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Doping Effect on the Two-layer Organic Solar Cell

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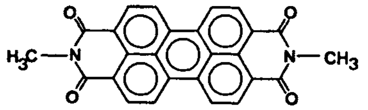
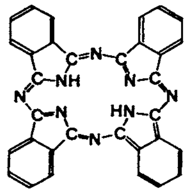
Doping effect on an organic solar cell composed of two-layer thin pigment films of metal-free phthalocyanine (H_2Pc) and perylene tetracarboxylic derivative (Me-PTC) was investigated. When H_2 or NH_3 was doped to the Me-PTC film during vacuum deposition, the photocurrent density drastically increased and the power conversion efficiency of the cell reached about 1% even under 75 mW cm^{-2} white light.

Last decade a large number of organic solar cells based on the photoelectrical properties of organic pigments or dyes have been reported. The organic solar cells reported up to date can be divided broadly into two categories; one is based on the Schottky junction with low-work-function metals$^{1,2)}$ and the other is based on the p-n junction with inorganic n-type semiconductors such as CdS and ZnO,$^{3,4)}$ since most of the organic pigments exhibit p-type character. Their conversion efficiency, however, has remained still quite low compared with that of silicon-based inorganic solar cells, especially under the intense light. Recently, Tang$^{5)}$ reported that a layered cell of two different pigments, copper phthalocyanine and perylene-based pigments, showed high conversion efficiency of near 1% with the photocurrent density of the order of milli-amperes. This type of cell seems to belong to the category of organic p-n junction, but no satisfactory explanation has not yet appeared for such high conversion. The distinctive progress, however, seems to provide a new avenue in developing organic solar cells for the practical use. In order to draw out the true semiconductor characteristics of organic pigments, therefore, the valency control is crucially important by doping well-identified impurity (dopant) into the thoroughly purified pigments.



(a) Me-PTC



(b) H_2Pc

Fig. 1. Chemical structure of pigments.

From this standpoint, we have investigated doping effects on the photovoltaic properties of the two-layer organic solar cell. In the present work, we would like to report the pronounced doping effect of H_2 gas to the purified perylene-based pigment which is conceivable to have the n-character.

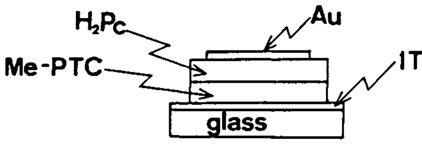


Fig. 2. The structure of two-layer organic solar cell.

Our two-layer cell constructed here is

composed of metal-free phthalocyanine (H_2Pc, Fig. 1(a)) and perylene tetracarboxylic derivative (Me-PTC, Fig. 1(b)) different from 3,4,9,10-perylenetetracarboxyl-bis-benzimidazole used by Tang.$^{5)}$ Me-PTC and H_2Pc were purchased from BASF and Tokyo Kasei Co. Ltd., respectively. Both the pigments were purified thoroughly three times at least by train sublimation technique with an appropriate temperature gradient in a furnace, since there is no other purification method for solvent-insoluble pigments. In either case of H_2Pc and Me-PTC a quantity of impurities was separated from the commercially available pigments by their first sublimation, but from second time no impurity zone was detected. The photovoltaic cells (Fig. 2) were fabricated by successive vacuum depositions without breaking the vacuum on an ITO glass plate under 5.3 x 10^{-4} Pa, and provided with a gold electrode. The film thickness was monitored by an oscillating quartz thickness meter (ULVAC, CRTM-1000). Gas doping was carried out by introducing H_2, NH_3, or O_2 gas (1.3 x 10^{-1}Pa) during the deposition of the pigments.

The photovoltaic properties were measured using an electrometer (Keithley, model 485) and a function generator (Hokuto Denko, Ltd., HB-104) under irradiation of broadly focused white light from 250 W metal halide lamp (Toshiba Co.). For the measurements of action spectra the monochromatic light from 500 W xenon lamp through a monochromator was used adjusting to a constant photon energy monitored by a thermopile (Eppley Lab. Inc.).

The curve (a) in Fig. 3 shows a typical photocurrent density - voltage (J - V) curve of the present two-layer organic solar cell. The voltage applied is referred to that on Au electrode. Film thickness of H_2Pc and Me-PTC is 40 nm as the best choice free from pin hole troubles. Upon the photo-irradiation, Me-PTC side showed negative photovoltage, and the cell gave the large short-circuit photocurrent, J_{sc}, of the milli-ampere order as much as Tang reported with a different perylene-based pigment. As a distinct feature of the present cell it should be noted that J_{sc} shows a quite linear dependence on the light intensity up to the intense illumination of 100 mW cm^{-2}.

