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Spectral Cosensitization in Organic Solar Cell with Mixed Film of Zinc Porphyrin and Merocyanine

Kohshin TAKAHASHI,* Kei HASHIMOTO, Teruhisa KOMURA, and Kazuhiko MURATA†
Department of Chemistry and Chemical Engineering, Faculty of Technology,
Kanazawa University, Kodatsuno, Kanazawa 920
†Tsukuba Research Laboratory, Nippon Shokubai Co. Ltd., Kannondai, Tsukuba 305

The Al/dye/Au sandwich–type photovoltaic cell with a mixed solid of 5,10,15,20–tetraphenylporphyrinatozinc (Zntpp) and 3–ethyl–5–[(3–ethyl–2(3H)–benzothiazolylidene)ethylidene]–2–thioxo–4–thiazolidinone (MC) exhibits a remarkably large energy conversion yield and a better spectral match with a solar spectrum, compared with a pure Zntpp or a MC solid.

Much attention has been drawn to the photovoltaic properties of organic films such as porphyrins and merocyanines from the standpoint of the conversion of solar to electrical energy.1–3) However, the energy conversion yield is small, and the light in a wide wavelength region cannot be utilized. Some work on photovoltaic properties of a sandwich–type cell with mixed films of chlorophyll a (chl a) and various photosynthetic pigments appeared because a high energy conversion yield can be expected from a simulation of a photosynthetic system in plants.4,5) In this cell, photocurrent was generated in a wider wavelength region, which is termed as a spectral sensitization, but the energy conversion yield was similar to that of pure chl a. Yamashita et al. 6,7) reported that organic photoelectrodes and photovoltaic cells based on p–n and p–p junctions between porphyrins and phthalocyanines exhibited a better spectral match with a solar spectrum and an enhanced photocurrent, which is called a spectral cosensitization. In this letter, we report that a spectral cosensitization effect is observed in the homogeneously mixed films of Zntpp and MC in Al/dye/Au sandwich–type cells. Such a remarkably enhanced photocurrent in the cell with homogeneously mixed dyes was not reported except for our previous letter.8)

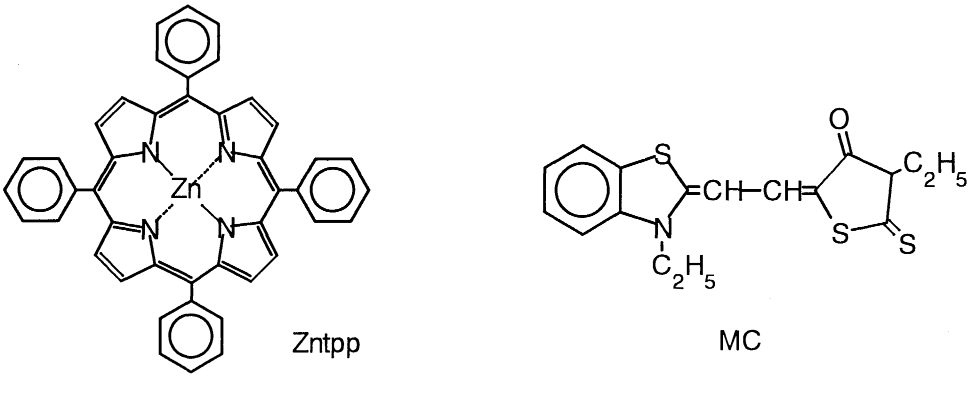

Fig. 1. Structures of Zntpp and MC.

Zntpp and MC as shown in Fig. 1 were synthesized and purified by literature methods.$^{9-11)}$ Sandwich-type photovoltaic cells of Al/dye/Au were fabricated as in the previous paper.$^{12)}$ The dye film (thickness, about 100 nm) were prepared by dropping a chloroform solution containing 2×10^{-2} mol·dm^{-3} of total dye onto an aluminum-coated glass substrate, which was rotated at the rate of 2000 rpm. The photocurrent action spectra were measured under the incident light of constant intensity (5 μW·cm^{-2} at the Al/dye interface) in all wavelength region. The other photocurrent measurements were carried out as in the previous paper.$^{12)}$

