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Contribution of Electric-Field-Induced Metal-Free Porphyrin Dication to Photocurrent in Mixed Solid of Metal-Free Porphyrin and *o*-Chloranil/Al Schottky-Barrier Cell

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Although a Al/H₂tpp (5, 10, 15, 20-tetraphenylporphyrin) Schottky-barrier cell did not show a clear rectification property because of the large electric resistance of the H₂tpp solid, the rectification property was remarkably improved when *o*-chloranil was added into the H₂tpp solid. The short-circuit dark-current was observed for the Al/dye cells with the mixed solid in contrast to that with the pure H₂tpp solid, and it increased with increasing molar ratio (R) of *o*-chloranil to H₂tpp. Furthermore, a much larger photocurrent was observed for the mixed-solid cells than for the pure H₂tpp cell, but in the former cells in contrast to the latter cell, the open-circuit photovoltage was approximately the same as the open-circuit dark-voltage. These results indicate that the photocurrent of the mixed-solid cells was from the photocorrosion of the Al electrode. The short-circuit photocurrent action spectra obtained by irradiating from the Al side followed the absorption spectra of the dye solid films on the Al substrate below the R value of about 1, but above $R = 1.5$, a clear difference was observed in the spectra. This difference arises because a small amount of metal-free porphyrin dications, which is hardly detected by UV-visible spectra, was produced in the immediate neighborhood of the Al electrode when spin-coated with a larger R value because of dark-corrosion of aluminum by both assistance of the hydrogen bonds (between H₂tpp and *o*-chloranil) and the electric field (in a Schottky barrier built during the spin coating). Thus the metal-free porphyrin dications efficiently underwent a photoinduced charge-separation by the potential gradient in the Schottky barrier.

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Much effort has been expended to attain efficient conversion from light energy to electric energy with photocells using organic dye solids.[1-30] But large efficiency has not been yet obtained for the photoconversion because the organic solids have large electric resistance, namely, small carrier density and/or small carrier mobility. In Al/dye Schottky-barrier cells with a series of porphyrin compounds having p-type conductance, relatively large photoconversion efficiency was obtained for the porphyrin, which is rather easily oxidized.[7,8] The reason is that a solid consisting of dye molecules with lower ionization threshold energy has a larger hole density as majority carrier because the oxidation of the dye molecules by the oxygen molecules physisorbed in the solid is easier, and eventually the solid has a relatively small resistivity. However, Gouterman et al. pointed out the possibility that when 5,10,15,20-tetraphenylporphyrinatomagnesium (Mgtpp) solid with a lower ionization energy contacted to low-workfunction Al, the observed photocurrent for the Schottky-barrier cell was from the photocorrosion of the Al electrode.[24] The proposal has been proved by us according to the observation of photocorrosion current in Al/dye cells using metal-free tetrabenzporphyrin, metal-free triazatetrabenzporphyrin, and metal-free phthalocyanine.[25]

To improve the photovoltaic properties, it has been tried to increase the hole density as majority carrier by adding an electron-acceptor such as iodine and *o*-chloranil, etc., to a dye solid with p-type conductance such as phthalocyanines,[26,27] porphyrins,[28,29] and merocyanines.[30] Although a larger photocurrent was observed with the Schottky-barrier cells using the mixed solids, we have doubted whether the photocurrent was really from the photoenergy conversion. Hence we have investigated again in detail the photovoltaic properties of Al/(H₂tpp + *o*-chloranil) Schottky-barrier cells reported previously by Harima et al.[28] and by us.[29]

Experimental

5,10,15,20-Tetraphenylporphyrin (H₂tpp) was synthesized and purified by methods described in the literature.[31] *o*-Chloranil, of reagent grade from Kanto Chemicals, was purified by recrystallization from acetone. Tetrachlorocatechol and trifluoroacetic acid were of reagent grade from Aldrich Chemicals and were used without further purification.

Al/dye/Au sandwich-type photovoltaic cells were fabricated as follows: first, semitransparent aluminum films with a thickness of about 22 nm were prepared on precleaned glass substrates by vacuum deposition at 0.01 Pa. Then the dye films were prepared on the aluminum-coated glass substrate (with a transmittance at 500 nm of $10 \pm 2\%$) by spin coating from the chloroform solutions containing various concentrations of H₂tpp and *o*-chloranil, where chloroform was used after distilling a guaranteed reagent from Nakarai Tesque. Finally a semitransparent gold film with a thickness of about 12 nm was formed on the dye films by vacuum deposition at 0.01 Pa. A slow deposition rate of less than 0.02 nm s⁻¹ was used to prevent short-circuiting of the cells. The photoactive area was confined to 0.25 cm². The thickness of the deposited Al and Au films was monitored by an Ulvac CRTM-5000 oscillating quartz thickness controller, and the thickness of the spin-coated dye films was evaluated by the amount of H₂tpp per unit area on the substrate. The amount was determined by a Hitachi U-3210 UV-visible spectrometer after dissolving the layer in chloroform. When the thickness in a unit of nanometers was necessary, it was estimated from the mixing molar ratio of H₂tpp and *o*-chloranil, the amount of H₂tpp on the substrate, and the density of the mixed dye solids. The mixing ratio in the mixed dye solid was regarded as the same as that in the spin-coating chloroform solution. The density of H₂tpp determined pycnometrically in a water and ethanol solvent mixture (3:7 by weight) was about 1.1 g cm⁻³, and the value of 1.1 g cm⁻³ was assumed as the density of the mixed dye layers.

The photocurrent action spectra were measured at a scan rate of 60 nm min⁻¹ for the incident light wavelength. The light intensity transmitted through the Al electrode was normalized to 20 μW cm⁻². To avoid any change of the photovoltaic properties with age, all electrical measurements were performed in air at a temperature of $22 \pm 3°C$ and a relative humidity of $40 \pm 10\%$, and within a few minutes after preparation of the cells. The light source consisted of a 750 W halogen tungsten lamp and a Jasco CT-10 monochromator with a Jasco scanning controller SDM-25C. The light intensity was monitored by an Advantest TQ-8210 optical power meter with a sil-

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icon photocell. The photocurrent was measured by an Advantest R-8240 electrometer, and was recorded by a Yokogawa Denki 3057 portable recorder. The bias was applied by a Hokuto Denko HB-104 function generator with the scan rate of 600 mV min^{-1} for the measurement of current-voltage curves.

