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EFFECTS OF HETERO- AND PERIPHERAL SUBSTITUTIONS ON PHOTOCURRENT QUANTUM YIELDS: *PARA*-SUBSTITUTED TETRAPHENYLDITHIAPORPHYRINS

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Replacement of two NH groups of the porphyrin in *meso*-tetraphenylporphinato core by two S atoms shifts the oxidation potential to the positive direction and increases the photocurrent quantum yields of the Al/Porphyrin/Ag cells. The previously observed correlation between the ease of oxidation of porphyrins and the higher quantum yields was confirmed in a series of *para*- substituted tetraphenyldithiaporphyrins.

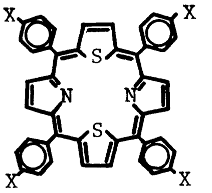
Effects of the central metal and peripheral substituents on the photovoltaic or photoelectrochemical properties of porphyrins have been extensively studied to build more efficient devices sensitized by the porphyrins for conversion of the solar energy into electric and/or chemical energy.[1-4] We previously reported a parallelism between the quantum yield and the oxidation potential found in two series of porphyrins: one with the same skeleton and different central metals and the other with the same central metal and modified skeletons. In other words, the more easily oxidized macrocycles exhibit the higher quantum yields.

In this paper we present effects of heterosubstitution in tetraphenylporphinato core and of peripheral substitution for *para*-substituted tetraphenyldithiaporphyrins [$(p\text{-X})S_2TPP$] on the photocurrent quantum yields.

The $(p\text{-X})S_2TPP$ used are shown in Fig. 1, which were prepared as described in reference.[5] An Al/Porphyrin/Ag sandwich system was used for measurement of the photocurrent quantum yields of sublimed microcrystalline films of the porphyrins. Film thickness of the porphyrins (about 100 nm) was measured with an Inficon XTM thickness monitor.

In Table 1 the photocurrent quantum yields with the oxidation half-wave potentials are given for $(p\text{-X})S_2TPP$, where X=CH_3, H and Cl, and the data for *para*-substituted tetraphenylporphyrins [$(p\text{-X})H_2TPP$] are included for comparison.

The replacement of two NH groups by two S atoms shifts the oxidation potentials of the porphyrins to more positive values but increases the photocurrent quantum yields. Thus S_2TPP are more efficient than H_2TPP, though the former are more difficult to oxidize than the latter. This may be attributed to a combination of the packing of porphyrin molecules and the extent of π-π overlap between the porphyrin rings, which facilitates the energy and electron transfer as assumed previously.[1] Probably the nonplanar structure of the photo-generated cation radicals ($S_2TPP^{+\cdot}$) is related with the finding that S_2TPP are more efficient than H_2TPP. Ulman *et al.*[6] found a similarity between the optical absorption spectrum of cation radicals of Se_2TPP and that of porphyrin diacids.



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1a X=OCH_3
1b X=H
1c X=Cl

Fig. 1 *Para*-substituted tetraphenyldithiaporphines used.

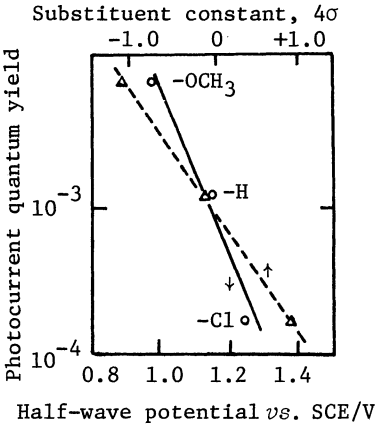

Fig. 2 Semi-log plots of the photocurrent quantum yields *vs.* the half-wave potentials of the first ring oxidation reactions and the substituent constants.

Table 1 Photocurrent quantum yields[a] and first ring oxidation half-wave potentials[b] of $(p\text{-}X)S_2TPP$ and $(p\text{-}X)H_2TPP$

Compound	λ/nm	Quantum yield	$E_{1/2}$ *vs.* SCE/V
$(p\text{-}OCH_3)S_2TPP$ (1a)	456	3.2×10^{-3}	0.98
S_2TPP (1b)	448	1.1×10^{-3}	1.16
$(p\text{-}Cl)S_2TPP$ (1c)	446	3.2×10^{-4}	1.25
$(p\text{-}OCH_3)H_2TPP$	440	1.2×10^{-3}	0.80
H_2TPP	445	3.2×10^{-4}	1.04
$(p\text{-}Cl)H_2TPP$	440	2.3×10^{-4}	1.11

[a] Quantum yield is defined as the number of the electrons produced per photon absorbed by the porphyrin film at low light intensities (about 0.1 mW/dm^2). [b] Oxidations at Pt in CH_2Cl_2 with 0.1 M tetrabutylammonium perchlorate.

Hence they concluded a similarity in structures of $Se_2TPP^{+\cdot}$ and the porphyrin diacid. The nonplanar conformation of the porphyrin diacids had been already determined by X-ray analysis.[7] In *meso*-tetraphenylporphine diacid the pyrrole rings are tilted alternately up and down, and the phenyl rings rotate toward the porphyrin plane. Similar inference may be applicable to $S_2TPP^{+\cdot}$, because the absorption spectrum of $S_2TPP^{+\cdot}$ resembles that of $Se_2TPP^{+\cdot}$.[8] Then the nonplanar conformation of $S_2TPP^{+\cdot}$ will result in a much larger π-π overlap between the pyrrole and the phenyl rings than the structure of $H_2TPP^{+\cdot}$. The enhanced conjugation of the phenyl substituents with the porphyrin ring facilitates the electron and energy transfer between neighboring molecules. Consequently, even if the structure change of $S_2TPP^{+\cdot}$ is small in solid films of the porphyrins, it brings about an increase of photocurrents and the quantum yields.

Figure 2 shows that the photocurrent quantum yields correlate exponentially with the first ring oxidation potentials of $(p\text{-}X)S_2TPP$ and also with the substituent constants[9] for the Hammett linear free-energy relationship.

Electron-donating substituents lower the oxidation potentials of the porphyrins and increase the photocurrent quantum yields. These results further support the previously observed correlation between the ease of oxidation of the porphyrins and the higher quantum yields.

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References

1) F.J. Kampas, K. Yamashita and J. Fajer, *Nature*, 284, 40 (1980).
2) K. Yamashita, K. Maenobe and J. Fajer, *Chem. Lett.*, 1980, 307.
3) K. Yamashita, K. Miyoshi, A. Osuka and H. Suzuki, *Chem. Lett.*, 1980, 627.
4) K. Yamashita, N. Kihara, H. Shimidzu and H. Suzuki, *Photochem. Photobiol.*, 35, 1 (1982).
5) A. Ulman and J. Manassen, *J. Am. Chem. Soc.*, 97, 6540 (1975).
6) A. Ulman, J. Manassen, F. Frolow and D. Rabinovich, *Inorg. Chem.*, 20, 1987 (1981).
7) A. Stone and E.B. Fleischer, *J. Am. Chem. Soc.*, 90, 2735 (1968).
8) J. Fajer, in personal communication.
9) D.H. McDaniel and H.C. Brown, *J. Org. Chem.*, 23, 420 (1958).

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