Effective Photocontrol of Micelle Formation by Malachite Green Derivative Carrying a Long Alkyl Chain

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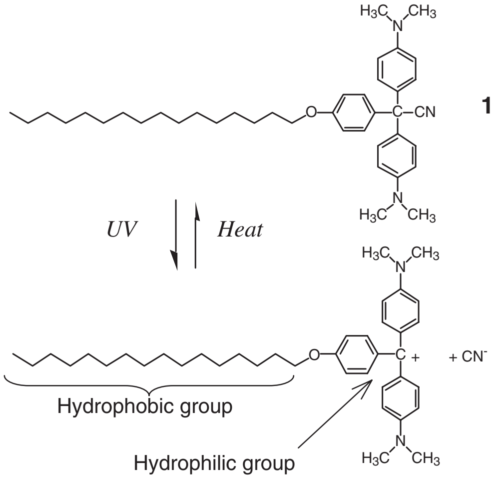
(Received February 12, 2004; CL-040165)

We designed Malachite Green leuconitrile carrying a long alkyl chain that is intended for a photoresponsive surfactant. The critical micelle concentration of cetyltrimethylammoium chloride solution containing the photoresponsive compound was decreased significantly by UV irradiation. The lipophilic photochromic compound realizes photochemical control of micelle formation.

The widespread use of surfactant mixtures for the industrial purpose has stimulated the interest of researchers in the control of formation and rupture of surfactant assemblies such as micelles. In aqueous solution, micelles solubilize lipophilic substance in their interior which consists of hydrophobic group of surfactant. Many studies aiming at the control of uptake and release of lipophilic substance were carried out by external stimulation using pH,[1] temperature,[2] and additives.[3] In particular, light is one of the most desirable stimulation for clean and rapid control of micelle formation.



Scheme 1.

Photochromic compounds such as azobenzene,[4–6] spiropyran,[7] and stilbene[8] were introduced to amphiphilic molecules for photochemical control of micelle and vesicle. Photoinduced trans–cis isomerization of azobenzene and stilbene derivatives induces a structural change, while photoirradiation of spiropyran derivatives generates a zwitter ion on the molecule. Nevertheless, photoinduced single-charge generation on amphiphilic molecules was scarcely reported. We have designed Malachite Green leuconitrile carrying a long alkyl chain **1** (Scheme 1), which controls micelle formation photochemically. Malachite Green leuconitrile, a triphenylmethane dye, undergoes photoionization by dissociating cyanide ion with a high quantum efficiency,[9,10] thus affording a positive charge generation on the molecule by UV irradiation. Therefore, when ionized photochemically, **1** exhibits both hydrophilicity by its triphenylmethyl cation and hydrophobicity by its long alkyl chain (Scheme 1). The photoionized charge is delocalized in the conjugate system of its triphenylmethane moiety including two nitrogen atoms at the dimethylaniline group and an oxygen atom at the hexadecyloxybenzene group. One of its resonance contributors is shown in Scheme 1. On the other hand, under dark condition, **1** behaves only as a lipophilic compound. Once it is irradiated by UV light, it turns into a cationic surfactant. Thus, a drastic effect on micelle formation is expected. Here we report the effective control of micelle formation by the photoresponsive Malachite Green surfactant **1**.

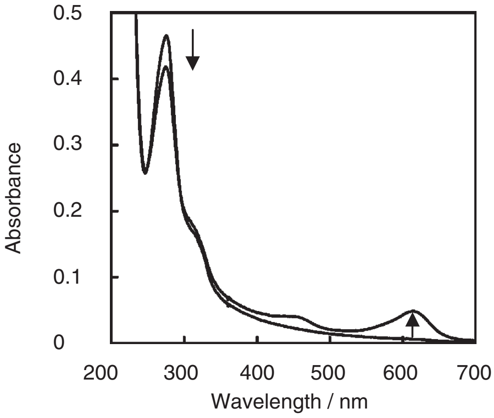


Figure 1. Absorption-spectral changes of 0.1 mol·dm^{-3} acetate buffer solution containing 1×10^{-3} mol·dm^{-3} CTAC and 1×10^{-5} mol·dm^{-3} Malachite Green derivative **1** under dark condition and after UV irradiation for 15 min. The arrows denote peaks changed by photoirradiation.

Bis[4-(*N*,*N*-dimethylamino)phenyl][4-(hexadecyloxy)phenyl]-acetonitrile (**1**) was synthesized by 4-lithiated *N*,*N*-dimethylaniline with methyl 4-hexadecyloxybenzoate, followed by cyanization of resulting Malachite Green hydroxide. The sample solutions for the photoresponsive micelle were 0.1 mol·dm^{-3} acetate buffer solution at pH 4.8 containing 1.0×10^{-5} mol·dm^{-3} **1** and an appropriate concentration of cetyltrimethylammoium chloride (CTAC). Even without photoirradiation, the ionization of **1** was strongly promoted in more acidic solutions than pH 4.0. When the pH of sample solution was above 5.0, the photoionized **1** was immediately hydroxylated and the positive charge on the Malachite Green moiety disappeared. Therefore, an appropriate buffer solution was necessary for all samples in this work. Cationic surfactant CTAC was added for dissolving electrically neutral **1**. The Malachite Green derivative **1** has the same length of hydrophobic chain as CTAC does. Hence, the Malachite Green derivative **1** ionized by UV irradiation is considered to participate in CTAC micelle formation. The light source (<330 nm) was a xenon lamp (500 W) equipped with a photoguide tube and a Toshiba UV-D33S color filter. The photoirradiation was carried out for 15 minutes. The critical micelle concentration (cmc) determination was performed by measuring the electric conductivity of sample solution.