The absorption spectra of the dye solid film formed on a glass slide and a semitransparent Al substrate with a transmittance at 500 nm of 50 ± 5% were recorded on a Hitachi U-3210 UV-visible spectrometer, and they were corrected for the absorption of the substrates.

Results and Discussion

Dependence of photocurrent action spectra on mixing ratio (R) of H_2tpp and o-chloranil.—Figure 1 shows the R dependence of photocurrent action spectra of Al/dye/Au cells with mixed solids of H_2tpp and o-chloranil and absorption spectra of their dye solid films on a semitransparent Al substrate, where R denotes the molar ratio of o-chloranil to H_2tpp in the solid film. Since it is known that H_2tpp solid has p-type conductance,[7] the dye solid and the Al electrode with low work function form a blocking contact. Therefore photoexcited H_2tpp molecules in an Al/H_2tpp/Au cell create free charges of electrons and holes by charge separation in the depletion layer
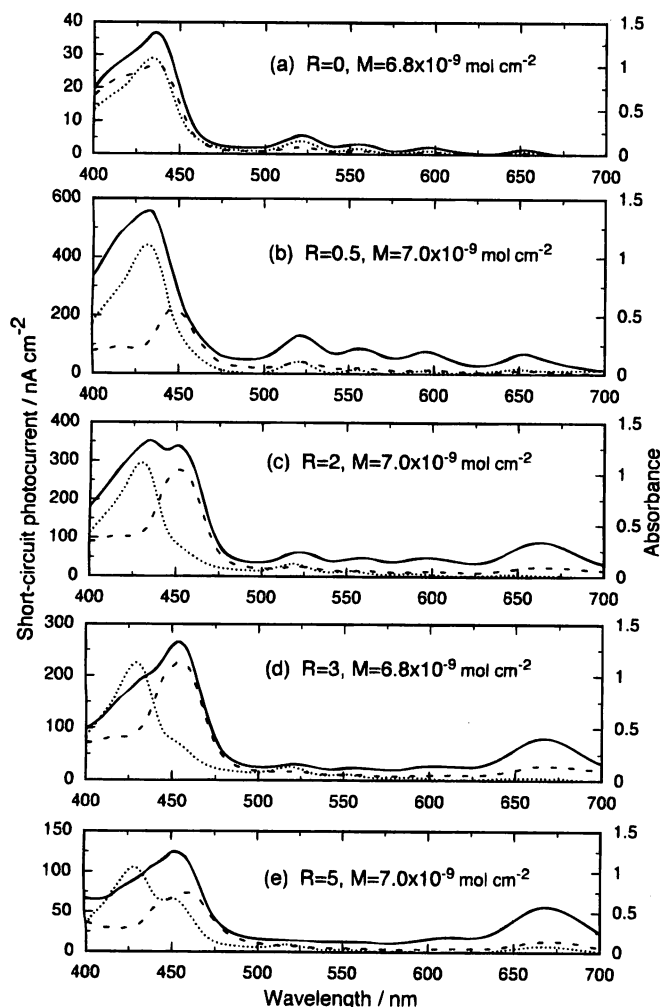

Figure 1. Photocurrent action spectra of Al/dye(M)/Au cells with pure H_2tpp solid (a) and mixed solids of H_2tpp and o-chloranil of $R = 0.5$ (b), $R = 2$ (c), $R = 3$ (d), and $R = 5$ (e), where M and R indicate the amount of H_2tpp per unit area on the electrode and the molar ratio of o-chloranil to H_2tpp in the solid film, respectively. The incident light intensity at the Al/dye and Au/dye interfaces was normalized to 20 μW cm^{-2}. The solid line represents irradiation from the Al side, dashed line represents irradiation from the Au side, and dotted line represents absorption spectra of dye solid films on the Al substrate.

forming near the Al/H_2tpp interface, and a short-circuit photocurrent flows from the Au electrode to the Al electrode through the external circuit. The photocurrent action spectrum obtained by irradiating from the Al side eventually followed the absorption spectrum of the H_2tpp solid film as shown in Fig. 1a. When the cell was irradiated from the Au side with ohmic contact, the photocurrent was smaller than that obtained by irradiating from the Al side. This reason is that incident photons are absorbed by the H_2tpp solid before reaching the photoactive Al/H_2tpp interface. However, the so-called optical filter effect as observed in the photocurrent was small even at the Soret band of H_2tpp which has very large absorption.

When a small amount of o-chloranil was added to the H_2tpp solid, the photocurrent of Al/mixed solid/Au cells became remarkably large, see Fig. 1b. Although the photocurrent action-spectra for the mixed solid cells irradiated from the Al side approximately followed the absorption spectra in analogy with the pure H_2tpp cell, the optical-filter effect at the Soret band became very large compared to the pure H_2tpp cell. On the other hand, in an Al/mixed solid of $R = 2$/Au cell with a large excess of o-chloranil to H_2tpp, the photocurrent action spectrum when irradiated from the Al side did not follow the absorption spectrum of the mixed solid, and a peak at 455 nm in the Soret band region as well as that at 665 nm in the Q band region were observed, see Fig. 1c. It is found from the optical filter effect that the active interface for the photocurrent generation was the Al/dye interface even when a large amount of o-chloranil was mixed with the H_2tpp solid. Thus, the mixed solid behaved as a p-type semiconductor. Further addition of o-chloranil led to disappearance of the peaks around 435, 520, 560, and 595 nm in the photocurrent action spectra. Thus only the two peaks at 455 nm in the Soret band region and at 665 nm in the Q band region were observed, see Fig. 1d and e. The assignment of the new peak at 455 nm, beside that at 435 nm, in the Soret band region and the new broad peak at 665 nm in the Q band region in the absorption spectra of the mixed solid of $R = 5$ on the semitransparent Al substrate is made in the following section.

