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Enhanced Quantum Yield in Porphyrin Heterodimer Solar Cells

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The Al/porphyrin/Au sandwich-type photovoltaic cell with a heterodimer solid of 5,10,15,20-tetraphenylporphyrinatozinc (Zntpp) and 5,10,15-triphenyl-20-(3-pyridyl)porphyrin (H_2pyp_3p) exhibits a remarkably large photocurrent quantum yield, compared with the cell with a pure Zntpp or an H_2pyp_3p solid.

Much attention has been drawn to the photovoltaic properties of porphyrin organic films from the standpoint of the conversion of solar to electrical energy.[1-4] However, the energy conversion yield is small because of the small intermolecular interaction between porphyrin molecules. An increase in the mobility and the concentration of a majority carrier is required in order to improve the energy conversion yield of the photovoltaic cells. In this letter, we report that the photocurrent quantum yield for mixed films of Zntpp and H_2pyp_3p is considerably larger than that for the pure porphyrin films in Al/porphyrin/Au sandwich-type cells.

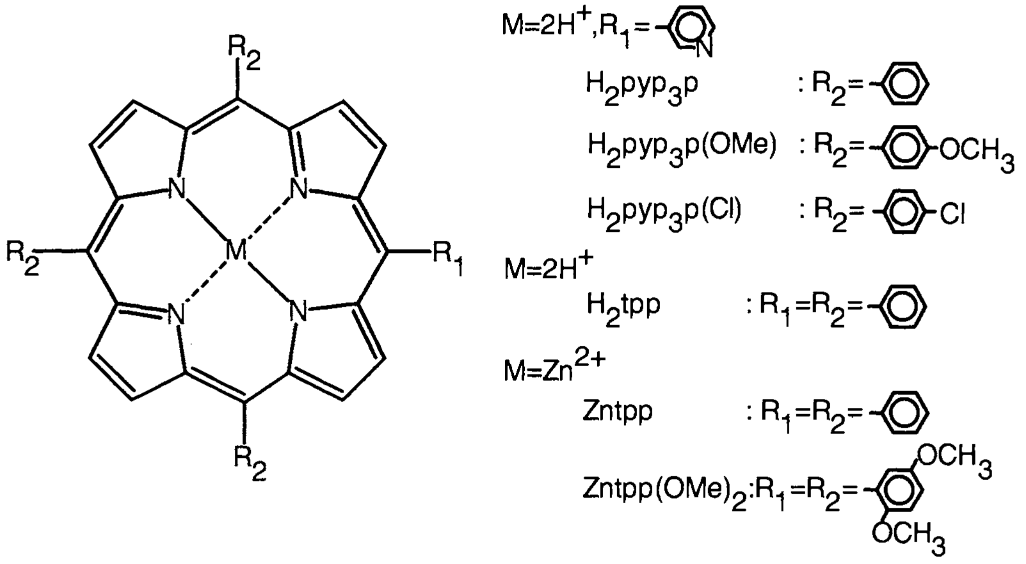

Fig. 1. Structure and abbreviations of porphyrins.

Porphyrin derivatives as shown in Fig. 1 were synthesized and purified by literature methods.[5,6] Sandwich-type photovoltaic cells of Al/porphyrin/Au were fabricated as the previous paper.[2] The porphyrin films (thickness, about 30 nm) were prepared by dropping the chloroform solution containing 1×10^{-2} mol·dm^{-3} of total porphyrin onto aluminum-coated glass substrate, which was rotated at the rate of about 1000 rpm. The photocurrent measurement was also carried out as the previous paper.[2]

