

Functionalization of Photoresponsive Molecular Assemblies Using the Inner Environments

(¹*Faculty of Science and Technology, Tokyo University of Science, Japan*)

○Masaaki Akamatsu¹

Keywords: Photochromism, Surfactant, Micelle, Confined space, Controlled release

1. Introduction

Photoresponsive molecular assemblies have promising applications, such as controlled release of drugs or active components and efficient heat transfers (Fig. 1). However, conventional systems require minutes or hours to induce significant variations in the properties, that is problematic for the practical applications. Lophine dimer that rapidly dissociates into two lophyl radicals upon ultraviolet (UV) light irradiation, and these radical species thermally recover to the initial dimer through recombination (Fig. 2). Although this thermal recombination reaction is extremely slow owing to free diffusion of the radicals in solution, Abe accomplished rapid recombination by covalently bounding two lophine units to inhibit diffusion of the radicals¹. We also demonstrated accelerated recombination of simple lophine dimers, solubilized in a micellar solution². This result indicates that inside of the micelles are useful for rapid recombination of the lophyl radicals. In this work, we tried rapid control of interfacial properties with the amphiphilic lophine dimers upon UV light irradiation. Furthermore, we monitored rapid morphological changes in the amphiphilic lophine dimer micelles and demonstrated photo-induced rapid controlled release of a solubilize by using an *in-situ* small-angle neutron scattering (SANS).

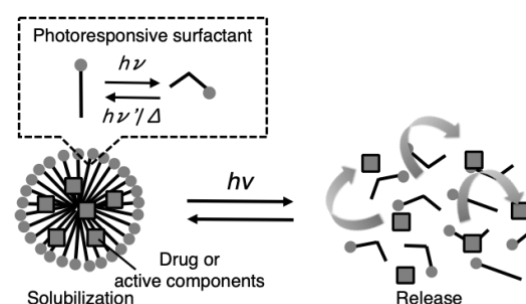


Fig. 1. Controlled release by using photoresponsive molecular assemblies.

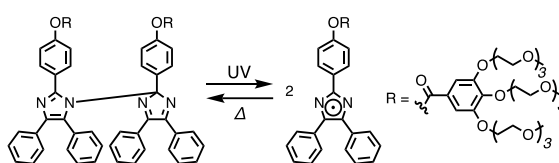


Fig. 2. Photoisomerization of the amphiphilic LPD (3TEG-LPD).

2. Experiment

The amphiphilic lophine dimer (3TEG-LPD) was synthesized (Fig. 2). Surface tension measurements were performed with the Wilhelmy plate method. SANS measurement of 5.0 mM 3TEG-LPD in D₂O was performed on SANS instrument (J-PARC MLF, BL-15 TAIKAN) equipped with an UV light irradiator and an UV/vis absorption spectrometer.

3. Results and Discussion

The photoisomerization of the amphiphilic lophine dimer (3TEG-LPD) in water was

evaluated by changes in the absorption band owing to the lophyl radical on the UV/vis absorption spectra upon UV light irradiation. The recombination rate of the lophyl radicals on a micellar solution of 3TEG-LPD was accelerated 800-fold in comparison with that in an organic solvent owing to restricted diffusion of the radical species. This result indicates that the confined and highly concentrated amphiphilic lophine dimer derivatives show rapid recombination of the lophyl radicals produced by UV light irradiation.

Rapid control of an interfacial property was investigated by using 3TEG-LPD. The static surface tension on the aqueous 3TEG-LPD solution decreased within several ten seconds upon UV light irradiation. Afterward, when the photoirradiation stopped, the surface tension immediately recovered to the original value. These reversible changes were repeatedly observed. The decrease in the surface tension value upon UV irradiation suggested that the produced lophyl radical, which is less bulky than the initial dimer form, efficiently adsorbs at the air/water interface. After the irradiation was stopped, the recombination of the lophyl radicals readily proceeded in the micelles of the bulk phase or in the Gibbs monolayer formed at the air/water interface. From these results, we successfully demonstrated reversible and quick control of the surface tension using fast dissociation of the lophine dimer upon photoirradiation and accelerated the recombination of the radicals in the micelles.

Next, we have monitored morphological changes in the 3TEG-LPD micelle by using SANS. Fig. 3 showed the *in-situ* SANS results of 3TEG-LPD in D₂O. By UV light irradiation, the SANS profiles changed rapidly and reversibly, which is due to elongation of the 3TEG-LPD micelle. Furthermore, rapid photo-induced release of calcein as a model drug, solubilized in the 3TEG-LPD micelle was successfully monitored by a fluorescence spectroscopy and the *in-situ* SANS.

In conclusion, we successfully demonstrated accelerated photoisomerization of amphiphilic lophine dimers with inside of the micelles and rapid control of surface tension of the aqueous solution by UV light irradiation. *in-situ* SANS measurements revealed rapid morphological change in the micelle and controlled release of the model drug^{3,4}.

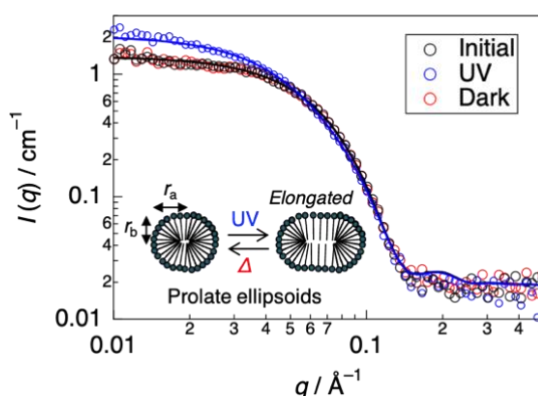


Fig. 3. SANS profiles of 3TEG-LPD in D₂O under UV light irradiation.

References 1) J. Abe et al. *J. Phys. Org. Chem.* **2007**, *20*, 857. 2) M. Akamatsu, H. Sakai, et al. *Chem. Lett.* **2018**, *47*, 113. 3) M. Akamatsu, K. Kobayashi, K. Sakai, H. Sakai. *Chem. Commun.* **2019**, *55*, 9769. *selected as outside back cover* 4) M. Akamatsu, K. Kobayashi, H. Iwase, Y. Sakaguchi, R. Tanaka, K. Sakai, H. Sakai. *Sci. Rep.* **2021**, *11*, 10574.