Metal-free porphyrin dication produced by corrosion of aluminum.—When the spin-coated films of the mixed solid containing a large excess of o-chloranil to H_2tpp were prepared on a glass plate and on a semitransparent Al substrate, the two absorption spectra were considerably different. Figure 2 shows the absorption spectra for the mixed solid films of $R = 5$. A single Soret peak was observed at 435 nm on the glass substrate, but additional peaks appeared at 455 and 665 nm on the Al substrate. The additional peaks may resemble absorption peaks of free base chlorin, which is a reduction product of H_2tpp. However, we believe that H_2tpp is not reduced to the chlorin in the mixed solid containing o-chloranil as an oxidant but o-chloranil is preferentially reduced to tetrachlorocatechol, because the reduction potentials of o-chloranil and H_2tpp in dichloromethane are -0.34 and -1.74 V vs. the oxidation potential of ferrocene (Fc$^+$/Fc), respectively, that is, o-chloranil is reduced much more easily than H_2tpp. Such absorption spectra on the Al substrate were not obtained by using p-chloranil instead of o-chloranil, and also they were not obtained by using 5,10,15,20-tetraphenylporphyrinatozinc (Zntpp) instead of H_2tpp. That is, such characteristic absorption spectra were obtained only by mixing H_2tpp and o-chloranil.

The absorbances at 455 nm of two kinds of mixed solid films ($R = 5$) which were prepared on the Al substrate by using a dehydrated chloroform and a water-saturated chloroform (data not shown) were compared. Even when the dehydration of chloroform was done by calcium hydride, the absorption shoulder at 455 nm was slightly observed because we cannot perfectly prevent the incorporation of moisture due to spin-coating in air. It is found that a larger amount of new species P, which was recognized by the absorption peaks at 455 and 665 nm, existed in the mixed film prepared from the chloroform containing a larger amount of water. Thus, water, which may be contained in the spin-coating chloroform solution and/or originate from moisture in air, is necessary to produce the new species P. We infer that the following chemical reactions pro-
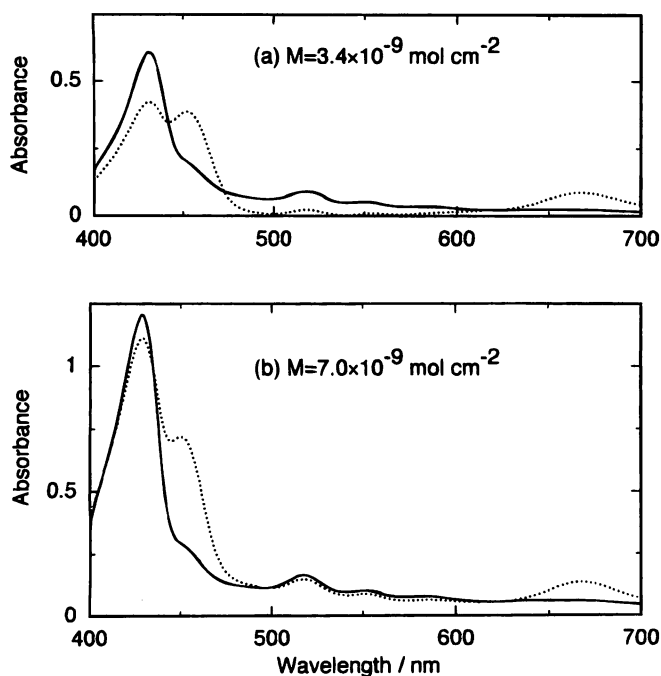
Figure 2. Absorption spectra of mixed solids films ($R = 5$) of H_2tpp and o-chloranil on the glass substrate (solid line) and the Al substrate (dotted line), where R indicates the molar ratio of o-chloranil to H_2tpp in the solid film. The amount (M) of H_2tpp per unit area on the substrates was (a) 3.4 × 10^{-9} and (b) 7.0 × 10^{-9} mol cm^{-2}.

ceeded at the Al/mixed solid interface when the spin-coated films of the mixed solids of H_2tpp and o-chloranil were made on the Al substrate. That is, at the same time that the aluminum reacted with water, produced protons and electrons reacted with o-chloranil

$$2Al + 6H_2O \rightarrow Al_2O_3 \cdot 3H_2O + 6H^+ + 6e^- \quad [1]$$

$$o\text{-chl} + 2H^+ + 2e^- \rightarrow tcc \quad [2]$$
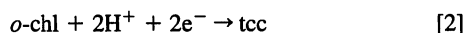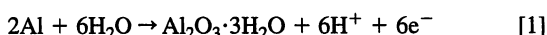
where o-chl and tcc represent o-chloranil and tetrachlorocatechol, respectively. Therefore, the species (produced near the Al substrate) such as tcc may take part in the production of the new species P. The oxidation product of aluminum at the Al/mixed solid interface in the dark may be Al_2O_3 although we cannot detect the product. This was reasoned by the fact that the transmittance of the Al electrode in the Al/dye Schottky-barrier cells increased under continuous illumination, see Ref. 25.

The shape of the spectrum for the mixed solid film ($R = 5$) on the glass substrate was independent of the thickness, but the shape of the spectrum on the Al substrate depended on the thickness. That is, the ratio of the peak intensity at 455 nm to that at 435 nm in the thinner film was larger than the ratio in the thicker film, see Fig. 2. This suggests that the molar ratio of the new species P to H_2tpp in the mixed film was larger in the vicinity of the Al substrate than in the bulk of the mixed solid. Figure 3 shows the thickness dependence of the absorbance at 665 nm of the mixed solid ($R = 5$) on the Al substrate, where the absorbance is approximately proportional to the concentration of the new species P because the H_2tpp hardly absorbs at this wavelength. Its dependence does not follow the Lambert-Beer's law. When it is assumed that the new species P is proportionally produced with the increase of an electric field in the depletion layer with a proposed function by Yamashita et al.,[32] its concentration at a distance x from the Al/dye interface is proportional to $\exp(-x/C)$. Therefore, its absorbance is shown by the following equation

