Photoelectrochemical Properties of Thin Films of Cadmium, Zinc, and Magnesium Porphyrins with Pyridyl Group

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Synopsis. Cadmium and zinc porphyrins with pyridyl or aminophenyl group gave smaller activation energy for the transfer of the carriers photoproduced in the solid thin film and larger cathodic photocurrent in quinhydrone solution than tetraphenylporphyrinato-cadmium and -zinc. The properties may be ascribed to the molecular arrangement of the porphyrins in the film.

It has been known that the peripheral substituent group and the central metal ion in a porphyrin largely influence the photoelectrochemical properties.[1-3] Yamashita reported that the photocurrent quantum yield increased with a decrease in the first ring oxidation potential of metalloporphyrins.[1] We previously reported that the pyridyl group in zinc porphyrins played an important role in the photoelectrochemical behavior bacause of its coordination to zinc in another porphyrin.[3] In this note, we report the photoelectrochemical properties of Cd, Zn, and Mg porphyrins with pyridyl or aminophenyl group.

Experimental

Tetraphenylporphyrin(H_2TPP),[4] 5-(4-pyridyl)-10,15,20-triphenylporphyrin (H_2PyP_3P),[5] and 5-(4-aminophenyl)-10,15,20-triphenylporphyrin($H_2P_{am}P_3P$)[6] were synthesized and purified by the literature method. Cd, Zn, and Mg porphyrins were also synthesized and purified by the literature method.[7-9] Porphyrin films were prepared on Pt plates by sublimation at pressure 4×10^{-3}Pa. The Pt plates were maintained at ambient temperature during the sublimation. Film electrodes were insulated from the electrolyte with epoxy resin except for the portion to be exposed to light (1 cm²). A 500 W xenon arc lamp (Ushio UXL-500D-O) was used as a white light source. The light was passed through a color filter (Toshiba L-39) and water, irradiated onto a film electrode in a N_2-purged solution thermostated at a constant temperature. The other experimental datails were described in the previous paper.[3]

Results and Discussion

In dark, the anodic currents were observed with Cd, Zn, and Mg porphyrin film electrodes above about 0.5 V vs. AgCl/Ag in 0.01 M quinhydrone aqueous solution containing 0.2 M KCl (at pH 4.7), but the currents were hardly observed below 0.5 V (1 M=1 mol dm⁻³). However, under illumination, the relatively large cathodic currents were obtained below the electrode potential of 0.4—0.6 V. The blocking contant was probably formed between a p-type semiconductor such as Cd, Zn, and Mg porphyrins and the electrolytic solution. Figure 1 shows the dependence of the short circuit photocurrents(i_p) of Cd porphyrins on the film thickness in 0.01 M quinhydrone aqueous solution containing 0.2 M KCl (at pH

4.7). The film electrode exhibited the maximum cathodic photocurrent(i_{max}) at a film thickness. The similar dependence was also observed with Zn and Mg porphyrins. The i_{max} values are summarized in Table 1.

The ease of the carrier formation and the mobility of the carrier photoproduced in the solid film may
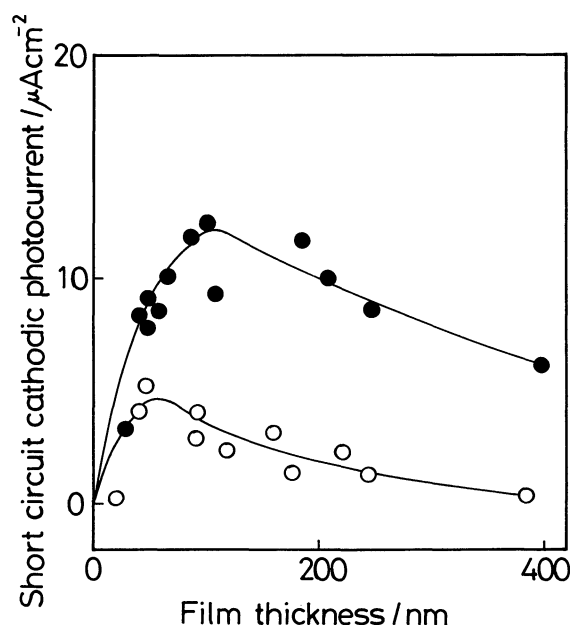
Fig. 1. Dependences of short circuit photocurrents of CdTPP (○) and CdPyP₃P (●) on film thickness in 0.01 M quinhydrone aqueous solution containing 0.2 M KCl (pH 4.7) at 25 °C.

