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Photovoltaic Properties of Porphyrin Thin Films Mixed with *o*-Chloranil

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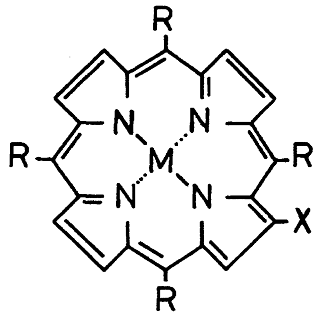
By mixing Zntpp solid with *o*-chloranil, the rectification and photovoltaic properties of Al/porphyrin/Au sandwich-type cell are improved (Zntpp: 5, 10, 15, 20-tetraphenylporphyrinatozinc). The improvement may be mainly attributable to an increase in the hole concentration as the majority carrier because of the electron transfer from Zntpp to *o*-chloranil in the ground state. In addition, by mixing H_2tpp solid with *o*-chloranil, the short circuit photocurrent of the sandwich-type cell increases although the rectification property is hardly improved (H_2tpp: 5, 10, 15, 20-tetraphenylporphyrin). The fluorescence intensity, the short circuit photocurrent and its temperature-dependence for various porphyrin solids mixed with *o*-chloranil are measured in order to clarify the photogeneration mechanism of charge carriers. The results suggest strongly that an exciplex formed between H_2tpp and *o*-chloranil molecules contributes to the photogeneration of charge carriers.

Much attention has been drawn to the photovoltaic properties of phthalocyanine,[1] merocyanine,[2] and porphyrin[3] organic films from the standpoint of the conversion of solar to electrical energy. The photovoltaic cells are roughly divided into three types by following blocking contacts, (a) the Schottky contact between metal with small work function and p-type organic semiconductor, (b) a p–n heterojunction between n-type inorganic and p-type organic semiconductors, and (c) a p–n heterojunction between n- and p-type organic semiconductors. However, their energy conversion yields are small because of the large resistance of organic solids. Therefore, the increase in the mobility and the concentration of the majority carrier is required in order to improve the energy conversion yield of the photovoltaic cells. We previously reported that the use of 5,10,15-triphenyl-20-(3-pyridyl)-porphyrinatozinc (Znpyp$_3$p) as an organic solid improved the photoelectrochemical properties because of the axial coordination of a pyridyl group in Znpyp$_3$p to zinc in another porphyrin.[4,5] Loutfy et al.[6] and Harima et al.[7] previously reported that, by mixing metal-free phthalocyanine, H_2tpp and Zntpp solids with an electron acceptor such as 2,4,7-trinitrofluorenone, iodine, tetracyanoquinodimethane, and *o*-chloranil, the fluorescence of the solids was quenched, and at the same time the energy conversion yield increased. However, the detailed mechanism for the increased photocurrent is not clear yet. The improvements may be ascribed to an increase in photoproduced carriers owing to an exciplex formation between the dye and the electron-acceptor molecules. However, in the case of I_2-mixed Zntpp solid, the enhanced photocurrent may be due to an increase in the hole concentration because of the electron transfer from Zntpp to I_2 in the dark. In this paper, we discuss in detail the reason of the improvement of photovoltaic properties for Al/porphyrin/Au sandwich-type cells by introducing *o*-chloranil into the porphyrin solids as shown in Fig. 1.



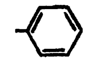
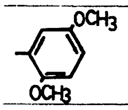
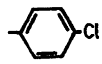
R	X	M	abbreviation
	H	H_2	H_2tpp
		Zn	Zntpp
		Mg	Mgtpp
		Al(Cl)	Altpp
	NO_2	Zn	Zntpp(NO_2)
	H	H_2	H_2tp(OMe)$_2$p
		Zn	Zntp(OMe)$_2$p
	H	H_2	H_2tp(Cl)p
		Zn	Zntp(Cl)p

Fig. 1. Structures and abbreviations of porphyrins.