$$A = A_0 [1 - \exp(-d/C)] \quad [3]$$

where A, A_0, d, and C denote the measured absorbance, the absorbance by the new species P of the mixed solid film with the infinite
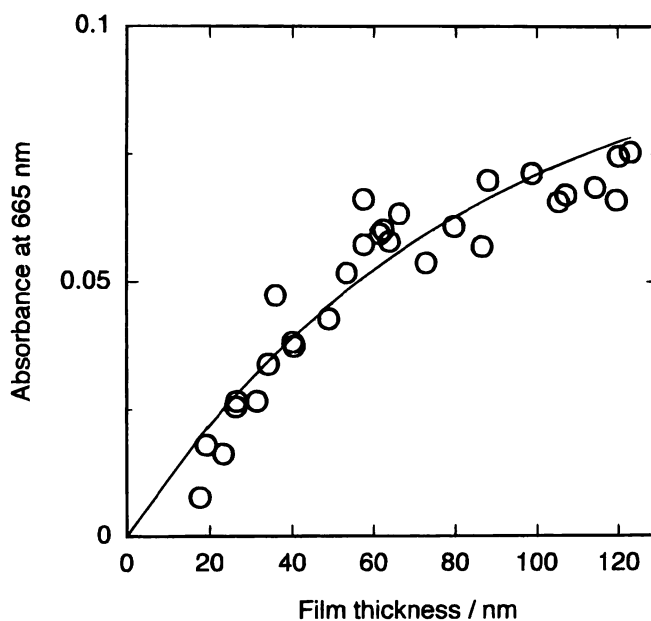
Figure 3. Thickness-dependence of absorbance at 665 nm for mixed solid films ($R = 5$) of H_2tpp and o-chloranil on the Al substrate, where R indicates the molar ratio of o-chloranil to H_2tpp in the solid film. The symbols are the experimental values, and the solid line is estimated by substituting $A_0 = 0.1$ and $C = 80$ nm in Eq. 3.

thickness, the film thickness, and the constant, respectively. The measured absorbance fitted well with our proposed equation, and a best consistency was obtained with $A_0 = 0.1$ and $C = 80$ nm.

The absorption spectrum of the solid film of metal-free porphyrin dication (H_4tpp^{2+}), which is an adduct of two protons to H_2tpp, on a glass plate is shown in Fig. 4, where the H_4tpp^{2+} solid film was prepared by spin-coating from a chloroform solution of H_4tpp^{2+} formed by adding fivefold molar trifluoroacetic acid to H_2tpp. [33] Since the observed absorption peaks at 455 and 665 nm consisted
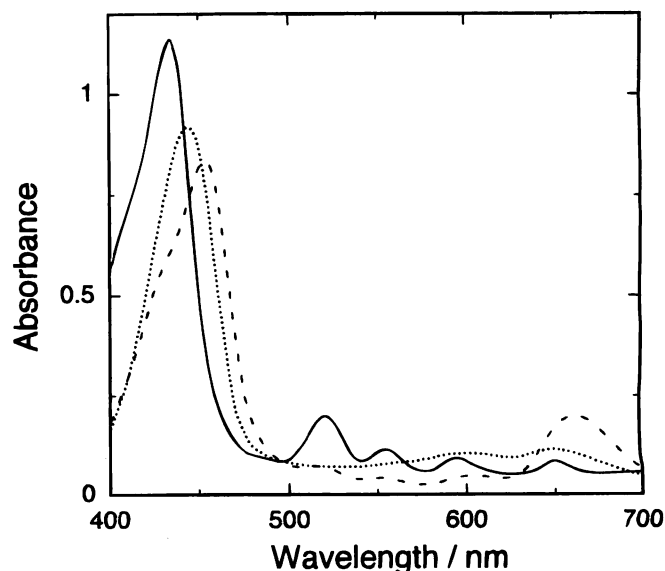
Figure 4. Absorption spectra of H_2tpp solid film (solid line), mixed solid film ($R = 5$) of H_2tpp and tetrachlorocatechol (dotted line), and mixed solid film ($R = 5$) of H_2tpp and trifluoroacetic acid (dashed line) on the glass substrate, where R indicates the molar ratio of tetrachlorocatechol or trifluoroacetic acid to H_2tpp in the spin-coating chloroform solution. The amount of H_2tpp per unit area on the substrate was about 6.8 × 10^{-9} mol cm^{-2}.

with those in the mixed solid film of $R = 5$ on the Al substrate, we assign that the new species P is H_4tpp^{2+}.

We infer that two hydroxy protons in tcc produced near the Al substrate are the proton source for the production of H_4tpp^{2+}, and a salt such as $(H_4tpp^{2+})(tcc^{2-})$ is produced, where tcc^{2-} indicates a dianion formed by an acid dissociation of tcc. To make sure whether the protonation to H_2tpp occurred by the tcc, we measured the absorption spectrum of the spin-coated film prepared on the glass plate from a chloroform solution containing fivefold molar tcc to H_2tpp, see Fig. 4. The spectrum indicates that the tcc functioned as the proton source, but its acidity was much weaker than trifluoroacetic acid, giving a smaller shift of the Soret peak.

An intensive peak at 1682 cm^{-1} and a weak peak at 1702 cm^{-1} were observed in the IR spectrum for a KBr pellet sample of *o*-chloranil, being assigned to the stretching vibration of the carbonyl group in *o*-chloranil. In the mixed sample of $R = 5$, a new intensive peak besides the two peaks appeared at 1689 cm^{-1}. This new signal was assigned to its stretching vibration in *o*-chloranil making a weak hydrogen bond with pyrrole protons in H_2tpp since H_2tpp has no signal in this wavenumber region. Only when such an *o*-chloranil forming the hydrogen bond with H_2tpp underwent the self-discharge reaction 2, the produced tcc may behave efficiently as the proton source for the production of the $(H_4tpp^{2+})(tcc^{2-})$ salt because the tcc molecules were very close to the H_2tpp molecules by the hydrogen bond.

The above results are summarized as follows; (*i*) when *o*-chloranil was mixed with H_2tpp, hydrogen bonds were formed, making the two molecules closer. (*ii*) The *o*-chloranil was reduced into tcc by protons and electrons from hydration of Al. (*iii*) H_4tpp^{2+} was produced because of the protonation to H_2tpp by the close tcc with an assistance of electric field built in a Schottky barrier, resulting in the formation of electric field-induced $(H_4tpp^{2+})(tcc^{2-})$. (*iv*) The newly appeared peaks at 455 and 665 nm both for photocurrent action spectra and absorption spectra in Fig. 1 originated from H_4tpp^{2+}. Why the action spectra did not follow the absorption spectra for $1.5 < R < 6$ was that excited H_4tpp^{2+} only near Al contributed to photocurrent generation. This is discussed in a later section.

