Two-phase photoreduction of quinones sensitized by porphyrins

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Keywords: porphyrin, quinone, Two-phase, photoreaction

Background. Artificial photosynthesis consists of three reactions: oxidation reaction, storage of redox equivalents, and reduction reaction. Storage of redox is indispensable because the oxidation reaction and reduction reaction are slower than the lifetime of the excited state and the charge separation state. Quinones and hydroquinones are responsible for this in plant photosynthesis. As an attempt for artificial utilization of this mechanism, Yusa et al. have reported a solution-phase photoreduction reaction of quinone using thiol as a reducing agent [1]). In this study, we investigated a two-phase reaction system that accumulates hydroquinone in the organic phase and the oxidation product of the reducing agent in the aqueous phase (Fig. 1).

Experiments. Ferrocene (42 μmol), hydrophobic quinone (13 μmol) and porphyrin (0.42 μmol) were dissolved in deuterated chloroform and placed in a Schlenk tube. An emulsifier was dissolved in heavy water and placed in the same Schlenk tube. The two-phase mixture was degassed by freeze-pump-thaw and irradiated with a yellow LED light at 30 ° C for 24 hours. The reaction was also carried out in the presence of an acid in the organic phase. After the photoreaction, the organic and aqueous phases were analyzed by ^{1}H NMR and UV-vis spectroscopy.

Results. It was observed that the aqueous phase was colored by ferrocenium ion, which is an oxidation product of ferrocene. The UV-Vis spectrum of the aqueous phase confirmed the presence of the ferrocenium ion (Fig. 2). The amount of produced ferrocenium ion was 0.94 μmol. When various acids were added as proton sources in the formation of hydroquinone, the aqueous phase was most strongly colored when acetic acid was added. From these facts, it is concluded that ferrocene functions as a reducing agent and ferrocene ion, which is an oxidation product, moves to the aqueous phase and is accumulated.

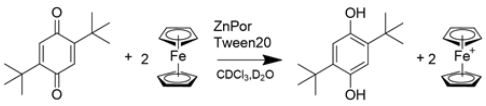

Figure 1 Assumed photoreduction reaction

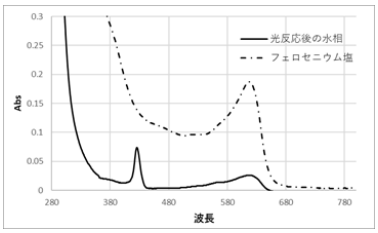

Figure 2 UV-Vis spectrum of aqueous phase after reaction The dot line is the absorption spectrum of ferrocenium tetrafluoroborate (0.63mmol/L) synthesized separately.

1) M. Yusa and T. Nagata, *Photochem. Photobiol. Sci.*, **2017**, 16, 1043-1048.