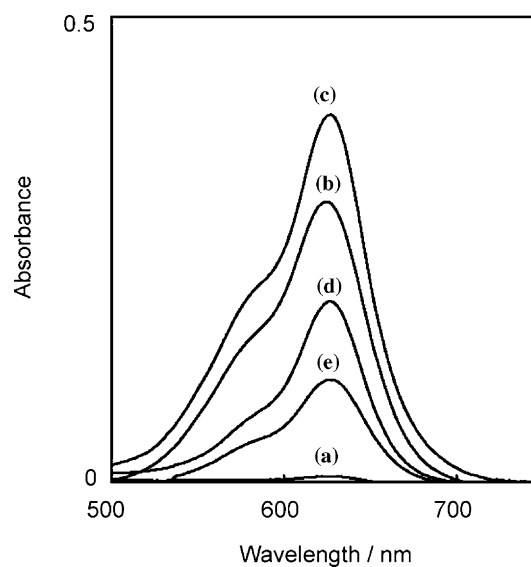


Figure 6. Absorption-spectral change of PVC membrane containing Malachite Green derivative **3** under dark condition (a) and after UV irradiation at pH 6 (b), pH 8 (c), pH 10 (d), and pH 12 (e).

potassium ion differs from that with sodium ion; the two adjacent crown rings of Malachite Green **1** are responsible for potassium ion binding and one of the crown ether ring is enough to bind a sodium ion. However, we did not find any significant difference in the photoinduced potential change for sodium ion and potassium ion as shown in Table 1.

Conclusion

The photoinduced potential change for plasticized PVC membranes containing a Malachite Green derivative was affected by its metal-ion complexing ability and by pH in aqueous solution. Thus, a perfect photoinduced switching in the potential response to metal-ion concentrations was realized by the membrane containing Malachite Green carrying a bis(crown ether) moiety **1**. Malachite Green **1** undergoes photoionization by UV irradiation, which induces release of complexed metal ion as a result of the electrostatic repulsion caused by the photoinduced cation species. This result may suggest a possibility for photochemical ion-selectivity switching between cation and anion. After UV irradiation, a positive charge of ionized Malachite Green is left on membrane surface and in turn attracts a negative charge. Thus, Malachite Green **1** might work as a cation sensor under dark condition and it is switched to an anion sensor by UV irradiation. The photochemical selectivity switching between cation and anion is expected to realize sophisticated ion-sensing systems, especially in aprotic organic solutions that do not bring about the protonation and hydroxylation of the photoinduced Malachite Green cationic species.

Acknowledgements

Financial support by Grant-in-Aids for Scientific Research (No.15750164 and No. 15350043) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan is gratefully acknowledged.

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