Experimental

Porphyrin derivatives as shown in Fig. 1 were synthesized and purified by literature methods.[8—12]

Sandwich-type photovoltaic cells of Al/porphyrin/Au were fabricated as follows.[7] Transparent aluminum films were firstly prepared onto precleaned glass substrate by vacuum deposition. The transmittance of the films was 20—40%. The porphyrin films were secondly prepared onto aluminum-coated glass substrate by spin coating. The glass substrates were rotated at the rate of about 1000—2000 rpm, and the chloroform solutions containing 2×10^{-2} M porphyrin and *o*-chloranil of various concentrations were dropped onto the substrates (1 M=1 mol dm^{-3}). The thickness of porphyrin films, measured by a Sloan Dektak 3030 surface profilometer, was 100—150nm. Finally gold films (transmittance, 30—60%) were formed on the porphyrin films by vacuum deposition to make an ohmic contact.

The light source consisting of a 150 W halogen tungsten lamp and a JASCO CT-25C monochromator was used only when the photocurrent action spectra, the photocurrent quantum yield and photocurrent-voltage curves were measured. The light intensity was monitored by an Ando AQ-1135E optical power meter with a silicon photocell. For the current-voltage characteristics measurement, the 440 nm light with an intensity of 17.9 μW cm^{-2} at the Al/porphyrin interface was used. The bias was applied by a Hokuto Denko HB-105 function generator with the scan rate of 500 mV min^{-1}, and the current was measured by a Keithley 617 electrometer. For the photocurrent action spectra, the light intensity was normalized to 30 μW cm^{-2} at the Al/porphyrin interface. These equipments were controlled and the measured data were recorded by a microcomputer through a GPIB interface. The other photocurrent measurements were performed by the light source consisting of a 500 W xenon arc lamp and an interference filter (λ_{max}=424 nm, $\Delta\lambda_{1/2}$ (half width) =15 nm). The light intensity at the Al/porphyrin interface was 200 μW cm^{-2}, and the short circuit photocurrent was measured by a Keithly 614 electrometer.

Cyclic voltammetry was performed in a N_2-purged dichloromethane solution, using a Pt wire (diameter, 0.1 mm) as the working electrode, a Pt wire as the counter electrode, and Ag/0.1 M $AgNO_3$ in acetonitrile solution as the reference electrode. The electrode potential was controlled by using a Hokuto Denko HA-501 potentiostat and a Hokuto Denko HB-104 function generator, and recorded on a Yokogawa Denki 3025 X–Y plotter. The average of the cathodic and anodic peak potentials, measured at the scan rate of 100 mV s^{-1}, was regarded as the half -wave potentials. The half-wave potential of ferrocene/ferrocenium ions (Fc/Fc$^+$) was used as the internal reference. The absorption and emission spectra were recorded on a Hitachi U-3210 spectrophotometer and a Shimadzu RF-540 spectrofluorometer equipped with a Hamamatzu Photonics R928 photomultiplier respectively. The infrared spectra were also taken on a JASCO FT/IR-3 fourier transform infrared spectrophotometer.

