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PHOTOELECTROCHEMICAL STUDIES OF METALLOTETRAPHENYLPORPHYRIN ELECTRODES

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Eight kinds of metallotetraphenylporphyrins(MeTPP's) evaporated onto platinum plates were utilized as photoelectrodes in a wet cell, and their photo-induced voltage and current were measured under oxygen atmosphere. The largest photovoltage(+0.6V) and cathodic photocurrent(4μA/cm^2 at +0.1V vs. SCE) were observed with the PdTPP electrode. The photovoltage decreased in the order Pd(0.6V)>H$_2$(0.4V) >Zn≈Cu(0.3V)>Mg(0.2V)>Pb(0.08V)>Ni(0.03V)>Co(~0V), and, in parallel with this trend, the photocurrent also decreased. It was found that the photoeffect of the MeTPP's was dependent on the oxidation potential except that the lifetime of the excited state of the porphyrin was extremely short.

The photoelectrochemical behaviors of various types of metalloporphyrin electrodes have extensively been studied in connection with the solar energy utilization and the fundamental understanding of the primary process in photosynthesis.$^{1-4)}$ One of the recent interests in this field is to elucidate the mechanism of photoelectrode process at the porphyrin/electrolyte interface.$^{2,4)}$ In order to proceed the photoelectrochemical reaction, an effective charge separation must occur at the primary step through the excited state of porphyrin. The recent investigation using porphyrin films on various kinds of metal plates has shown that charge carriers are generated at the porphyrin/solution interface, and the lowest triplet exciton has been assumed as the most probable precursor for the charge separation.$^{4)}$ On the other hand, a comparison between the photoelectrochemical behaviors and the physicochemical properties such as the oxidation potential or the luminescence behavior of metalloporphyrins seems to provide significant information regarding the mechanisms of the charge separation process. However, little is known about the difference of the photoelectrochemical properties accompanying the variation of the central metal of porphyrins.

In the present study, eight kinds of metallotetraphenylporphyrins(MeTPP's) were used as photoelectrodes, and their photo-induced voltage and current were measured. As a result, it was found that a good correlation existed between the photovoltage and the oxidation potential of the MeTPP's except that the lifetime of the excited state of the porphyrin was extremely short. These results will briefly be reported in this communication.

Tetraphenylporphyrin(TPP) was synthesized by the condensation of benzaldehyde and pyrrole in propionic acid.$^{5)}$ As the product contained approximately 3% tetraphenylchlorin(TPC) as an impurity, it was purified by the treatment with 2,3-dichloro-5,6-dicyanobenzoquinone, followed by the chromatographic separation to remove completely any trace of TPC.$^{6)}$ The following complexes were prepared by the literature procedures, and purified, if necessary, by passing through an alumina or cellulose column: MgTPP,[7)] ZnTPP,[8)] PbTPP,[8)] CoTPP,[8)] CuTPP,[8)] NiTPP,[8)] and PdTPP.[9)] The purity of each complex was confirmed by the optical absorption spectrum in benzene solution.

The porphyrin electrode was prepared by the vacuum sublimation of MeTPP onto a platinum plate, the backside of which was connected to a copper lead wire by soldering and sealed by epoxy resin in order to insulate the bare metal surface from the electrolyte solution. The schematic illustration of the electrode is shown in Fig. 1. The area of the porphyrin electrode was about $0.4\,\mathrm{cm}^2$. The saturated calomel electrode(SCE) and the platinum-gauze were used as the reference and the counter electrodes, respectively. The electrolyte solution was 0.1M sodium sulfate solution, and oxygen was bubbled into the electrolyte as an electron acceptor. The photovoltage was detected with a voltmeter (internal impedance: $>10^9\Omega$) and the photocurrent was measured with a potentiostat under the voltage-controlled condition at +0.1V vs. SCE where the set voltage nearly corresponded to the rest potential of the porphyrin electrodes under oxygen atmosphere. These apparatuses were constructed at this laboratory using appropriate operational-amplifiers. Photo-irradiation was carried out through the Pyrex glass($\lambda_{trans}>300$nm) of electrolytic cell with a 1 kw projector lamp (Kondo Sylvania Co., Ltd., KP-12) equipped with a cold filter to remove heat radiant. For the measurement of action spectra, the chopped light(30Hz) through a monochrometer (JASCO, CT-25N) was irradiated on the working electrode, and the resulting potential change across a 5 kΩ load resistor between the working and the counter electrodes was amplified using a pre-amplifier(×100) and a lock-in amplifier (JASCO, LA-126). The amount of MeTPP on the platinum plate was determined spectrophotometrically after dissolving in benzene.