Table 1. The Maximum Photocurrent (i_{max}),[a] the Activation Energy of the Transfer of the Photoproduced Carrier (ΔE), and the First Ring Oxidation Potential (E_{ox})[b] for Mg, Cd, and Zn Porphyrins

Porphyrin	$i_{max}/\mu A\ cm^{-2}$	$\Delta E/eV$	E_{ox}/V
ZnTPP	3	0.18	0.46
ZnPyP₃P	11	0.14	0.49
ZnP$_{am}$P₃P	13	0.14	0.46
CdTPP	4	0.22	0.38
CdPyP₃P	12	0.13	0.42
MgTPP	15	0.16	0.26
MgPyP₃P	7	0.16	0.33

a) Measured at 25 °C. b) Measured against Ag/0.01 M AgNO₃ in acetonitrile, Solvent: N,N-dimethylformamide.
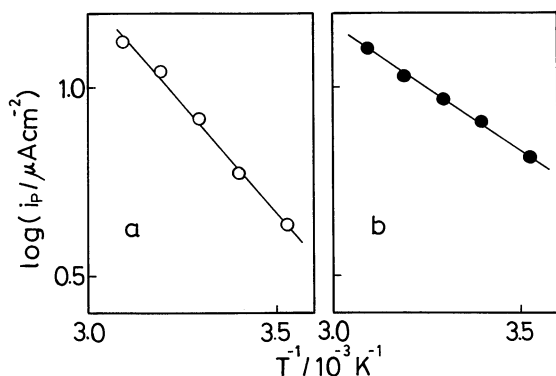
Fig. 2. Plots of log i_p vs. T^{-1} for CdTPP (a, thickness 60 nm) and CdPyP₃P (b, thickness 100 nm). i_p and T denote the short circuit cathodic photocurrent and the absolute temperature, respectively.

largely influence the photocurrent quantum yield. The former and the latter were evaluated by the first ring oxidation potential (E_{ox})[1] and the potential barrier hindering carrier transport (ΔE)[10], respectively. The E_{ox} values were also summarized in Table 1. The ΔE value was determined by the following equation,[10]

$$i = i_0 \exp(-\Delta E/kT), \qquad (1)$$

where i is the photocurrent at a constant applied voltage, i_0 is a constant, k is Boltzman constant, and T is an absolute temperature. The ΔE value is independent on the applied voltage. The i_p values between 10 and 50 °C were used instead of i. Figure 2 shows plots of log i_p vs. T^{-1} for Cd porphyrins. It was identified from an increase in the i_p value with an increase in temperature that these films had the semiconductive property. These plots gave straight lines, and the slope (ΔE) of CdPyP₃P was smaller than that of CdTPP. Since the ΔE values of the two porphyrin films were obtained at the same experimental conditions, the difference between two ΔE values was attributed to the difference of an intrinsic property between two porphyrin films. Therefore, the result exhibited that the carriers photoproduced in CdPyP₃P film transfered easier than those in CdTPP film. The plots of Zn and Mg porphyrins also gave straight lines. The ΔE values of Cd, Zn, and Mg porphyrins are summarized in Table 1. The values were independent on the film thickness.

It was found by means of scanning electron microscopy and X-ray diffraction spectrography that these ZnTPP and ZnPyP₃P films were uniform and amorphous. We previously clarified from the absorption and resonance Raman spectra of ZnPyP₃P film that the pyridyl group in porphyrin coordinated to zinc in another porphyrin.[3] Further, Fleischer et al. reported the long linear chain structure of a polymer of ZnPyP₃P by means of X-ray crystallography.[11] Zn porphyrin with one aminophenyl group and Cd porphyrin with one pyridyl group can also form a

linear polymer in the solid film because a 1:1 complex was formed between aniline and ZnTPP, and between pyridine and CdTPP,[12] respectively. Therefore, in the solid film, ZnPyP₃P, ZnP$_{am}$P₃P, and CdPyP₃P must have larger interactions between neighbouring molecules and more orderly molecular arrangement than ZnTPP and CdTPP. The ΔE values of ZnPyP₃P, ZnP$_{am}$P₃P, and CdPyP₃P consequently became smaller than those of ZnTPP and CdTPP, respectively.

In the porphyrin film with the very small conductivity $(10^{-13}$—10^{-10}S cm^{-1} [3]$)$, the effective charge separation of electrons and holes photoproduced in a space charge layer may be achieved by the easy transfer of the photoproduced carriers. Since the E_{ox} values of ZnPyP₃P, ZnP$_{am}$P₃P, and CdPyP₃P were approximately equal to those of ZnTPP and CdTPP, respectively, the carrier formation in ZnPyP₃P, ZnP$_{am}$P₃P, and CdPyP₃P films were as easy as that in ZnTPP and CdTPP films. ZnPyP₃P, ZnP$_{am}$P₃P, and CdPyP₃P nevertheless exhibited larger short circuit photocurrent than ZnTPP and CdTPP. The mobility of the photoproduced carriers probably played an important role in the photoelectrochemical behavior of Zn and Cd porphyrin films.

On the other hand, the ΔE value of MgPyP₃P was equal to that of MgTPP, but the i_{max} value of MgPyP₃P was smaller than that of MgTPP. MgPyP₃P can not form the long linear chain structure in the film because a 1:1 complex was hardly formed between pyridine and MgTPP.[12] The result implied that the photocurrent was largely influenced by the ease of the carrier formation in Mg porphyrins. That is to say, the i_{max} value increased with a decrease in the E_{ox} value of the metalloporphyrins with no long linear chain structure, as demonstrated by Yamashita.[1]

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