Results and Discussion

The photocurrent flowing from Au to Al is observed with the external circuit of Al/porphyrin/Au sandwich-type photovoltaic cells, when illumination is carried out from the Al/porphyrin interface. This direction of the photocurrent is defined as positive, and, in all photocurrent measurements, light is illuminated from the active interface of Al/p-type porphyrin. The mixing of H_2tpp solid with *o*-chloranil results in a remarkable increase in the short circuit photocurrent of the sandwich-type cell as exhibited by Harima et al.,[7] and also the mixing of Zntpp solid with *o*-chloranil indicates the same increase in the photocurrent. Figure 2 shows the short circuit photocurrent action spectra of Al/Zntpp/Au and Al/H_2tpp/Au sandwich-type cells with and without *o*-chloranil. The action spectra are approximately the same as the absorption spectra of the porphyrin solid films even when *o*-chloranil is introduced into the porphyrin solids. Therefore, the results imply that the excited porphyrins contribute to the generation of the photocurrent. The photocurrent quantum yield at an incident light of 433 nm (30 μW cm^{-2}) and an ambient temperature changes from 1.5% for pure Zntpp to 6.9% for *o*-chloranil-mixed Zntpp (mole ratio =1), and from 0.29% for pure H_2tpp to 4.4% for *o*-chloranil-mixed H_2tpp (mole ratio =1). Figure 3 shows the current-voltage characteristics of Al/Zntpp/Au and Al/H_2tpp/Au sandwich-type photovoltaic cells with and without *o*-chloranil. The Al/pure Zntpp/Au cell in the dark does not exhibit a clear rectification behavior because of the very small conductance of the film (3×10^{-13} S cm^{-1}),[4] although Zntpp solid is known as a p-type semiconductor. However, a clear rectification property is observed by introducing *o*-chloranil into the solid. The result suggests that in the dark the hole concentration as the majority carrier increases by mixing Zntpp solid with *o*-chloranil because of the electron transfer from Zntpp to *o*-chloranil in the ground state. Therefore, it is inferred that a potential slope formed at the interface of Al/*o*-chloranil-mixed Zntpp becomes larger than that of Al/pure Zntpp, and eventually that the photogenerated electrons and holes at the interface of Al/*o*-chloranil-mixed Zntpp are separated more efficiently. The inferences may be supported from the fact that the larger photocurrents are obtained by introducing *o*-chloranil into Zntpp solid. Moreover, the mixing of H_2tpp solid with *o*-chloranil results in an increase in the photocurrent. However, the rectification property is hardly improved. Therefore, the enhanced photocurrent may not be attributable to the increase of the hole concentration as the majority carrier in the dark. The reason for such an increase in the photocurrent by introducing *o*-chloranil into H_2tpp solid is discussed later in detail.

Figure 4 shows the relationship between the first ring oxidation potential ($E_{ox}{}^{1st}$) of porphyrins and the short circuit photocurrent of the photovoltaic cells. Half-wave potentials of porphyrins in solutions are summarized in Table 1. The short circuit photocurrent (i_0) of Al/pure porphyrin/Au cells proportionally increases with decreasing the value of $E_{ox}{}^{1st}$ as demonstrated by Yamashita.[3] When porphyrin solid is mixed with *o*-chloranil at mole ratio of 1, the short circuit photocurrent (i_m) of Al/*o*-chloranil-mixed porphyrin/Au cells increases. However, the linear relation between the values of $E_{ox}{}^{1st}$ and i_m is not obtained. Figure 5 shows the correlation between alterations in S_1 emission intensity $(1-(F_m/F_0))$ and the short circuit photocurrent (i_m/i_0), where F_m and F_0 correspond to the $Q_{0,1}$fluorescence intensities from porphyrin solid with

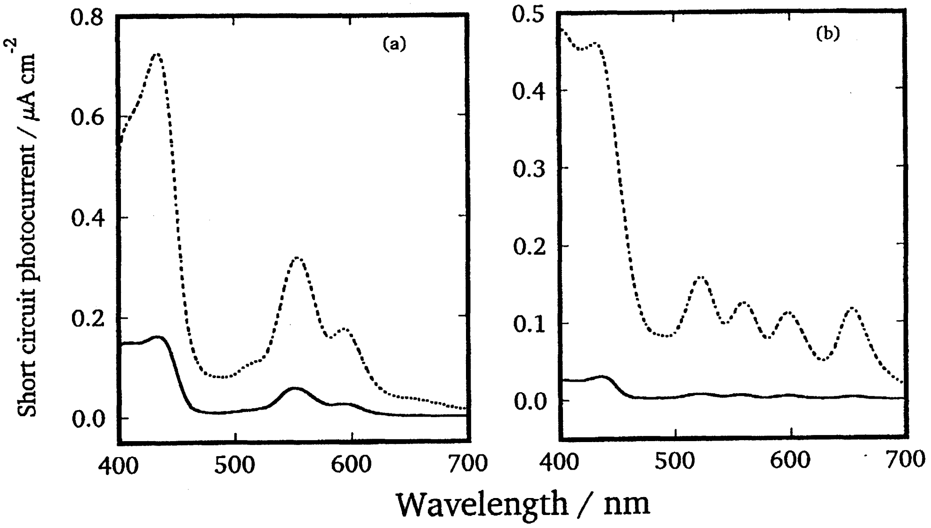


Fig. 2. Short circuit photocurrent action spectra of Al/Zntpp/Au (a) and Al/H_2tpp/Au (b) sandwich-type cells at ambient temperature. The solid and broken lines denote the porphyrin solid thin films without and with o-chloranil (mole ratio =1), respectively.