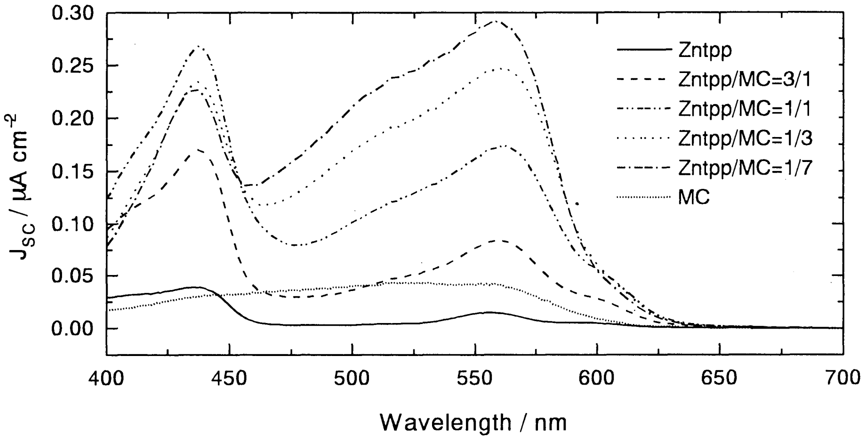

Fig. 2. Photocurrent action spectra of Al/dye/Au cells with pure and mixed dye films of Zntpp and MC. The incident light intensity was 5 μW·cm^{-2} at the Al/dye interface.

It is known that pure Zntpp and MC solids behave as p-type semiconductors.$^{1,3)}$ Therefore, the photocurrent flowing from Au to Al is observed in the external circuit of the photovoltaic cells, when illumination is performed from the Al/dye interface which forms a MIS(Metal-Insulator-Semiconductor)-type junction. The mixed films of Zntpp and MC behave as a p-type semiconductor. In all photocurrent measurements, a sample is illuminated from the active interface of Al/dye because the photocurrent remarkably decreases due to an optical filtering effect of the dyes when illumination is carried out from the Au/dye interface. Figure 2 shows the dependence of the short-circuit-photocurrent (J_{SC}) action spectra on the mixing ratio (R) of Zntpp and MC, which is defined as the mole ratio of Zntpp to total dye. The cells with the mixed solids exhibit remarkable increments of the photocurrent and the utilization efficiency of the light in a wide wavelength region (so-called spectral cosensitization), compared with pure Zntpp or MC solids. The action spectra are similar to the absorption spectra of the dye films although the profile varies with the R value. Figure 3 shows the relationship between the R value and the short-circuit-photocurrent quantum yield (ϕ) at 440 nm and 560 nm, and the relationship between the R value and the absorbance of the mixed film (thickness, about 20 nm). The ϕ value at 440 nm is 1.8% for R=0 (pure MC) and 2.2% for R=1 (pure Zntpp), and the maximum value of 15% for R=0.5. At 560 nm, the ϕ values of 1.8% and 0.65% are obtained for R=0 and 1, respectively, and the maximum value of 13% for R=0.125. Thus, we obtain larger ϕ value for the mixed solids than that for pure solids. Moreover, we obtain the open-circuit photovoltage (V_{OC}) of 0.80 V, the short-circuit photocurrent (J_{SC}) of 0.64 μA·cm^{-2}, the fill factor (ff) of 0.20, and the energy conversion yield (η) of 0.68% for the mixed solid of R=0.5 at 440 nm, and also

V_{oc}=0.95 V, J_{sc}=0.71 μA·cm^{-2}, ff=0.15, and η=0.66% for the mixed solid of R=0.125 at 560 nm when illuminated with the intensity of 15 μW·cm^{-2} at Al/dye interface. Figure 4 shows the UV–vis absorption spectra of the pure and mixed (R=0.5) films (thickness, 20 nm), and the spectra estimated from the simple summation of the absorbance of the two pure films. The absorption peak for the Q region of Zntpp in the mixed solid is observed at longer wavelength than that in the pure Zntpp solid. The absorption peak in MC around 480 nm disappears in the absorption spectra for the mixed film of R=0.5. Furthermore, the IR spectra exhibit an exceptional decrease of the absorption intensity at 1673 cm^{-1}, that signal is assigned to the stretching vibration of carbonyl group in MC, with the addition of Zntpp into MC. The signal is not observed at all for the mixed solid of R≥0.6. These results imply that a ground–state complex with a strong electronic interaction is formed between Zntpp and MC in the mixed solid due to the coordination of the carbonyl group in MC to the Zn ion in Zntpp. Because the rectification property in the dark is slightly improved for the cell of the mixed dyes, the carrier density increases and the resistance of the mixed dye film should decrease. Therefore, the increase in the photocurrent is partly ascribed to the decrease in the resistance. However, the small fill factors suggest that the cells with mixed solids of Zntpp and MC still have a high series resistance. The enhanced photocurrent must be limited by another mechanism. We tentatively assign that the cosensitization is due to a long–life excited complex of Zntpp and MC.