Dark-current from corrosion of aluminum electrode in Al/mixed solid/Au cells.—The current-voltage curve for an Al/H_2tpp/Au cell is shown in Fig. 5a. The curve showed a slight rectification property because of a large resistance of H_2tpp solid (ca. 10^{14} Ω cm), even though the H_2tpp solid has a p-type conductance. Figures 5b, c, and d show the current-voltage curves for Al/dye/Au cells with the mixed solids of $R = 0.5$, 2, and 3, respectively. When a slight amount of *o*-chloranil was added into the H_2tpp solid, a large dark-current flowed from the Al electrode to the Au electrode through the external circuit by applying the positive bias of more than about 0.8 V to the Au with respect to the Al; that is, the rectification property was remarkably improved. Figure 6 shows the R dependence of the series resistance for the Al/mixed solid/Au cells, where the resistance was estimated from the slope of the current-voltage curve in the forward-bias region. The resistance decreased remarkably by the slight addition of *o*-chloranil, and it exhibited a minimum around $R = 0.5$ to 1, but further addition led to a gradual increase of the resistance. This indicates that the hole density in the mixed solid considerably increased compared to that in the pure H_2tpp solid. The oxidation potential of H_2tpp and the reduction potential of *o*-chloranil in dichloromethane are 0.53 and −0.34 V vs. Fc^+/Fc, respectively, thus *o*-chloranil cannot oxidize H_2tpp thermodynamically. However, it may be possible for *o*-chloranil to oxidize H_2tpp to H_2tpp^+ in the presence of H^+ because the reduction product of *o*-chloranil is stabilized to tetrachlorocatechol by H^+ and eventually the oxidation power of *o*-chloranil becomes large. Therefore, the hole density in the solid increased with added *o*-chloranil, and the electric resistance of the mixed solid eventually decreased. However, at an R value above 1, the electronic interaction among H_2tpp molecules may become weak because of a diluting effect of H_2tpp by *o*-chloranil, resulting in a smaller hole mobility that brings a larger resistance.
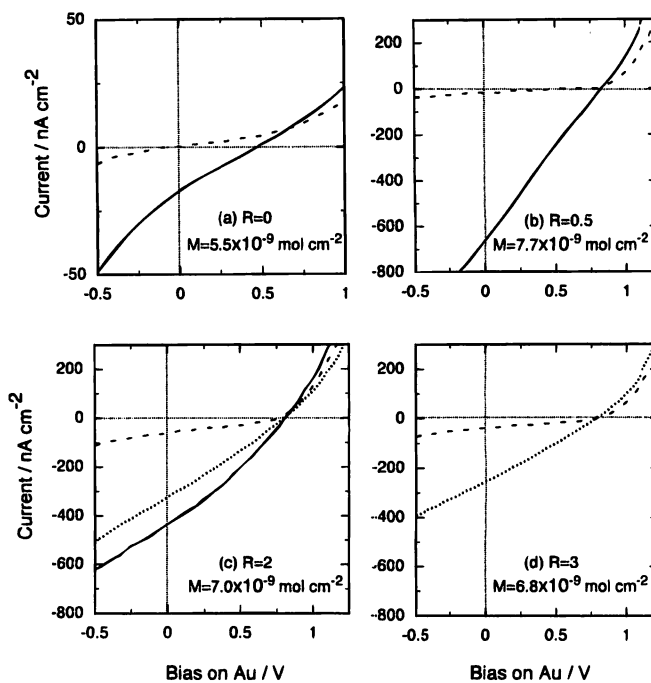
Figure 5. Dark current-voltage (dashed line) and photocurrent-voltage characteristics for the irradiation by 435 nm (solid line) and 455 nm (dotted line) monochromatic lights from the Al side in Al/dye(*M*)/Au cells with pure H_2tpp solid (a) and mixed solids of H_2tpp and *o*-chloranil of $R = 0.5$ (b), $R = 2$ (c), and $R = 3$ (d), where M and R indicate the amount of H_2tpp per unit area on the electrode and the molar ratio of *o*-chloranil to H_2tpp in the solid film, respectively. The incident light intensity at the Al/dye interface was normalized to 20 μW cm^{-2}.

In the cells with the mixed solid in contrast to those with the pure H_2tpp solid, a short-circuit dark-current (J_{sc}^d) flowed from the Au electrode to the Al electrode through the external circuit as shown in Fig. 5. Figure 7 shows the R dependence of the J_{sc}^d value. The J_{sc}^d increased with added *o*-chloranil below $R = 3$. We infer that the following reactions occurred in the mixed solid cells: an oxidation reac-
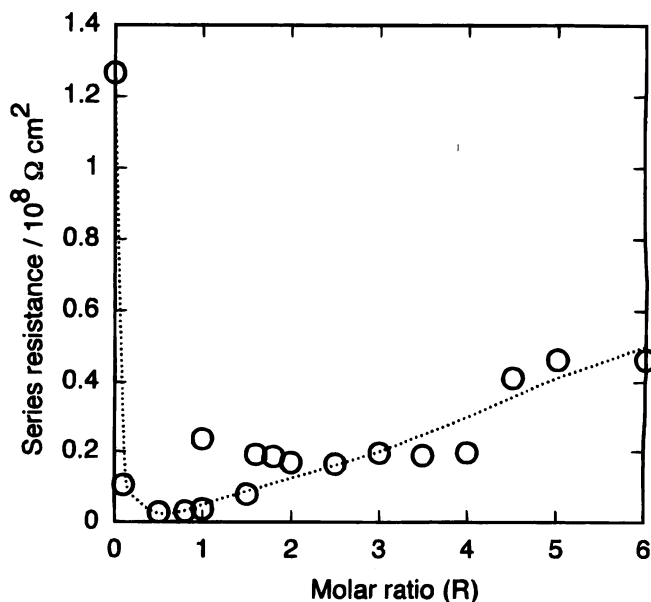
Figure 6. R dependence of series resistance of Al/mixed solid/Au cells, where R indicates the molar ratio of *o*-chloranil to H_2tpp in the solid film. The amount of H_2tpp per unit area on the electrode was $(5.2 \pm 0.9) \times 10^{-9}$ mol cm^{-2}.
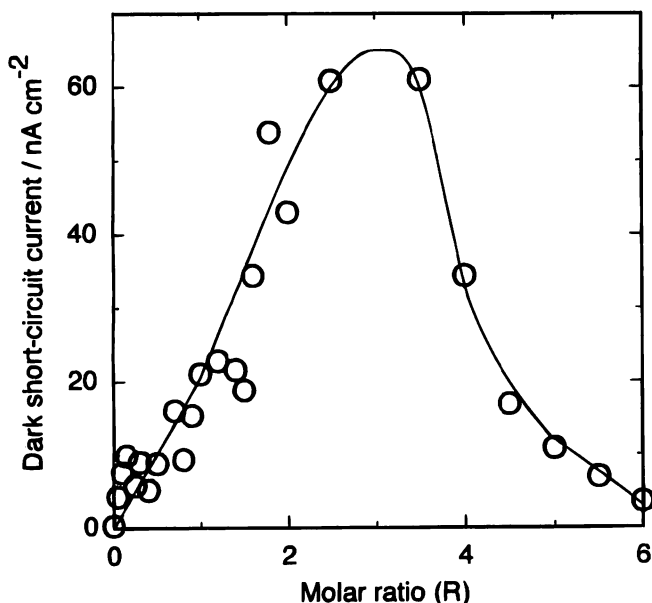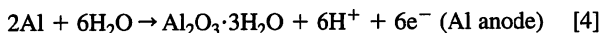
Figure 7. R dependence of dark short-circuit current of Al/mixed solid/Au cells, where R indicates the molar ratio of o-chloranil to H_2tpp in the solid film. The amount of H_2tpp per unit area on the electrode was $(6.3 \pm 0.9) \times 10^{-9}$ mol cm^{-2}.

