Spatiotemporal Control of Photochromic Reactions Based on Oxygen Transfer Suppressed in Supramolecular Gel

Sota Fujisaki,[a] Yoshinori Okayasu,[a] Yuki Nagai,[a] Yoichi Kobayashi[a,b]
[a]*Department of Applied Chemistry, College of Life Sciences, Ritsumeikan University. E-mail: ykobayas@fc.ritsumei.ac.jp*
[b]*PRESTO JST*

In photofunctional materials utilizing triplet excitons, preventing triplet quenching by molecular oxygen (O_2) is an important issue. On the other hand, if the triplet quenching process can be arbitrarily controlled rather than simply prevented, it will lead to the development of unique photoresponsivity. In this study, we focus on the photochromic reaction of anthraquinone (AQ, Fig. 1a) as a model reaction.[1] The colorless and nonemissive AQ form is converted to the yellow and emissive AQH_2 form via photoexcitation to the S_1 state and subsequent intersystem crossing to the T_1 state, while the AQH_2 form is reversibly oxidized to AQ by O_2. We achieved spatiotemporal control of this photochromic reaction based on O_2 transfer suppressed in a supramolecular gel.[2]

A supramolecular gel was prepared by adding a gelator to a methanol solution of AQ containing triethylamine as a singlet oxygen scavenger. When this gel was irradiated with 365-nm light, a new absorption peak at around 400 nm was produced due to the photoreduction to AOH_2 (Fig. 1b). Interestingly, the absorbance at 400 nm remained unchanged for the initial stage of the photoirradiation and began to increase several tens of seconds after starting the irradiation. This unique behavior is explained as follows; At first, the photogenerated T_1 state of AQ is quenched by O_2 dissolved in the gel to produce singlet oxygen and then the singlet oxygen is consumed mainly by reaction with triethylamine. Because O_2 supply from the air through diffusion and convection is efficiently suppressed due to the supramolecular gel network, the O_2 concentration in the gel is gradually decreased, which finally triggers the photoreduction of AQ via the T_1 state. In addition, while the AQH_2 showed a lifetime of over 1 hour in the gel state, the decoloration was completed instantly upon the gel-to-sol transition by heating. This is because the sol state allows quick O_2 supply from the air in contrast to the gel state. Moreover, spatiotemporal patterning and on-demand erasing of the photochromic reaction were conducted to demonstrate the potential in application to cryptography and display devices.

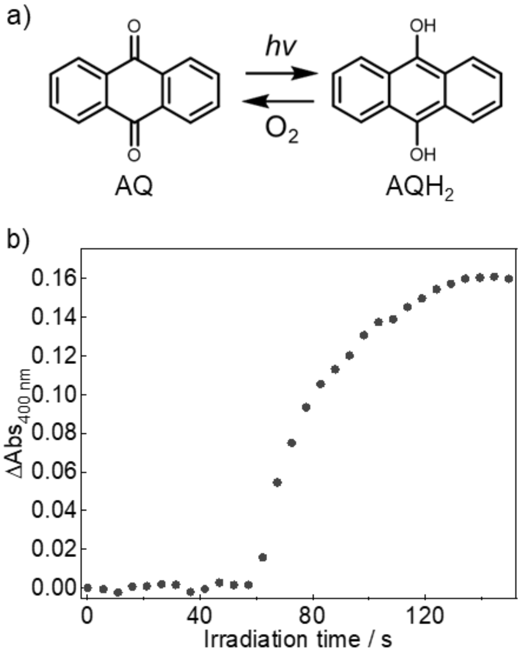

Fig.1 a) Photochromic reaction of AQ, b) Absorbance change of the MeOH gel of AQ under 365-nm light irradiation.

1) K. Hamanoue, T. Nakayama, Y. Yamamoto, K. Sawada, Y. Yuhara, H. Teranishi., *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1121.
2) P. Duan, N. Yanai, H. Nagatomi, N. Kimizuka, *J. Am. Chem. Soc.* **2015**, *137*, 1887.