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n-TYPE SEMICONDUCTING BEHAVIOR OF 5,10,15,20-TETRA(3-PYRIDYL)PORPHYRIN

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The photovoltaic effects observed for the indium-tin oxide (ITO)/5,10,15,20-tetra(3-pyridyl)porphyrin (TPyP)/Al cell are consistent with the existence of a Schottky junction at the interface between ITO and TPyP, which acts as an n-type semiconductor. The effects of O_2 and H_2 on the short-circuit photocurrents and the presence of a blocking contact at the TPyP/p-type porphyrin junction are explained in terms of the n-type semiconducting behavior of TPyP.

Up to date the most efficient cells based on solid porphyrin films on Al reached photocurrent quantum yields of 20-30% with power conversion efficiencies of 1-2% and generated open-circuit voltages greater than 1 V.1,2) However, in order to build more efficient devices it is necessary to establish a technology for controlling electric and/or photoelectric properties of the solid porphyrins. For organic semiconductors the control of the type of conductance by doping electron donors or acceptors is fairly difficult in comparison with cases of inorganic semiconductors. Organic compounds belonging to the same groups usually show the same type of conductance.3) For example, triphenylmethane dyes such as malachite green and crystal violet are n-type semiconductors and, on the other hand, phthalocyanines and the porphyrins studied so far have been characterized as p-type semiconductors.

In this paper we present evidence that substitution of phenyl groups of a 5,10,15,20-tetraphenylporphyrin (TPP) molecule by pyridyl groups leads to a change from the p-type to the n-type conductance, and that organic p-n junctions can be made from the porphyrins.

The cell used was a sandwich type: M/P/M', where M or M' is either indium-tin oxide (ITO) (∿0.1 μm), Al, Ag or Au (∿0.01 μm) and P is 5,10,15,20-tetra-(3-pyridyl)porphyrin (TPyP) or 5,10,15,20-tetraphenylporphinatozinc(II) (ZnTPP) at 0.1-0.3 μm thick. The details of fabrication are described in the previous paper.[4)] Current passing from Al to ITO through the cell is taken to be positive. The photocurrents have been normalized in such a way that the intensity of the incident light on the interface between the porphyrin and ITO or Al is constant (∿4.35×10^{12} photons cm^{-2} s^{-1}).

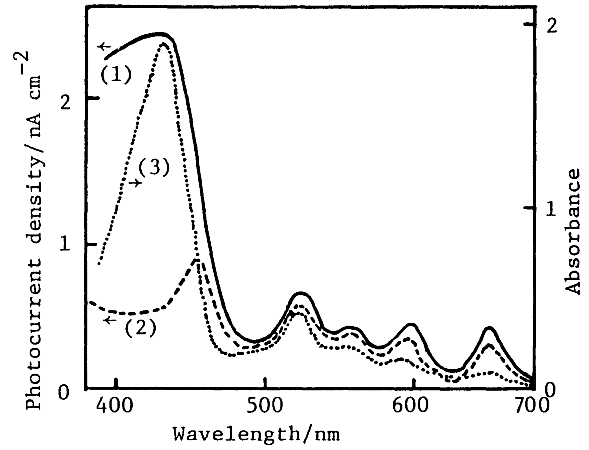

Fig. 1. Photocurrent action spectra of the ITO/TPyP (∿0.1 μm)/Al cell and the optical absorption spectrum of the TPyP film. Curves (1) and (2) are the action spectra obtained on illumination of the ITO and Al electrodes, respectively. Curve (3) is the absorption spectrum of the TPyP film.