tion of aluminum occurred between the Al electrode and water adsorbed in the dye solid

$$2Al + 6H_2O \rightarrow Al_2O_3 \cdot 3H_2O + 6H^+ + 6e^- \text{ (Al anode)} \quad [4]$$

At the same time, the H_2tpp molecules in the immediate neighborhood of the Al electrode were oxidized to porphyrin radical cations (H_2tpp$^+$) by o-chloranil and the produced protons, and the o-chloranil was reduced to tcc

$$2H_2tpp + o\text{-chl} + 2H^+ \rightarrow 2H_2tpp^+ + tcc \quad [5]$$
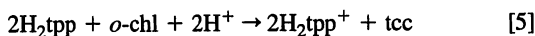
H_2tpp molecules bound to o-chloranil molecules by the weak hydrogen bonds may be easily oxidized. When the H_2tpp$^+$ combined with electron by a self-discharge, the overall reaction was represented by combination of reactions 1 and 2. On the other hand, when the hole [h$^+$(H_2tpp)] originating from the H_2tpp$^+$ migrated to the Au cathode by a potential gradient built in the depletion layer near the Al/dye interface, h$^+$(Au cathode) in Eq. 7 combined with e$^-$ (Al anode) in Eq. 4 in the external circuit. Eventually, J_{sc}^d increasing up to $R = 3$ was observed because of an increased rate of the chemical reactions 4 and 5

$$H_2tpp^+ \rightarrow H_2tpp + h^+(H_2tpp) \quad [6]$$

$$h^+(H_2tpp) \rightarrow h^+(Au \text{ cathode}) \quad [7]$$
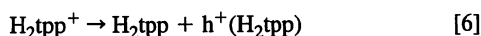
However J_{sc}^d decreased with added o-chloranil above $R = 4$, because the large electric resistance of the mixed solid limited the magnitude of J_{sc}^d and eventually chemical reaction 5 in the dark proceeded rather slowly above $R = 4$.

Photocurrent from photocorrosion of aluminum electrode in Al/mixed solid/Au cells.—A photocurrent and an open-circuit photovoltage were observed for the Al/H_2tpp/Au cell. As shown in Fig. 5a, the photocurrent increased with increasing reverse bias. This is interpreted as a space-charge limitation in the large resistance of the H_2tpp solid. In the Al/mixed solid of H_2tpp and o-chloranil/Au cells, the photocurrent increased remarkably compared to J_{sc}^d but the open-circuit photovoltage was approximately the same as the open-circuit dark voltage; see Fig. 5b, c, and d. This suggests that the oxidation rate of H_2tpp by o-chloranil and H$^+$ (the reaction rate of Eq. 5) was much faster under illumination than in the dark, because the pho-

toexcited H_2tpp (*H_2tpp) was oxidized much more easily than the H_2tpp in the ground state

$$2*H_2tpp + o\text{-chl} + 2H^+ \rightarrow 2H_2tpp^+ + tcc \quad [8]$$
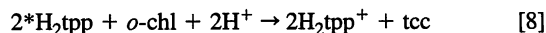
Under continuous illumination to the mixed solid cells, the photocurrent decayed rapidly, the transmittance of the semitransparent Al anode increased, and further the series resistance increased. This suggests that the photocurrent generation turned a part of the Al electrode into aluminum oxide,[9] that is, the photocurrent was due to the photocorrosion of the Al electrode.

Rate-determining step for photocorrosion of aluminum electrode in Al/mixed solid/Au cells.—The magnitude of the photocurrent from the photocorrosion of the Al electrode for the Al/mixed solid of H_2tpp and o-chloranil/Au cell depended largely on the R value. Figure 8 shows the R dependence of the short-circuit photocurrent quantum yield (ϕ) obtained by irradiating monochromatic light of 435, 455, and 665 nm from the Al side in the Al/dye/Au cells. The ϕ values in a unit of percent were estimated by the following equation