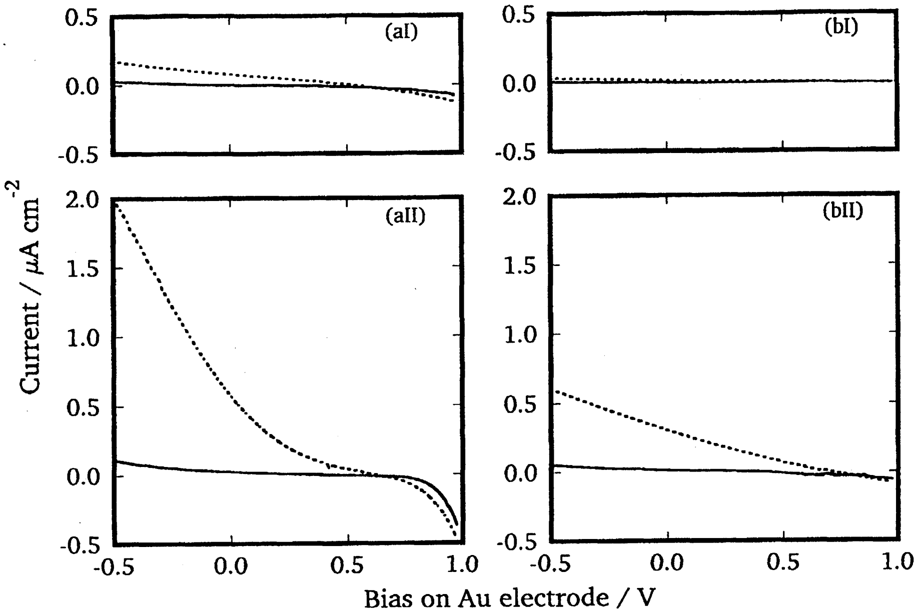


Fig. 3. Dark current–voltage (——) and photocurrent–voltage (- - -) characteristics for Al/Zntpp/Au (a) and Al/H_2tpp/Au (b) cells at ambient temperature. I and II denote the porphyrin solid thin films without and with o-chloranil (mole ratio =1), respectively.

and without o-chloranil respectively (mole ratio =1). In the case of the metal porphyrins, which are oxidized easier than the metal-free porphyrins, the i_m/i_0 values are approximately constant and relatively small in spite of the effective fluorescence quenching arising from mixing of o-chloranil. The result suggests that, by mixing metal porphyrin solids as well as Zntpp one with o-chloranil, the hole concentration as the majority carrier increases in the dark, and eventually that this increase mainly brings about the enhanced photocurrent. On the other hand, the i_m/i_0 values of the metal-free porphyrins are relatively large. The infrared spectra exhibit that the signal at 3318 cm^{-1} for pure H_2tpp solid, which is assigned to N–H stretching vibration of pyrrole part in H_2tpp, shifts to lower wavenumber by introducing o-chloranil into the solid (difference (mole ratio =1), 5 cm^{-1}). The result implies that the very weak hydrogen bond is partly formed between pyrrole protons of H_2tpp and carbonyl oxygens of o-chloranil. Therefore, an exciplex with the intermolecular charge transfer character may be produced when the very weakly aggregated molecules are photoexcited. We tentatively infer that the enhanced photocurrent for the metal-free porphyrins is ascribed to the exciplex formation. That is,