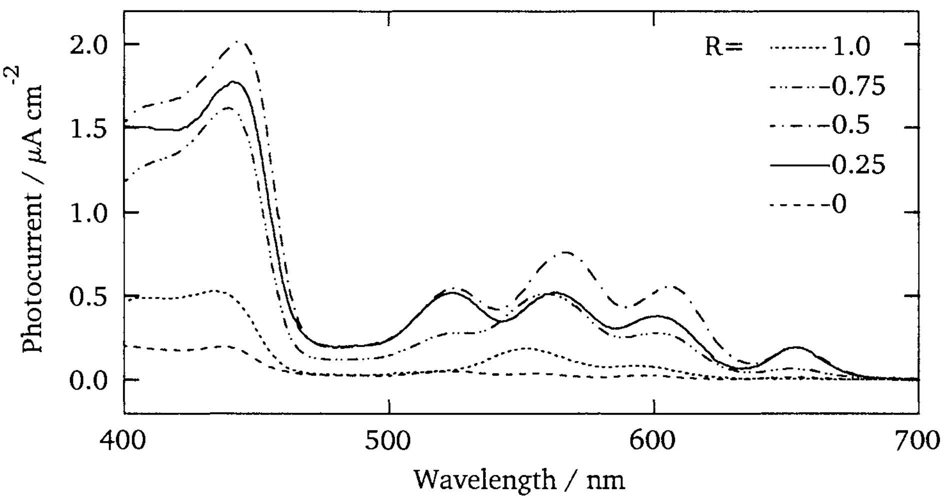

Fig. 2. Photocurrent action spectra of Al/porphyrin/Au cells with pure and mixed porphyrin films of Zntpp and H_2pyp_3p. The incident light intensity was normalized to 60 μW·cm^{-2} at the Al/porphyrin interface.

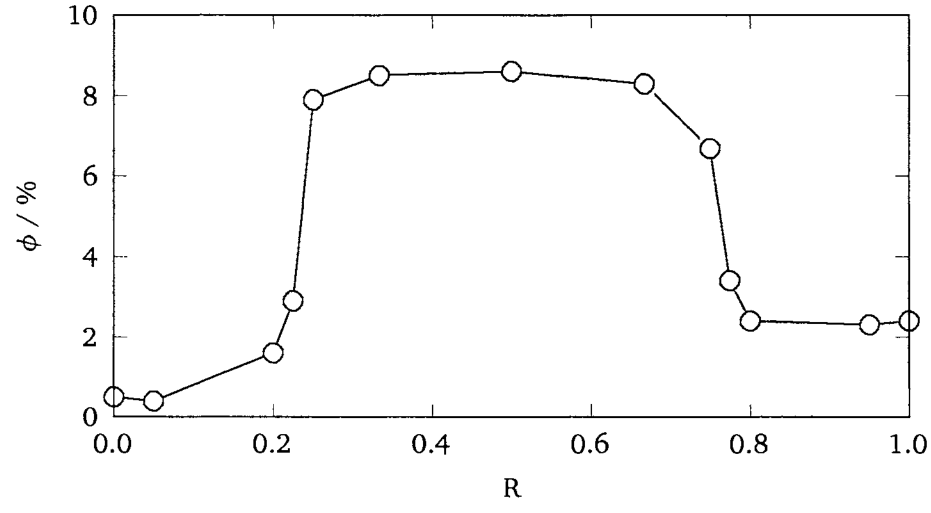

Fig. 3. Photocurrent quantum yield (φ) of Al/mixed porphyrin film of Zntpp and H_2pyp_3p/Au cell as a function of the mixing ratio (R) with an incident light of 440 nm (35 μW·cm^{-2}).