Figure 1 shows a typical absorption-spectral change of the sample solution before and after UV irradiation. An absorption peak around 270 nm decreasing by UV irradiation was assigned to the electrically neutral leuconitrile form of **1**. Its ionized form was confirmed by a peak at 610 nm after UV irradiation, indicating the photoinduced ionization of **1**.

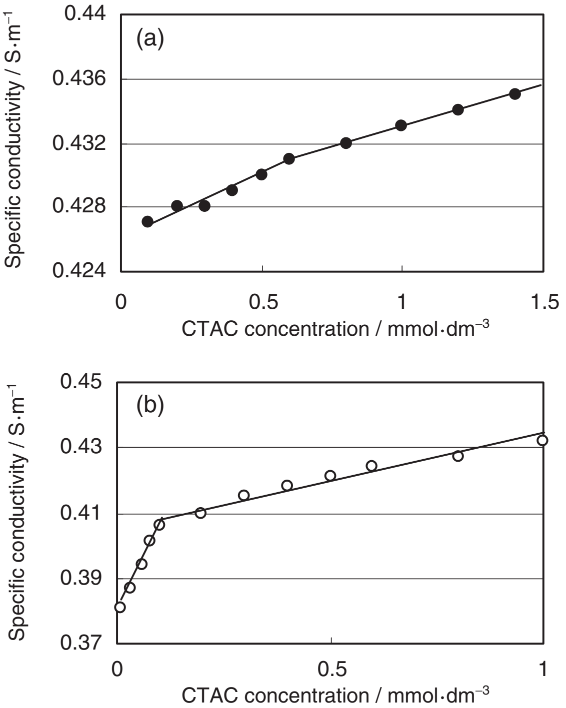


Figure 2. Specific conductivity of 0.1 mol·dm^{-3} acetate buffer solution containing CTAC and 1×10^{-5} mol·dm^{-3} Malachite Green derivative **1** as a function of CTAC concentration under dark condition (a) and after UV irradiation (b).

Figure 2 shows the dependence of specific conductivity of the sample solutions on CTAC concentration. The specific conductivity increased linearly with CTAC concentration and the slope of the conductivity curve changes abruptly at a certain concentration. The cmc values correspond to the bending point on the conductivity curve.[11] Under dark condition, the cmc was found to be 0.6 mmol·dm^{-3} (Figure 2a), which is smaller than a reported value (1.3 mmol·dm^{-3}) for CTAC.[12] Since addition of electrolytes such as NaCl generally diminishes cmc values of surfactants,[12,13] the smaller cmc value was caused by acetate ions for pH buffer in our samples. UV irradiation decreased the cmc to 0.1 mmol·dm^{-3} (Figure 2b). This is probably because the photoionized **1** behaves as cationic surfactant; a smaller amount of CTAC was consequently required to form the micelle. This "cmc shift" indicates that photochemical control of micelle formation can be accomplished by the Malachite Green derivative **1**.

The drastic cmc change is obviously induced by the remarkable feature of **1**, i.e. photogenerated amphiphilicity from the simply lipophilic substance. However, Malachite Green surfactant **1** gave a greater effect on CTAC micelle than expected because the amount of 1.0×10^{-5} mol·dm^{-3} for **1** might be too small to cause the cmc change from 0.6 mmol·dm^{-3} to 0.1 mmol·dm^{-3}. We consider that the geometry of ionized **1** and photogenerated electrolyte are responsible for it. Since the photoionized **1** has a bigger hydrophilic head group than CTAC does, it affects the shape or aggregation number of CTAC micelle. Israelachvili et al. reported the relationship between cmc and micelle aggregation number and the influence of micelle shape on cmc.[13] Though the data of the micelle shape and aggregation number for the present system have not been obtained yet, one may speculate that the big head group of the Malachite Green surfactant **1** affects the cmc considerably. Another plausible factor that we should consider is the electrolytic property in micelle solution generated by the photochemical ionization of **1** corresponding to its cationic dye and cyanide ion (Scheme 1). As discussed above, the addition of electrolyte lowers the cmc and therefore photogenerated ions also contribute to the decreased cmc.

We conclude that photochemical control of micelle formation was achieved by the Malachite Green leuconitrile carrying a long alkyl chain **1**. Furthermore, a slight amount of **1** caused such a significant decrease of the cmc by UV irradiation. Photocontrol of uptaking and releasing oily substance may be expected to be realized by this Malachite Green derivative **1** system. Studies concerning the micelle shape, aggregation number, and Malachite Green location in micelle are now under way.

Financial support by Grant-in-Aids for Scientific Research (No.15750164 and No. 15350043) from the Japan Society of the Primotion of Science is gratefully acknowledged.

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