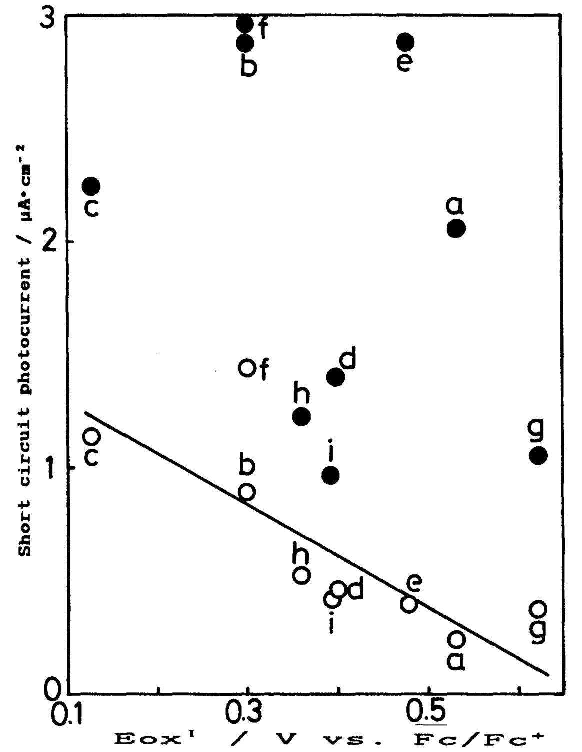


Fig. 4. The dependence of the short circuit photocurrent for Al/pure porphyrin/Au (○) and Al/*o*-chloranil-mixed porphyrin (mole ratio =1)/Au (●) cells on the first ring oxidation potential of porphyrins (E_{ox}^{1st}) at ambient temperature. a: $\mathrm{H_2tpp}$, b: Zntpp, c: Mgtpp, d: Altpp, e: $\mathrm{H_2tp(OMe)_2p}$, f: $\mathrm{Zntp(OMe)_2p}$, g: $\mathrm{H_2tp(Cl)p}$, h: Zntp(Cl)p, i: $\mathrm{Zntpp(NO_2)}$.

Table 1. Half-Wave Potentials[a] of Porphyrins in Dichloromethane at Ambient Temperature

Porphyrin	Reduction potential/V		Oxidation potential/V	
	2nd	1st	1st	2nd
$\mathrm{H_2tpp}$	−2.09	−1.74	0.53	
Zntpp		−1.83	0.30	
Mgtpp			0.13	0.43
Altpp		−1.69	0.40	
$\mathrm{H_2tp(OMe)_2p}$		−1.76	0.48	0.75
$\mathrm{Zntp(OMe)_2p}$		−1.88	0.30	
$\mathrm{H_2tp(Cl)p}$		−1.66	0.62	0.82
Zntp(Cl)p			0.36	0.65
$\mathrm{Zntpp(NO_2)}$		−1.54	0.39	

[a] The half-wave potential of ferrocene/ferrocenium ion (Fc/Fc$^+$) was used as the internal reference.

the charge separation of the exciplex may occur more effectively than that of the excited pure porphyrin in the potential barrier at the Al/porphyrin interface. Figure 6 shows the effect of *o*- and *p*-chloranil mixing on the short circuit photocurrent and fluorescence intensity for Zntpp and $\mathrm{H_2tpp}$ solids. The fluorescence quenching efficiency increases with mixing of *o*-chloranil, and at the same time the photocurrent also increases. The same effect is obtained by introducing *o*-bromanil into porphyrin solids. The fluorescence of porphyrin solids is also quenched by introducing *p*-chloranil. However, the photocurrent remarkably decreases with an increase in the mixing ratio of *p*-chloranil, of which first reduction potential (−0.44 V) is slightly more negative than that of *o*-chloranil (−0.34 V). The same depression effect is