The photocurrent flowing from Au to Al is observed with the external circuit of the photovoltaic cells, when illumination is performed from the Al/porphyrin interface. On the other hand, when illumination is carried out from the Au/porphyrin interface, the photocurrent decreases due to a filter effect of the porphyrin film. Therefore, in all photocurrent measurements, light is illuminated from the active interface of Al/porphyrin. Figure 2 shows the dependence of the short-circuit-photocurrent action spectra on the mixing ratio (R) of Zntpp and H_2pyp_3p, which is defined as the mole ratio of Zntpp to total porphyrin. The cells with the mixed solids (R=0.25-0.75) indicate a remarkable increase of the photocurrent, compared with pure Zntpp and H_2pyp_3p solids. Moreover, the action spectra are approximately the same as the absorption spectra of the porphyrin films, although the profile varies with the R value. Figure 3 shows the relation between the R value and the short-circuit-photocurrent quantum yield (ϕ) at an incident light of 440 nm (35 $\mu W \cdot cm^{-2}$) and an ambient temperature. The ϕ value changes from 0.44% for R=0 (pure H_2pyp_3p) to approximately 8% for R=0.25-0.75, and further 2.4% for R=1 (pure Zntpp). On the contrary, the ϕ value for the photovoltaic cell with an equimolar mixed solid of Zntpp and H_2tpp (5,10,15,20-tetraphenyl porphyrin) is 1.1%. Fleischer et al. reported the coordination of pyridyl group in H_2pyp_3p to the zinc center in Zntpp in chloroform.7) Therefore, in the mixed solid of Zntpp and H_2pyp_3p, a porphyrin heterodimer may be formed between the two porphyrin molecules by the coordination. In fact, the absorption peak in the Q region of Zntpp in the mixed solid is observed at longer wavelength than that in the pure Zntpp solid because of the axial coordination of pyridyl group in H_2pyp_3p to zinc in Zntpp. The increase of the ϕ value may be ascribed to the heterodimer formation. The Al/porphyrin/Au sandwich-type cell with the porphyrin heterodimer exhibits the open circuit photovoltage of 1.1 V, but does not show a clear rectification behavior in the dark in a similar manner as the cells with pure Zntpp and H_2pyp_3p. The result indicates that the porphyrin heterodimer in the ground state does not bring about the increase of the concentration of holes as majority carriers. The ϕ value of the photovoltaic cells with various porphyrin heterodimers (R=0.5) are summarized in Table 1. $H_2pyp_3p(OMe)$ (5,10,15-tri(4-methoxyphenyl)-20-(3-pyridyl)porphyrin) and $H_2pyp_3p(Cl)$ (5,10,15-tri(4-chlorophenyl)-20-(3-pyridyl)porphyrin) as well as H_2pyp_3p are used as the coordinating porphyrin, and Zntpp and $Zntpp(OMe)_2$ (5,10,15,20-tetra(2,5-dimethoxyphenyl)porphyrinatozinc) as the host porphyrin. The maximum ϕ value of 13.2% is obtained for the cell with a heterodimer solid consisting of $H_2pyp_3p(Cl)$ and $Zntpp(OMe)_2$ (R=0.5). The fluorescence spectra of the mixed porphyrin solids were also measured. The fluorescence of Zntpp is completely quenched by the introduction of Zntpp into H_2pyp_3p solid because of the energy transfer from the excited Zntpp to H_2pyp_3p. On the other hand, the fluorescence of H_2pyp_3p is also slightly quenched. That is, the enhanced photocurrent for the heterodimer solids may be correlated to the fluorescence quenching. We tentatively infer from the results that an exciplex is formed in the porphyrin heterodimer solid, and that it contributes to the increase of the photogenerated charge carriers.

In conclusion, the large ϕ values are obtained in the wide range of R=0.25-0.75 in the mixed solids of Zntpp and H_2pyp_3p as shown in Figs. 2 and 3, and also the photocurrent action spectra change with the R value. The result suggests that a porphyrin heterodimer formed between the two porphyrin molecules acts as a photoreaction center, and further that a monomeric porphyrin acts as a photon collector. Such a photovoltaic property is particularly interesting from the standpoint of the photosynthesis model. That is, in this simple solar cell, the porphyrin heterodimer behaves as the special pair of the photosynthetic reaction center,8) and the monomeric porphyrin as the antenna pigment, and further the potential barrier at the Al/porphyrin interface as the multi-step redox chain for the charge separation.

Table 1. Photocurrent quantum yield (ϕ/%) for pure and equimolar mixed porphyrin films in Al/porphyrin/Au sandwich-type photovoltaic cells with an incident light of 440 nm (35 $\mu W \cdot cm^{-2}$)

Pure porphyrin film		Equimolar mixed porphyrin film	
H_2tpp	0.86	H_2tpp-Zntpp	1.1
H_2pyp$_3$p	0.44	H_2tpp-Zntpp(OMe)$_2$	1.4
H_2pyp$_3$p(OMe)	1.4	H_2pyp$_3$p-Zntpp	8.6
H_2pyp$_3$p(Cl)	0.60	H_2pyp$_3$p-Zntpp(OMe)$_2$	11.1
Zntpp	2.4	H_2pyp$_3$p(OMe)-Zntpp	4.1
Zntpp(OMe)$_2$	2.3	H_2pyp$_3$p(OMe)-Zntpp(OMe)$_2$	7.9
		H_2pyp$_3$p(Cl)-Zntpp	8.8
		H_2pyp$_3$p(Cl)-Zntpp(OMe)$_2$	13.2

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