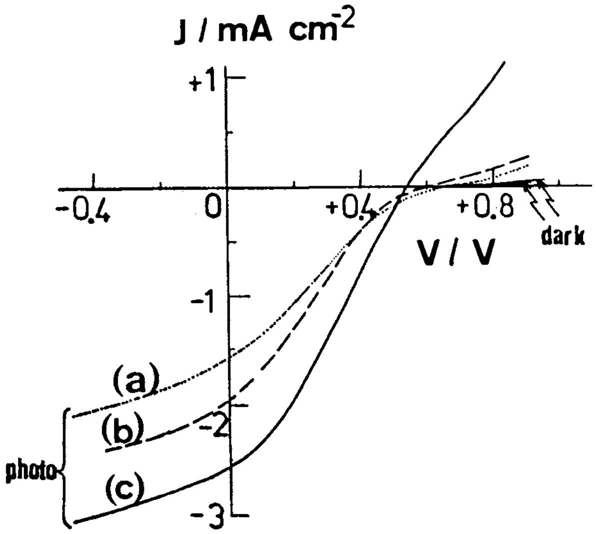


Fig. 3. J-V characteristics of ITO/Me-PTC (40 nm)/H_2Pc(40 nm)/Au cell. White light (76 mW cm^{-2}) was irradiated through ITO. Dopants for Me-PTC are as follows; (a) undoped, (b) NH_3, (c) H_2.

Figure 4 shows the spectral dependence of the current quantum efficiency of J_{sc}, which is evaluated by Eq. 1.

$$\Phi^{o}\ (\%) = (n_e/n_{ph}{}^{o}) \times 100 \qquad (1)$$

Here, n_e is the number of carriers collected in the short-circuit condition and $n_{ph}{}^{o}$ the number of photons absorbed by two organic layers. It can be seen from the comparison with their absorption spectra that the present two-layer cell responds mainly in the absorption regions of Me-PTC and H_2Pc for the respective irradiation from H_2Pc and Me-PTC sides. Thus, the pronounced masking effects clearly indicate that the active region for the charge carrier separation locates near the junction between two pigment films.

Doping of H_2 or NH_3 donor gas to the Me-

PTC pigment layer, which is conceivable to be n-type, showed drastic effects in the cell performance as shown in Fig. 3, curves (b) and (c). Especially, J_{sc} increased from 1.6 to 2.5 mA cm^{-2} in the case of H_2 doping and hence the maximum quantum efficiency improved from 10% to 25% (Fig. 5). Even after 20 days we could clearly observe these doping effects. On the other hand, doping of O_2 acceptor gas to the p-type H_2Pc gave no significant effect since the measurements were carried out in air. The detailed results of the doping effects are given in Table 1.

The results obtained presently on the doping effects of H_2 to the Me-PTC pigment, are summarized as follows. (1) The photocurrent density drastically increased, (2) fill factor was also improved, and (3) the forward current increased in dark as well as in photo. The results of (2) and (3) can be reasonably understood as a result of the improvement of the carrier transport properties of the Me-PTC film. In order to confirm this interpretation, we measured the surface conductivity of the Me-PTC film using a comb-type electrode in various gas atmosphere. Apparently, the conductivity increased about 10 times in H_2 atmosphere or under vacuum condition compared to that in O_2. Since it is unlikely that O_2 or H_2 takes charge of carrier generation interacting with the perylene pigments in dark, O_2 in the Me-PTC film is considered to act as an electron trap which may disturb the electron conduction in n-like pigments. Stated reversely, the present results indicate explicitly that perylene-based pigments behave as an n-type organic semiconductor. Therefore, the main doping effects of H_2 is considered to be due to the replacement of H_2 for O_2 acting as an electron trap in the evaporated Me-PTC film. There remains, however, another effect of some interaction between the pigments and H_2, because the appreciable spectral change in absorption spectrum was observed by H_2 doping, although as little as shown in Fig. 4.

The present drastic increase in the photocurrent density can not be explained simply

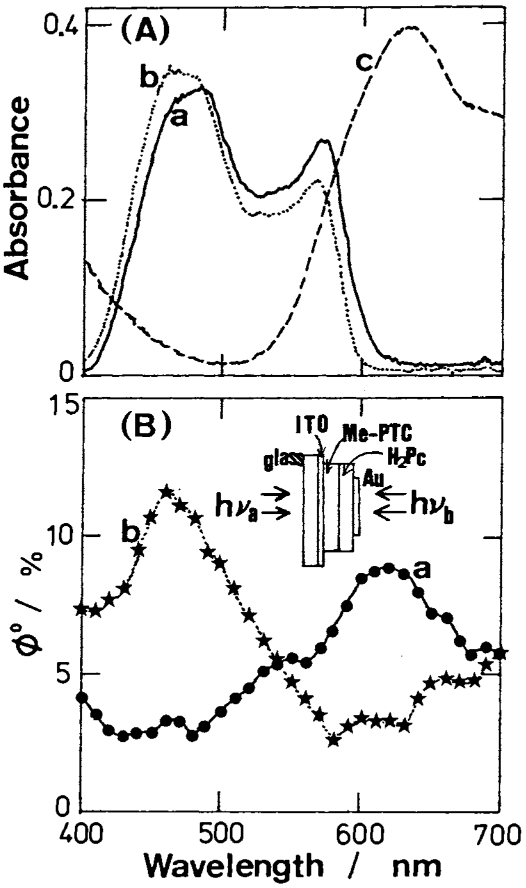


Fig. 4. (A) Absorption spectra of the 40 nm-thick pigment films. (a) Me-PTC, (b) H_2 doped Me-PTC, and (c) H_2Pc. (B) Spectral dependence of Φ^0 for undoped cell. Cell structure is the same as Fig. 3. Directions of the light irradiation are indicated in the figure.