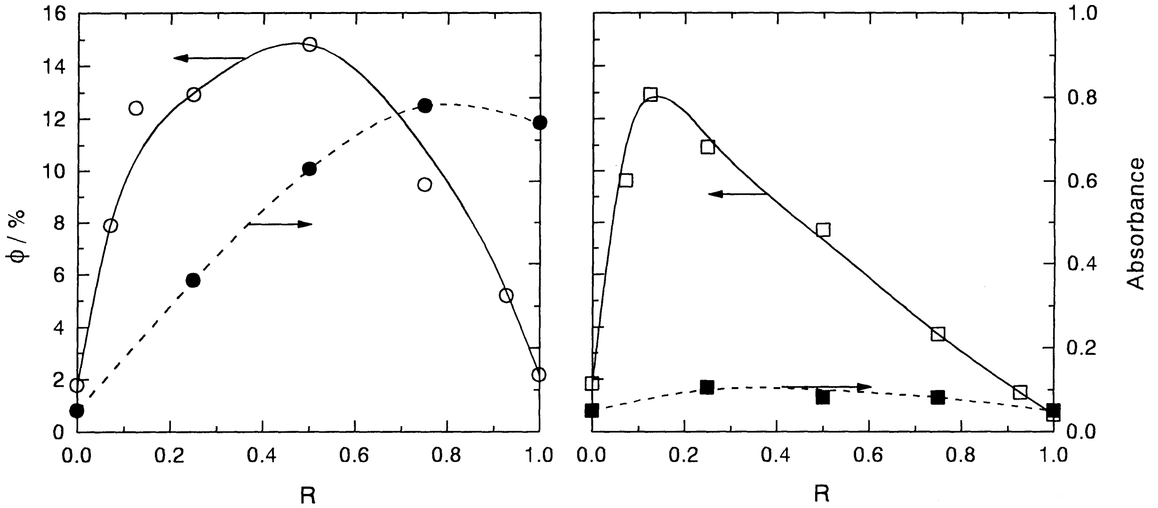

Fig. 3. Photocurrent quantum yields (φ) of Al/mixed dye/Au cells at the incident lights of 440 nm (○) and 560 nm (□), and the absorbance of the mixed film (thickness, 20 nm) at 440 nm (●) and 560 nm (■) as a function of the mixing ratio (R).

In conclusion, the photovoltaic cell with the mixed solid of Zntpp and MC can convert the light energy into the electrical energy more effectively than those with pure Zntpp and MC. This is probably ascribed to the formation of the ground–state complex with the strong electronic interaction. The complex in the vicinity of the MIS–type junction at the Al/dye interface may be photo–excited by the direct excitation and the exciton migration from the monomeric dye to the complex, and then the net charge can be produced by the charge separation of the excited complex at this interface with the potential barrier. The exciton migration from MC molecules may occur easier than that from Zntpp molecules because the relatively large φ is obtained for the smaller R value even though the absorbance is relatively small (Fig. 3). Such a photovoltaic property is particularly interesting from the standpoint of the photosynthetic model. That is , in this simple solar cell, the Zntpp–MC complex behaves as the special pair of the photosynthetic reaction center,[13] and the monomeric MC or Zntpp as the antenna pigment, and further the potential barrier at the Al/dye interface as the multi–step redox chain for the charge separation. Although Diarra et al.[5] already reported photovoltaic properties of mixed monolayer of chl a and carotenoid canthaxanthin from the viewpoint of the photosynthetic model, the energy conversion yield is considerably smaller than that for our system.

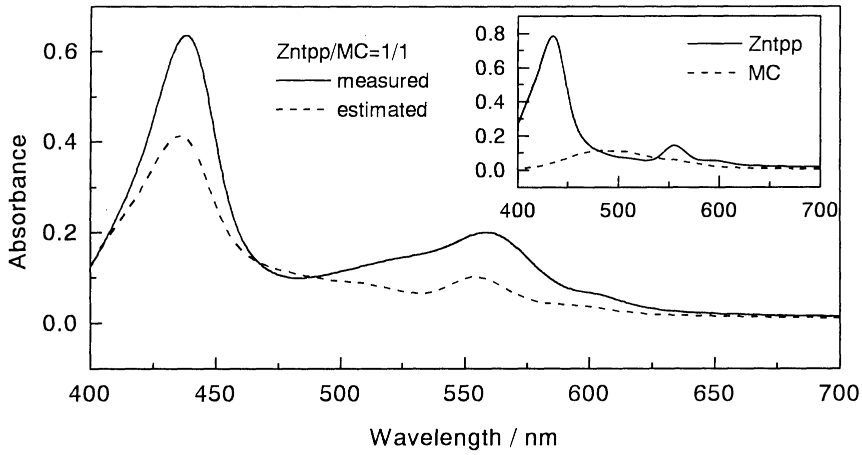

Fig. 4. Absorption spectra of pure Zntpp, pure MC, and equimolar mixed films of 20 nm thickness, and an estimated absorption spectrum of the equimolar mixed film.

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