$$\phi = 124 \, J_{sc}/(I_0 \, \lambda) \quad [9]$$

where J_{sc} is the short-circuit photocurrent in units of nA cm^{-2}, I_0 (μW cm^{-2}) is the light intensity at the Al/dye interface, and λ (nm) is the incident wavelength. The photocurrent originating from the excited H_2tpp is mainly obtained when irradiated at 435 nm monochromatic light, but the observed photocurrents by irradiating at 455 and 655 nm contain both contributions from the excited H_2tpp and H_4tpp^{2+}. Since the concentration of H_4tpp^{2+} increased with added o-chloranil, the R dependence of the ϕ values was different for different irradiation wavelengths. Namely, the ϕ_{435} value exhibited a maximum around $R = 1$, and the ϕ_{455} and ϕ_{665} values exhibited maxima around $R = 2$ to 4, where the subscripts denote the incident wavelength. The R dependence of the ϕ_{435} did not fit with that of the J_{sc}^d but with that of the series resistance (see Fig. 6 and 7), suggesting that the photocurrent was limited only by the resistance because the photochemical reaction 8 proceeded very rapidly in contrast to the chemical reaction 5 in the dark. Therefore, a much smaller
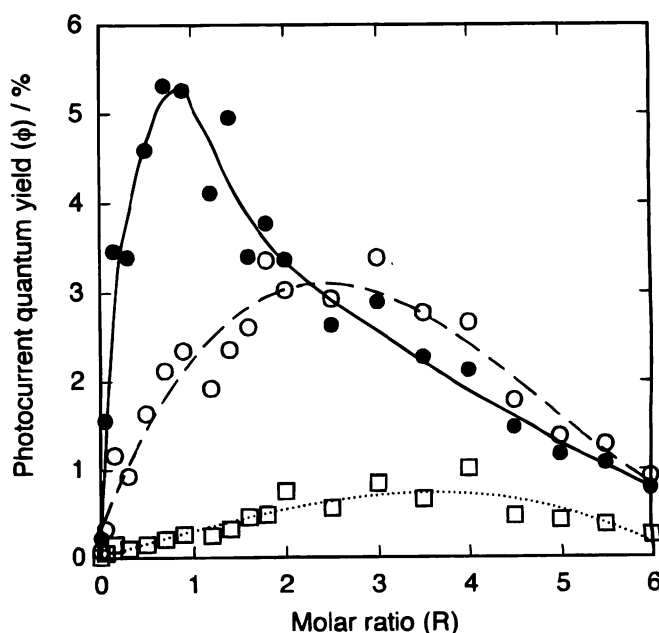
Figure 8. R dependence of short-circuit photocurrent quantum yield (ϕ) at 435 (●), 455 (○), and 665 nm (□) for irradiation from the Al side in Au/mixed solid/Au cells, where R indicates the molar ratio of o-chloranil to H_2tpp in the solid film. The amount of H_2tpp per unit area on the electrode was $(6.3 \pm 0.9) \times 10^{-9}$ mol cm^{-2}, and the incident light intensity at the Al/dye interface was $8.3 \pm 2 \, \mu$W cm^{-2}.

amount of o-chloranil is required to facilitate reaction 8. The H_2tpp^+ produced by the photochemical reaction 8 in the vicinity of the Al anode behaves as free holes which can move in the mixed dye solid by a hopping mechanism, and the photocurrent is observed only when the holes arrive at the Au cathode across the solid film. Thus, its magnitude was limited by electronic properties such as the resistivity of the dye solid.

We assumed that Eq. 8 consisted of two elementary reactions of a charge-separation of $*H_2tpp$ in the depletion layer and a consumption of the produced electrons (by Eq. 10) and the produced H^+ (by Eq. 4)

$$*H_2tpp \rightarrow e^-(H_2tpp) + h^+(H_2tpp) \quad [10]$$

$$o\text{-chl} + 2H^+ + 2e^-(H_2tpp) \rightarrow tcc \quad [11]$$
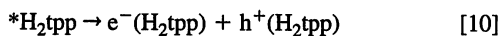
where $e^-(H_2tpp)$ and $h^+(H_2tpp)$ imply free electrons and free holes which can move in the solid, respectively. If the photocharge-separation reaction 10, of which the efficiency may be low because of a charge recombination, proceeds much more slowly than chemical reaction 11, the former efficiency in the depletion layer limits the magnitude of the photocurrent from the photocorrosion in a manner similar to that in organic solar cells.

To confirm the prediction that the charge-separation reaction 10 is a rate-determining step, we examined whether the dependence of the optical-filter effect (as observed in the photocurrent) on the film thickness as plotted in Fig. 9 was reproduced by the Yamashita model[32] applied to Schottky-type porphyrin organic solar cells. This model contains the assumptions that the photogenerated charge carriers are attributable to the dissociation of excitons diffusing toward the Schottky barrier in the electric field, and that the quantum efficiency of carrier generation is not constant over the dye layer but exponential at the barrier assuming exponential distribution of dopant O_2. Figure 9 also shows the calculated lines for the optical

Figure 9. Plot of the value of $\phi(Au)/\phi(Al)$ at Soret peak wavelength of H_2tpp as a function of the thickness of dye film. The optical-filter effect is represented by $\phi(Au)/\phi(Al)$, where $\phi(Au)$ is the short-circuit photocurrent quantum yield at the Soret peak of H_2tpp for the irradiation from the Au side and $\phi(Al)$ is that for the irradiation from the Al side. Symbols are the experimental values, and lines are estimated by calculation: (□) $R = 0$; (solid line) $W_{ap} = 18$ nm, $L_{exc} = 6$ nm; (●) $R = 0.1$; (broken line) $W_{ap} = 6$ nm, $L_{exc} = 10$ nm; (○) $R = 0.5$; (dotted line) $W_{ap} = 6$ nm, $L_{exc} = 8$ nm, where R indicates the molar ratio of o-chloranil to H_2tpp in the solid film, and W_{ap} and L_{exc} indicate apparent barrier width and exciton diffusion length, respectively.

Table I. Apparent barrier width (W_{ap}) and exciton diffusion length (L_{exc}) for the Al/mixed solid of H_2tpp and o-chloranil Schottky-barrier cell.

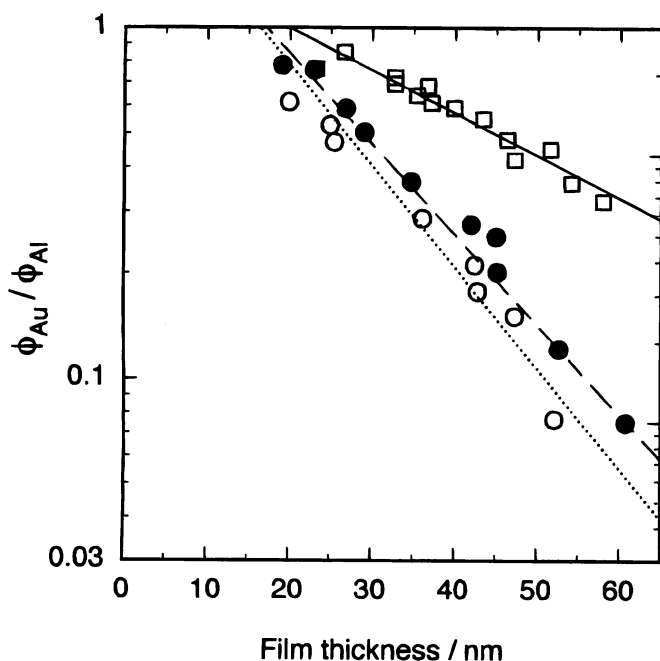| Mixing ratio	λ^a (nm)	α^b (nm^{-1})	W_{ap} (nm)	L_{exc} (nm)
0	440	0.061	22 ± 4	8 ± 4
0.1	435	0.063	6 ± 2	10 ± 4
0.5	435	0.064	6 ± 2	8 ± 2

