## Substituent Effects in Photoreduction of Cationic Porphyrins

(Graduate School of Science and Technology, Meijo University) OTakumi Ogawa, Toshi Nagata

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**Background.** In plant photosynthesis, the electrons produced by  $H_2O$  oxidation are temporarily transferred to quinones. In this respect, electron transfer of quinones can be one of the important subjects of artificial photosynthesis. Yusa *et al.* reported photoreduction of quinones using a reducing agent and a photosensitizer.<sup>1</sup> However, since this reaction does not separate the products, it is desirable to develop a way to separate the oxidation and reduction products into two phases.

In this study, we performed photoreaction of cationic porphyrins and thiols in homogeneous systems, with the aim of expanding the photoreaction to two-phase systems. In the course of the study, we accidentally found that porphyrin ring was reduced by photoreaction. To investigate this phenomenon in detail, photoreaction was carried out with various cationic porphyrins. Specifically, we varied the positions of the positive charges and investigated how they affected such photoreduction.

<u>Photoreactions.</u> Porphyrin (2 µmol) and thiol (200 µmol) were dissolved in deuterated methanol (0.6 mL) and placed into a J-Young NMR tube in a glove box. The mixtures were irradiated with yellow LED ( $\lambda = 593$  nm) for 24 h at 30°C. After photoreaction, the reaction mixtures were examined by UV-vis spectra and <sup>1</sup>H NMR spectra.

**<u>Results.</u>** After the photoreaction with 4-TMPyPZn, the <sup>1</sup>H NMR signals of  $\beta$  -protons of the porphyrin ring disappeared and new signals appeared in the range of 5-7 ppm. The UV-vis spectra suggested that the products have a phlorin-like structure. The conversion of the photoreaction was examined by the UV-vis spectra from the decrease of the Soret band around 430 nm. The conversion increased in the order 3- < 2- < 4- for the position of the methyl group. These results can be attributed to the difference in the intensity of delocalization of the positive charge to the porphyrin ring.



Figure. (a) the studied porphyrins. (b) <sup>1</sup>H NMR of 4-TMPyPZn before and after photoreaction. (c) UV-vis spectra of each porphyrin after photoreaction.

1) M. Yusa et al., Photochem. Photobiol. Sci., 2017, 16, 1043-1048.