Figure 2(A) shows the potential change for the ZnTPP electrode on irradiation under oxygen atmosphere. About +0.3V of open circuit photovoltage was obtained. The magnitude of the photovoltage was proportional to the logarithm of the light intensity. However, when a bare platinum electrode (corresponded to ca. 5% area of the ZnTPP electrode surface) was linked in parallel with the ZnTPP electrode, a little photovoltage was observed owing to the electrical leak through the bare platinum electrode as shown in Fig. 2(B). Accordingly, we paid much attention to insulate the porphyrin electrode from the electrolyte, and it was coated with epoxy resin several times to

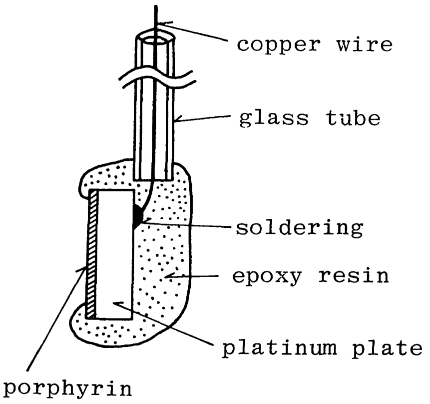

Fig. 1. Porphyrin electrode.

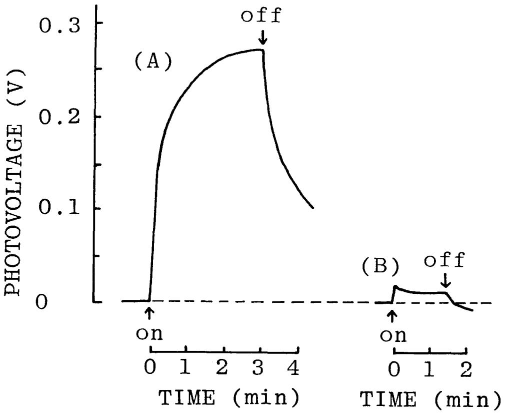

Fig. 2. Photovoltage for ZnTPP electrode. (A) ZnTPP electrode. (B) ZnTPP electrode combined with bare Pt electrode.

Table 1. Photovoltage, photocurrent, oxidation potential, and luminescence data for metalloporphyrins

Metal	Photovoltage[a] (V)	Photocurrent[a] (μA/cm^2, +0.1V vs. SCE)	Oxid. Pot.[b] (V vs. SCE)	Fluorescence Int.[c]	Phosphorescence Int.[c]	Triplet State Lifetime[c] (msec)
H_2	0.4	2	0.95	VS	VW	14
Mg	0.2	0.6	0.54	S	W	160
Zn	0.3	1	0.71	M	M	83
Pb	0.08	0.2	0.63		VW	≤ 0.5
Co(II)	~0	~0	0.32		NONE[d]	—
Cu(II)	0.3	0.6	0.90		VS	0.10
Ni(II)	0.03	0.08	1.04		NONE[d]	—
Pd(II)	0.6	4	1.02		VS	2.0

a) Photovoltage and photocurrent: This work. They are positive and cathodic, respectively.
b) Oxidation potential:
R.H.Felton, in "The Porphyrins", Vol.V, Ed. D.Dolphin, Academic Press, New York (1979), p.53ff.
c) Luminescence intensity and lifetime at 77K (mesoporphyrin-IX-dimethylester (Mg: etioporphyrin II)): R.S.Becker and J.B.Allison, J.Phys.Chem., 67, 2662, 2669(1963).
d) D.Eastwood and M.Gouterman, J.Mol.Spectrosc., 35, 359(1970).

ensure the insulation. When nitrogen was bubbled into the electrolyte in place of oxygen, the photovoltage gradually decreased, and finally almost diminished. This fact indicates that oxygen acts as a good electron acceptor from the excited porphyrin. The addition of other electron acceptor such as p-benzoquinone or methylviologen was also found to enhance the photovoltage. The photovoltage under oxygen atmosphere showed nearly constant value of +0.3V at the thickness from 200 to 2000 A of the ZnTPP layer. Although the reproducibility of the photocurrent compared with that of the photovoltage was relatively poor, the largest cathodic photocurrent(1~2μA/cm^2) was observed at the thickness around 500 A on repetition of the measurements. With the increase in the thickness of the ZnTPP layer, the photocurrent tended to decrease owing to the increase in the electrical resistance of the layer.