Figure 1 displays the action spectra of short-circuit photocurrents for the ITO/TPyP/Al cell with the optical absorption spectrum of a sublimed film of TPyP. The action spectrum (1) obtained on illumination of the ITO electrode resembles the absorption spectrum (3). However, the action spectrum (2) obtained on illumination of the Al electrode is different in shape from the spectra (1) and (3), although the photocurrents flow from Al to ITO through the porphyrin layer regardless of the direction of irradiation. These findings are ascribed to an optical filtering effect of the porphyrin phase[5)] and suggest that only the light absorbed near the ITO (blocking) contact is effective in producing charge carriers and that an ohmic or a near ohmic contact is formed at the TPyP/Al interface. Similar photovoltaic features were observed for cells with Ag and Au contacts in place of the ITO contact. These results are contrary to those predicted from the *p*-type semiconducting behavior observed for the porphyrins studied so far.[1)] For example, the strong rectifying and photovoltaic effects observed for the ITO/ZnTPP/Al cell, where ZnTPP is well-known as a typical *p*-type porphyrin, are attributed to the blocking contact of ZnTPP with Al and not to the ITO contact (Fig. 2). The conduction- and valence-band edges are bent downwards at the ZnTPP/Al interface under short-circuit conditions. The ZnTPP/Ag or Au interface is not photoactive because the contact at the junction is ohmic.

Figure 3 shows the voltage dependence of photocurrents for the ITO/TPyP/Al cell. In this case, it should be noted that more photoactive region is not the

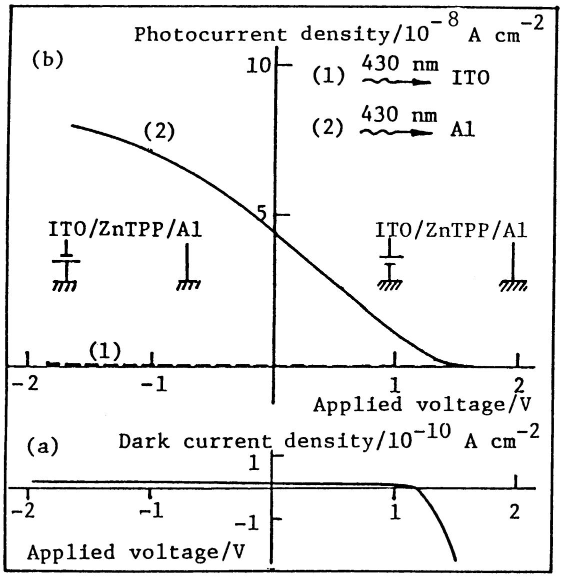

Fig. 2. Current-voltage characteristics of the ITO/ZnTPP(∿0.1 μm)/Al cell.
(a) dark current-voltage curve.
(b) photocurrent-voltage curves. Curves (1) and (2) were obtained on illumination of the ITO and Al electrodes at 430 nm, respectively.

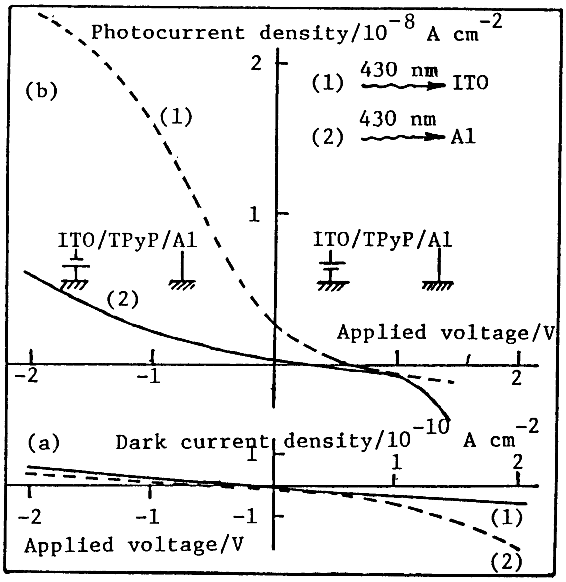

Fig. 3. Current-voltage characteristics of the ITO/TPyP(∿0.1 μm)/Al cell.
(a) dark current-voltage curves. Curves (1) and (2) were obtained for the cell in air (O_2) and in vacuum (∿10^{-4} Pa).
(b) photocurrent-voltage curves. Curves (1) and (2) were obtained on illumination of the ITO and Al electrodes for the cell in air at 430 nm.

interface of the porphyrin TPyP with Al, but that with ITO, and there the conduction- and valence-band edges are bent upwards under short-circuit conditions. In principle, a similar upward band-bending may be produced at the contact of ITO with a *p*-type porphyrin, if the Fermi level of the porphyrin lies above that of ITO. However, such a contact usually becomes ohmic for the majority carriers (holes) and thus no obvious photoresponce is observed when the ITO/porphyrin interface is illuminated. Hence, it is assumed that TPyP is not a *p*-type porphyrin, but an *n*-type. This assumption is consistent with the rectification effect observed for the ITO/TPyP/Al cell under reduced pressure (∿10^{-4} Pa) [Fig. 3(a)].