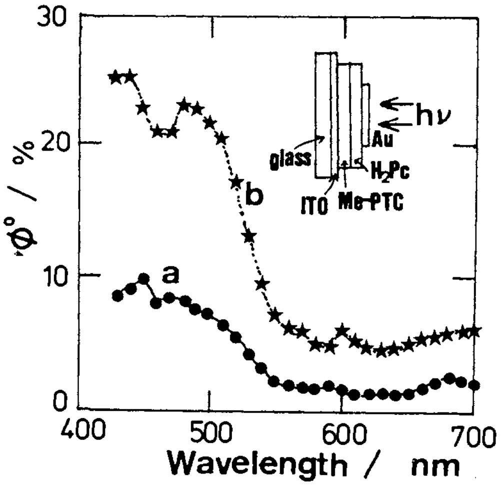


Fig. 5. Spectral dependence of Φ^0 in ITO/Me-PTC/H_2Pc/Au cell. Light was irradiated through Au. (a) undoped, (b) H_2 was doped only to Me-PTC.

by the improvement of the conductivity of the Me-PTC film. The results shown in Fig. 5 indicate that the carrier generation efficiency also increased by H_2 doping. Since the shape of action spectrum, however, did not change as much as to be significant by H_2 doping, this effect is not attributed to the spectral sensitization effect. Taking into account that the charge generation is much responsible to the field built up between two pigment layers with different Fermi level (E_F), the present result can be explained by the shift of E_F in Me-PTC by H_2 doping. Actually, we recognized the E_F shift of Me-PTC about 0.1 eV toward negative direction by H_2 doping from the measurements of the built-in potentials in Al/Me-PTC junction. This may cause the increase of the built-in potential within the p-n junction also between H_2Pc and Me-PTC pigments, which gives rise to the increase of carrier generation efficiency. In Fig. 6 the energy diagrams of Me-PTC and H_2Pc pigments based on the conventional band model are depicted. The V.B. levels were measured by the atmospheric photo-electron emission analysis (Rikenkeiki, AC-1)[6] and E_Fs were evaluated from the built-in potentials against Al metal, respectively.

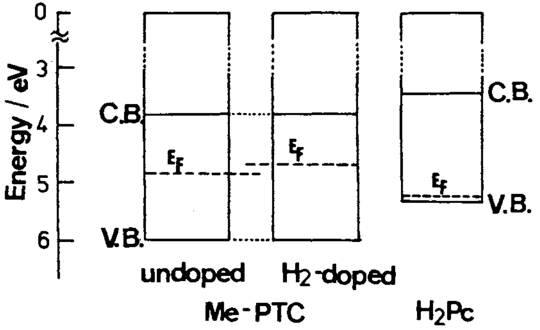


Fig. 6. Energy diagram of Me-PTC and H_2Pc. C.B., V.B. and E_F denote the conduction band, the valence band, and the Fermi level, respectively.

Table 1. Cell Performance

Dopant to Me-PTC	Light[a)] /nm	J_{sc} /μA cm^{-2}	V_{oc}/V	ff	η^o b) /%
Undoped	white	1570	0.66[c)]	0.22	0.41
	460	16	0.21	0.26	0.57
	570	61	0.37	0.32	1.10
	630	33	0.30	0.29	0.69
H_2	white	2570	0.55	0.30	0.77
	460	39	0.24	0.30	1.81
	570	110	0.37	0.35	2.17
	630	59	0.30	0.32	1.35
NH_3	white	1960	0.58	0.23	0.49
	460	22	0.26	0.31	1.17
	570	90	0.39	0.35	1.87
	630	37	0.30	0.32	1.35

a) Light was irradiated through ITO. Light intensity is as follows; 76 mW cm^{-2} (white), 0.604 mW cm^{-2} (460 nm), 1.24 mW cm^{-2} (570 nm), 0.759 mW cm^{-2}(630 nm).
b) η^0 is the power conversion efficiency for the light energy absorbed by two organic layer.
c) When O_2 acting as electron trap in Me-PTC was removed under vacuum, V_{oc} of the undoped cell decreased to 0.46 V due to the increase of the forward photocurrent. This value is smaller than that of H_2-doped cell and consistent with the negative E_F shift by H_2 doping.

In summary, we showed the effectiveness of the H_2 doping to n-type pigment semiconductor for the improvement of organic solar cells. As a result the conversion efficiency reached about 1% even under intense light irradiation of 76 mW cm^{-2} and more than 2% under monochromatic light of 570 nm (1.24 mW cm^{-2}) for the H_2-doped two-layer cell. The present results provide a possibility to improve organic solar cell further by searching for appropriate solid dopants.

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