The photovoltage and the photocurrent for various MeTPP electrodes with the layer thickness of ca. 500 A are shown in Table 1. The measurements of action spectra were also carried out for all the porphyrins, and it was confirmed that the appearance of the photoeffect was not due to the contamination of H_2TPP. For example, in Fig. 3 are shown the optical absorption spectrum of PbTPP sublimed on a glass plate and the action spectrum of the photocurrent on the PbTPP electrode. The largest values of photo-

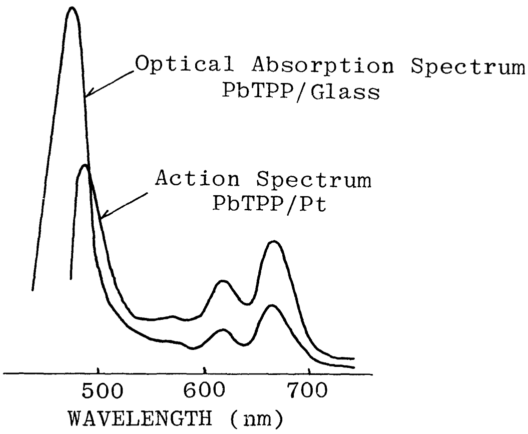

Fig. 3. Optical absorption spectrum of PbTPP/ glass, and action spectrum of PbTPP/Pt electrode.

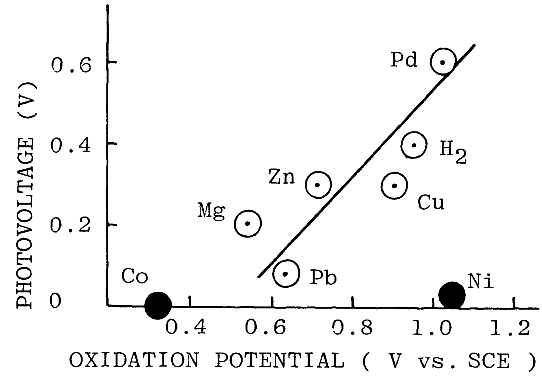

Fig. 4. Plot of photovoltage vs. oxidation potential.

voltage(0.6V) and photocurrent($4\mu A/cm^2$ at +0.1V vs. SCE) were obtained with the PdTPP electrode. The photovoltage decreased in the order Pd(0.6V)>H_2(0.4V)>Zn≃Cu(0.3V)>Mg (0.2V)>Pb(0.08V)>Ni(0.03V)>CO(~0V), and, in parallel with this trend, the photocurrent also decreased.

Included in Table 1 for comparison are the oxidation potential of the MeTPP's10) and the luminescence data of metal derivatives of mesoporphyrin-IX-dimethylester.11) However, because the kind of porphyrin referred in the luminescence data differs from TPP, it is inevitable to examine the difference of the photoeffect accompanying the change of porphyrin ligands. Although the photovoltage and the photocurrent for the mesoporphyrin-IX-dimethylester and octaethylporphyrin electrodes as the example of different ligands were measured, no significant difference of the photoeffect among these porphyrins was observed, indicating that the photoeffect was little affected by the difference of the porphyrin ligands. Therefore, the photoeffect is mainly attributed to the kind of central metal ions, and it may be possible to make some correlation between the observed photoeffect and the physicochemical properties of these metalloporphyrins.

Based upon the above considerations, we discuss the correlation among the various experimental data shown in Table 1. The most probable cause for the order of the photoeffect might be due to the difference of the oxidation potential of the MeTPP's. Furthermore, the lifetime of the excited porphyrin should also be important, because the photoelectrode process is associated with the electron transfer from the excited state of the porphyrin. As is shown in Fig. 4, there is a good correlation between the photovoltage and the oxidation potential of the MeTPP's except for black circles which show non-luminescent porphyrins at 77 K, indicating that the oxidation potential is important for the appearance of the photoeffect. The small photovoltage for the non-luminescent porphyrins suggests that the photoeffect cannot be exhibited if the lifetime of the excited state of the porphyrin is extremely short. Thus, it can be concluded that the photoeffect of various metalloporphyrins is largely dependent on the oxidation potential, and at the same time the lifetime of the excited state also affects the charge separation process.

Further investigations are now in progress concerning with the detailed mechanism of the photoelectrode process of metalloporphyrins in wet cell.

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