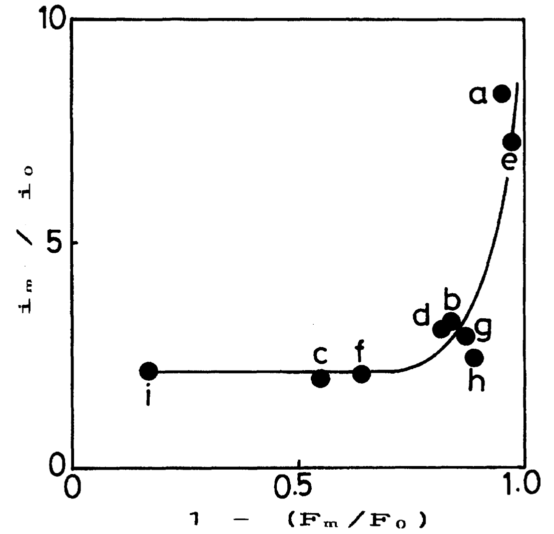


Fig. 5. The relation between i_m/i_0 and $(1-(F_m/F_0))$ at ambient temperature. i_m/i_0 Denotes the ratio of the short circuit photocurrents of Al/*o*-chloranil-mixed porphyrin (mole ratio=1)/Au cell to Al/pure porphyrin/Au cell, and also F_m/F_0 the ratio of $Q_{0,1}$ fluorescence intensities of the porphyrin solid film with *o*-chloranil (mole ratio =1) to pure porphyrin solid film. a: $\mathrm{H_2tpp}$, b: Zntpp, c: Mgtpp, d: Altpp, e: $\mathrm{H_2tp(OMe)_2p}$, f: $\mathrm{Zntp(OMe)_2p}$, g: $\mathrm{H_2tp(Cl)p}$, h: Zntp(Cl)p, i: $\mathrm{Zntpp(NO_2)}$.

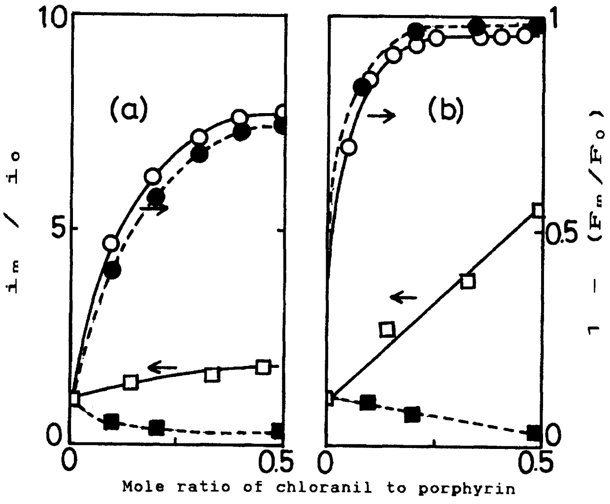


Fig. 6. The effect of *o*-chloranil (□,○) and *p*-chloranil (■,●) mixing on the short circuit photocurrent (□,■) and $Q_{0,1}$ fluorescence intensity (○,●) for Zntpp (a) and $\mathrm{H_2tpp}$ (b) solid thin films at ambient temperature.

also observed by introducing *p*-bromanil, *p*-benzoquinone, and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone into porphyrin solids. The resistance of the porphyrin films may merely increase by mixing with *p*-chloranil, and eventually the photocurrent of the photovoltaic cells may decrease. *p*-Chloranil molecules cannot approach the porphyrin ones as closely as *o*-chloranil ones, and consequently the ground state complex or the exciplex, of which the formation probably enhances the photocurrent, may not be produced between *p*-chloranil and porphyrin molecules. At present, we cannot clearly explain the difference of the photovoltaic effect on *o*- and *p*-chloranil mixing.

The activation energy (ΔE) for the migration of the photogenerated charge carriers in porphyrin solids is estimated from the dependence of the short circuit photocurrent (i) for Al/porphyrin/Au sandwich-type cells on the measurement temperature (T),

$$i = A\exp\left(-\Delta E/kT\right) \qquad (1)$$

where A, k, and T are constant, Boltzman constant, and absolute temperature respectively. The i values increase with an increase in the temperature. The relations between the reciprocal of T and log (i) are shown in Fig. 7. The plots give straight lines in the range from 5 to 40°C. The ΔE values of pure Zntpp and H_2tpp solids are 0.15 and 0.17 eV respectively, and those of *o*-chloranil-mixed Zntpp and H_2tpp solids (mole ratio =1) are 0.26 and 0.30 eV respectively. The mixing of *o*-chloranil may result in smaller intermolecular interaction between porphyrin molecules, and eventually the decrease in the mobility of charge carriers. However, the mixing of *o*-chloranil results in an increase in the photocurrent of the photovoltaic cells. The fact also suggests that the increase of charge carriers in the dark and/or under illumination significantly contributes to the enhanced photocurrent. The following Stern–Volmer equation may be valid for the homogeneous *o*-chloranil-mixed porphyrin solids,