[a] Wavelength of incident light.
[b] Extinction coefficient defined by $I = I_0 \exp(-\alpha d)$, where I and I_0 denote the transmitted and incident lights, respectively, and d is the film thickness.

filter effect at $R = 0$ (pure H_2tpp), 0.1, and 0.5. Since the estimated lines by the proposed model approximately agree with the experimental plots, it is found that the rate-determining step of reaction 8 is the photoinduced charge-separation reaction 10. The apparent width of the Schottky barrier (W_{ap}) and the exciton diffusion length (L_{exc}) obtained by this simulation are summarized in Table I. W_{ap} decreased rapidly from 22 nm (for the pure H_2tpp) to 6 nm (for the mixed solid of $R = 0.1$) by adding o-chloranil in H_2tpp as predicted from the strong increase of the hole density by this addition,[21] but W_{ap} at $R = 0.5$ was the same as that at $R = 0.1$. On the other hand, L_{exc} indicated constant values of about 8 nm in spite of the addition of o-chloranil.

The potential step corresponding to the open-circuit voltage (V_{oc}) may exist in the Schottky barrier under the short-circuit condition. Thus the potential gradient is estimated roughly from the ratio of the V_{oc}/e and W_{ap} values because W_{ap} is the distance where the potential step V_{oc} becomes 1/e. Since the V_{oc} values for the cells with the dye solids of $R = 0$, 0.1, and 0.5 were about 0.5, 0.8, and 0.8 V under illumination, respectively, the estimated potential gradients were about 10^4 V cm^{-1} at $R = 0$ and 10^5 V cm^{-1} at $0 < R < 1$. Hence one cause of the increased ϕ value by adding o-chloranil was the efficient photocharge-separation originating from the steep potential slope in the Schottky barrier.

Photocurrent from photocorrosion of aluminum electrode by excited metal-free porphyrin dication in Al/mixed solid/Au cells.— The absorption peaks at 455 and 665 nm in the absorption spectra of the mixed solid on the Al substrate originated from H_4tpp^{2+} as mentioned in an earlier section. Therefore, the photocurrent peaks observed at 455 and 665 nm in the photocurrent action spectra of the Al/dye/Au cells with the mixed solid of more than $R = 1.5$ were attributable to a charge separation of the excited H_4tpp^{2+} ($*H_4tpp^{2+}$) in the depletion layer. However, even when H_4tpp^{2+} was weakly detected in the absorption spectra, the contribution of $*H_4tpp^{2+}$ in the photocurrent action spectra was considerably large, see Fig. 1c and d. This is reasonably explained by the concentration of H_4tpp^{2+} and the efficiency of the photocharge-separation in the depletion layer close to the Al/dye interface as represented by Eq. 3 and the Yamashita model, respectively. This implies that, even when the total amount of H_4tpp^{2+} is not enough for UV-visible detection, its concentration is relatively high in the immediate neighborhood of the Al electrode because the distribution of H_4tpp^{2+} in the dye layer is not constant but exponential, and that the excited H_4tpp^{2+} underwent efficient charge-separation. Although it is predicted that the photocurrent by $*H_4tpp^{2+}$ increases as the concentration of H_4tpp^{2+} increases, that means the photocurrent generates from the singlet state of $*H_4tpp^{2+}$ and not from exciplex, the ϕ_{455} and ϕ_{665} values exhibited maxima around $R = 2$ to 4 because the resistance of the mixed solid limited the photocurrent at larger R region. In fact, the series resistance increased gradually above $R = 1$ as shown in Fig. 6 perhaps due to the decrease of hole mobility by a diluting effect of H_2tpp with o-chloranil and the decrease of hole density. The decrease of hole density is supported from the result that C in Eq. 3 corresponding to W_{ap} in the depletion layer was a large value of

about 80 nm for $R = 5$. That is, the hole density decreases because the increased H_4tpp^{2+} is not oxidized as easily as H_2tpp, and eventually the physisorbed O_2 and the mixed o-chloranil in the solid can hardly act as electron acceptors.

Conclusion

When the mixed-dye solid films were prepared on the Al substrate by spin coating from chloroform solutions containing a large excess of o-chloranil to H_2tpp, H_4tpp^{2+} was produced in the vicinity of the Al substrate because of the corrosion of aluminum aided by both the hydrogen bonds (between H_2tpp and o-chloranil) and the electric field (in a Schottky barrier built during the spin coating). The observed photocurrent for the Al/dye/Au cells with the mixed solids of H_2tpp and o-chloranil was attributable to the photocorrosion of the Al electrode by o-chloranil and water as presented by the following overall reaction

$$6*Por + 2Al + 3o\text{-chl} + 3H_2O \rightarrow 6Por + Al_2O_3 + 3tcc \quad [12]$$
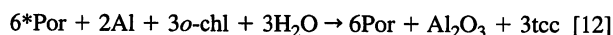
where *Por and Por denote H_2tpp or H_4tpp^{2+} in the excited state and in the ground state, respectively. Since the rate-determining step of the photocorrosion was the charge-separation process of the excited species in the depletion layer, the molar ratio of $*H_2tpp$ and $*H_4tpp^{2+}$ in the vicinity of the Al electrode limited the shape of the photocurrent action spectra. Hence the photocurrent action spectra of the cells with the mixed solids of more than about $R = 1.5$ did not follow the absorption spectra of the mixed solids on the Al substrate reflecting the total amount of H_4tpp^{2+}. Thus, we could plainly observe the photoinduced charge-separation profile at the photoactive Al/porphyrin interface because of the production of the electric-field-induced H_4tpp^{2+} by the corrosion of the Al substrate.

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