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# SUBSTITUENT EFFECTS ON THE PHOTOCURRENT QUANTUM YIELDS OF PARA-SUBSTITUTED TETRAPHENYLPORPHYRINS

Kazuo YAMASHITA*
*Faculty of Integrated Arts and Sciences, Hiroshima University, Hiroshima 730*
Keiko Miyoshi, Atsuhiro OSUKA, and Hitomi SUZUKI
*Department of Chemistry, Faculty of Science, Ehime University, Matsuyama 790*

The photocurrent quantum yields of para-substituted tetraphenylporphyrins were found to be increased by electron-donating groups. Semi-logarithmic plots of the quantum yields *vs.* the half-wave potentials for the first ring oxidations of the porphyrins or the Hammett $\sigma$ of substituents yielded a linear relationship.

For a given porphyrinic ligand the photocurrent quantum yield of metalloporphyrins paralleled the half-wave potential for the first ring oxidation.[1)] In other words, the more easily oxidized porphyrins exhibited the higher quantum yields of the photocurrents. The most efficient cell of the porphyrins such as magnesium porphin and tetraphenylporphyrin reaches the quantum yield of about 0.2. The effect of central metal on the oxidation potential of the porphyrins can be explained by a variation in the electrostatic forces which are introduced into the porphyrin cavity by the different metal ions as well as the effects on the basicity of the porphyrin ring.[2)] Up to date, however, no systematic study has been reported for the effects of electron-donating or electron-withdrawing groups on the periphery of the porphyrin ring upon the photocurrent quantum yield.

In this communication, we present the substituent effects on the photocurrent quantum yield for para-substituted tetraphenylporphyrins ((p-X)TPP$H_2$) in Al/(p-X)TPP$H_2$/Ag sandwich systems. These porphyrins were prepared by the modified Rothemund method[3)] and purified according to the literature procedure.[4)]

Figure 1 shows the absorption and action spectrum for a (p-$CH_3$)TPP$H_2$ film, which was prepared by sublimation under *ca.* $10^{-3}$ Pa and 150 nm thick. The action spectrum was corrected for both the variation of photon flux with wavelength of the incident light source and the transmission of the aluminum film. The slight shift of the peaks for the action spectrum to longer wavelength is attributed to surface recombination described previously.[5)]

Semi-logarithmic plots of the photocurrent quantum yields measured at 440 nm *vs.* the half-wave potentials of (p-X)TPP$H_2$, where X = $OCH_3$, $CH_3$, H and Cl, are illustrated in Fig. 2. The half-wave potentials were measured as the potential halfway between the oxidation and reduction peak for a given couple in dichloromethane containing 0.1 M tetra-*n*-butylammonium perchlorate.[6,7)] The exponential correlation of the quantum yield with the half-wave potential of the porphyrin was the same as that observed in

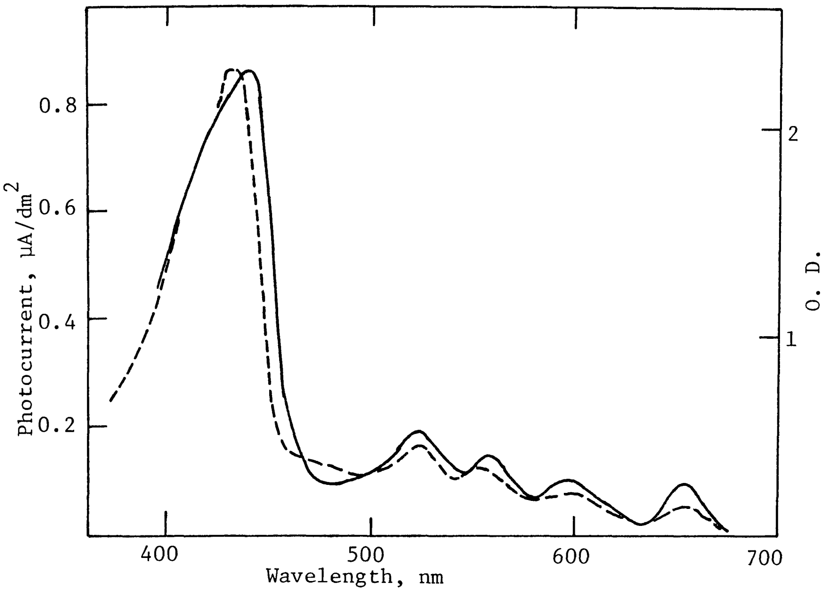

Fig. 1 Absorption and action spectra for a film of (p-$CH_3$)-$TPPH_2$.

Dashed and solid lines denote the absorption and action spectra. Illumination was done through the Al in the Al/(p-$CH_3$)$TPPH_2$/Ag cell at zero bias.

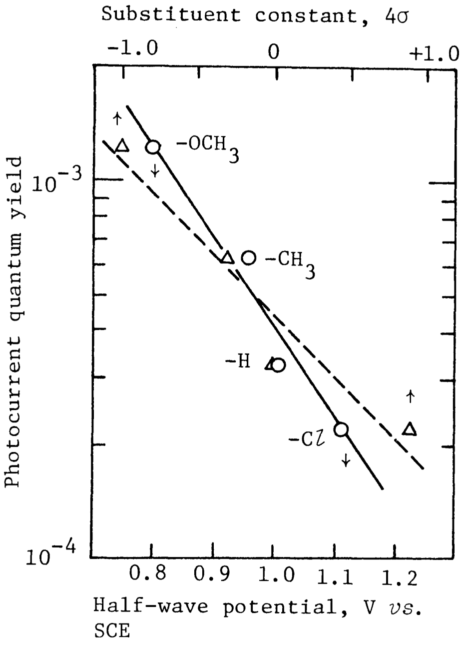

Fig. 2 Semi-log plots of the photocurrent quantum yields *vs.* the half-wave potentials of the first ring oxidation reactions for (p-X)$TPPH_2$ or substituent constants.

the case where the central metal ions were changed[1, 5] (see a solid line). Thus, the electron-donating groups such as -$OCH_3$ and -$CH_3$ at the para-positions of phenyl rings significantly affect to increase the quantum yield.

Since the shift in the half-wave potential of the (p-X)$TPPH_2$, as a result of changing the substituent X, has been found to obey the Hammett linear free-energy relationship,[7] we obtain the following equation,

$$\log\frac{\phi_X}{\phi_H} \propto \Delta E_{1/2} = 4\sigma\rho \qquad (1)$$

where $\phi_X$ is the photocurrent quantum yield for the (p-X)$TPPH_2$, $\Delta E_{1/2}$ the difference in half-wave potentials of the (p-X)$TPPH_2$ and (p-H)$TPPH_2$, σ the substituent constant and ρ is the reaction constant. As shown in Fig. 2, semi-logarithmic plots of the $\phi_X$ values *vs.* McDaniel and Brown[8] substituent constants 4σ, which were used as the total substituent constants for the four phenyl rings, gave similarly a linear relationship ( a dashed line).

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