Figure 4 illustrates the effects of H_2 and O_2 on the action spectra of short-circuit photocurrents for the ITO/TPyP/Al cell. Measurement of the changes of photoelectric or dark conductivity of cells caused by O_2 and H_2 is very useful to establish the type of conductance of dyes, where the increase (decrease) of conductivity in H_2 (O_2) indicates *n*-type conductance.3) The increase (decrease) of the photocurrent observed for the ITO/TPyP/Al cell in H_2 (O_2) agrees with the assumption that TPyP is an *n*-type organic semiconductor. For comparison, we have confirmed that the photocurrent for the ITO/ZnTPP/Al cell increases in O_2 owing to the *p*-type semiconducting behavior of ZnTPP itself.

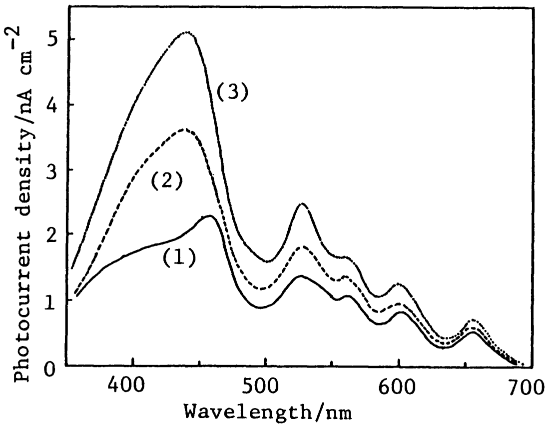

Fig. 4. Effects of O_2 and H_2 on the action spectra of the ITO/TPyP($\sim$0.3 µm)/Al cell under irradiation of the ITO electrode at zero bias. Curves (1), (2), and (3) are the action spectra obtained for the cell in air (O_2), vacuum ($\sim 10^{-4}$ Pa) and H_2 ($\sim 10^5$ Pa).

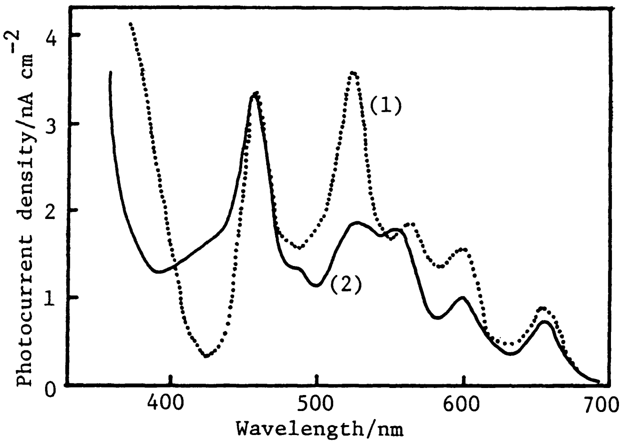

Fig. 5. Action spectra of short-circuit photocurrents for the ITO/ZnTPP($\sim$0.2 µm)/TPyP($\sim$0.1 µm)/Al cell. Curves (1) and (2) were obtained under illumination of the ITO and Al electrodes, respectively.

Figure 5 shows the photocurrent action spectra obtained for the cell made from ZnTPP and TPyP. Without regard of the direction of irradiation the optical filtering effect is observed, and the photocurrents flow in the same direction from Al to ITO through the ZnTPP/TPyP interface. The direction of the photocurrent coincides with that of the light-induced currents at inorganic *p-n* junctions. Therefore, it is deduced that the ZnTPP/TPyP interface is the most photoactive region in the cell and that an organic *p-n* junction is formed at the ZnTPP/TPyP interface, where TPyP acts as an *n*-type semiconductor.

At present we are not in a position to comment on the reason why TPyP behaves as an *n*-type semiconductor. However, we know some cases where the substitution of methine groups by nitrogen atoms leads to the change from the *p*-type to the *n*-type nature.$^{3)}$

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