$$F_0/F_m = 1 + K_{sv}\cdot m \qquad (2)$$

$$K_{sv} = \tau_0\cdot k_q \qquad (3)$$

where K_{sv} and m indicate Stern–Volmer constant and the mole ratio of *o*-chloranil to porphyrin respectively, and also τ_0 and k_q indicate the fluorescence lifetime (or exciton lifetime) of pure porphyrin molecules in the solids and the fluorescence quenching kinetic constant respectively. Figure 8 shows the relationships between m and F_0/F_m for Zntpp and H_2tpp solids. The plots give straight lines in the range from m=0 to m=0.3, and therefore, it is estimated that the K_{sv} values are 8.5 for Zntpp solid and 61.0 for H_2tpp solid respectively. Since the τ_0 values are 0.9 ns for Zntpp solid and 0.31 ns for H_2tpp one respectively,[13] it is estimated that the k_q values are 9.4×10^9 s^{-1} for Zntpp solid and 2.0×10^{11} s^{-1} for H_2tpp one respectively. It is found that the exciplex formation is influenced more significantly by k_q

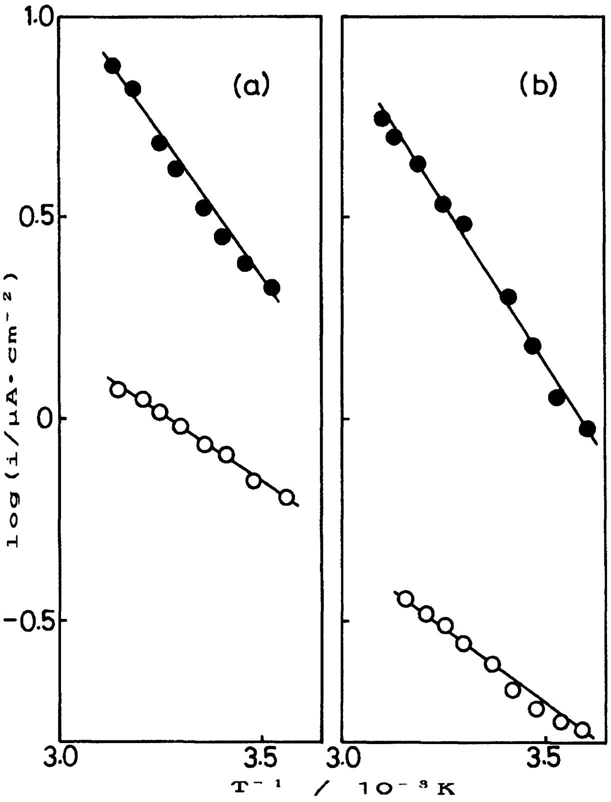


Fig. 7. The relation between log (i) and T^{-1} for Al/Zntpp/Au (a) and Al/H_2tpp/Au (b) cells. ○ and ● denote the porphyrin solid thin films without and with *o*-chloranil (mole ratio =1), respectively. i and T also denote the short circuit photocurrent and the absolute temperature, respectively.

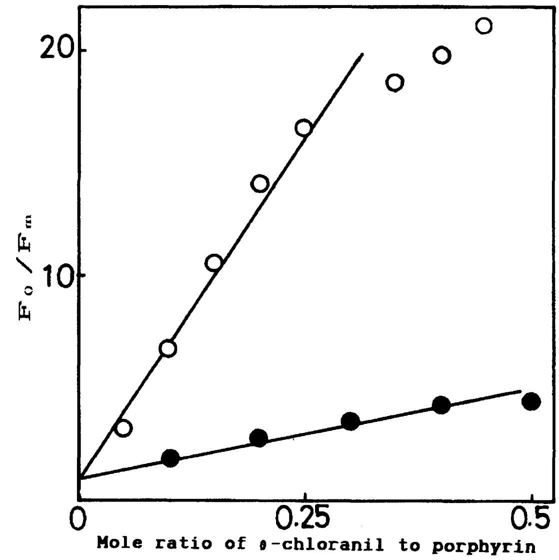


Fig. 8. Stern–Volmer plots for the fluorescences of Zntpp (●) and H_2tpp (○) solid thin films at ambient temperature.

than τ_0. That is, the exciton diffusion rate of H_2tpp may be larger than that of Zntpp.

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