Porphyrin dye-sensitization of polythiophene in a conjugated polymer/TiO2 p-n hetero-junction solar cell

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Porphyrin dye-sensitization of polythiophene in a conjugated polymer/TiO_2 p-n hetero-junction solar cell

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Abstract

In the blended solid of poly(3-hexylthiophene-2,5-diyl) (P3HT) and porphyrin (TPP) / TiO_2 p-n hetero-junction solar cells, a photo-induced charge transfer between P3HT and TPP accelerated the charge separation in the depletion layer formed at the P3HT+TPP/TiO_2 interface, enhancing the photovoltaic properties. For the blended cell containing zinc porphyrin as TPP, the energy conversion yield of 0.26 % was obtained under the illumination of solar simulated light AM1.5-100 mW/cm^2.

Keywords: Organic solar cell; Porphyrin; Polythiophene; Photo-induced charge transfer

1. Introduction

We have examined the performance of organic solar cells with blended solid films consisting of a conjugated polymer as a charge-transporting material and a dye as a light-harvesting compound. We have reported that an enhanced photocurrent was observed for an Al/organic solid Schottky-barrier cell with a blended solid film of a conjugated polymer such as regioregular polythiophene and a dye such as a porphyrin or a merocyanine [1-4]. However in the cell, the aluminum electrode was photo-corroded under illumination [5].

Recently, p-n hetero-junction solar cells composed of inorganic semiconductors as electron-transporting materials and conjugated polymers as light-harvesting and hole-transporting compounds have been studied [6-11]. For example, Savenji et al. studied a solar cell consisting of a dense TiO_2 thin film and a poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] MEH-PPV [6], Huynh et. al. studied a cell consisting of CdSe nano-rods and poly(3-hexylthiophene-2,5-diyl) P3HT [7], and Arango et. al. reported on a cell consisting of TiO_2 nano-particles and poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] MDMO-PPV [8]. These solar cells were relatively photo-stable, but the energy conversion efficiency was low due to the low light-harvesting ability of the conjugated polymer films.

We think that combining both a blended solid and an inorganic semiconductor promises further improvement in solar cell performance. We previously reported on solar cells composed of a dense TiO_2 thin film and a blended film such as P3HT＋merocyanine dye or MEH-PPV+laser emitting dye DCM [12, 13]. The performance of the blended cells was enhanced compared to the pure P3HT or MEH-PPV cell, but the energy conversion yield was still very low. To attain a practical use of this type solar cell, it is necessary to accumulate many data on the blended cells. In this paper, we report an improvement in the photovoltaic properties of a TiO_2/P3HT/Au sandwich-type solar cell sensitized with a porphyrin dye.

2. Experimental

Chemicals. Regioregular poly(3-hexylthiophene-2,5-diyl) P3HT was purchased from Aldrich Chemicals and used without further purification. Metal-free and zinc porphyrins were synthesized and purified as the literature method [14]. The employed organic compounds and their abbreviations are shown in Fig.1.

Preparation and characteristics of TiO_2 thin film. A TiO_2 sol solution prepared by Rengakuji's method [15] was spin-coated on a transparent conducting oxide plate of F-doped SnO_2 (TCO, Asahi Glass Co. Ltd., 10 Ω/□) at 2000 r.p.m. The sample was dried at 100 ˚C for 1 h, then annealed at 450 ˚C for 1 h. The process from the spin-coating to the annealing was repeated twice. The solid film is transparent and dense, and the type of crystal lattice is anatase. The film thickness was about 500 nm. The AFM images of the TiO_2 surface on the TCO substrate as well as the TCO surface were shown in Fig. 2. The TiO_2 surface was considerably flat compared to the bare TCO. The surface morphology and the thickness of the TiO_2 thin film were observed with a SII Nano Technology Inc. SPI3800N atomic force microscope (AFM).

Cell fabrication and photocurrent measurements. A schematic structure of the TiO_2/organic solid/Au sandwich-type solar cell is shown in Fig.1. To confine the photoactive area to 0.25 cm^2, an insulator SiO_x film of 100 nm thickness was deposited on the TiO_2 by a vacuum evaporation method. The organic solid film was coated onto the TiO_2 by spin-coating. The gold film with thickness of about 25 nm was deposited onto the organic solid film by the vacuum evaporation.

The photocurrent-voltage characteristics were measured using a simulated solar light source in the intensity range of AM1.5-100 mW/cm^2 at a scan rate of 500 mV/min. The simulated solar light was obtained by a Kansai Kagakukikai XES-502S, and the light intensity was monitored by a SCIENTECH 365 power and energy meter.

The action spectra were measured at a scan rate of 60 nm/min. The light source consisting

of a 750 W halogen tungsten lamp and a Jasco CT-10 monochromator with a scanning controller SDM-25C was used. The light intensity was monitored by an Advantest TQ-8210 optical power meter with a silicon photocell. The photocurrent was measured by an Advantest R-8240 electrometer and was recorded by a Yokogawa Denki 3057 portable recorder.

The ionization potential of organic solids in air was estimated from a photoelectron spectroscopy (PESA) by a Riken Keiki model AC-2 [16]. The absorption spectra of organic solids were measured by a Hitachi U-3310 spectrophotometer.

3. Results and Discussion

Photovoltaic characteristics of the solar cells. We previously reported that a Schottky-barrier was formed at the interface between the low work functional Al and P3HT or porphyrin (TPP) with a p-type conductance [1, 2, 4]. The bottom energy level of the conduction band of TiO_2 was 3.8-4.2 eV [6, 8, 9], being nearly equal to the work function of Al. Therefore a p-n hetero-junction or a Schottky-barrier may be formed at the interface between TiO_2 and P3HT or TPP.

Figure 3 shows typical current-voltage characteristics of P3HT+ZnTPP and P3HT+H_2TPP solar cells in the dark and under an illumination of AM1.5-100 mW/cm^2. Figure 4 shows the mixing molar ratio R dependence of photovoltaic properties such as the short-circuit photocurrent J_{sc}, open-circuit photovoltage V_{oc}, fill factor FF, and energy conversion efficiency η under an illumination of AM1.5-100 mW/cm^2, where R was defined as the molar ratio of porphyrin to thiophene unit in P3HT and the film thickness d of the blended solid was about 60 nm The values of J_{sc}=0.34 mA/cm^2, V_{oc}=0.24 V, FF=0.31, and η=0.025 % were obtained for the pure P3HT solar cell. The performance of the pure Zntpp and H_2TPP solar cells cannot be obtained because of the short-circuit of the cells. On the other hand, the photovoltaic properties were remarkably enhanced by blending ZnTPP or H_2TPP to P3HT. For a P3HT+ZnTPP blended cell with R=0.4, the values of J_{sc}=1.11 mA/cm^2, V_{oc}=0.50 V, and FF=0.48 were observed, consequently the maximum value of η=0.26 % were

obtained. For a P3HT+ H_2TPP blended cell with R=0.1, the values of J_{sc}=0.68 mA/cm^2, V_{oc}=0.34 V, and FF=0.48 were observed, the maximum value of η=0.11 % were consequently obtained. The enhanced photovoltaic properties for the blended cells with various porphyrins were summarized in Table 1. The reason for the enhanced performance in the blended cells will be discussed later.

Figure 5a shows the photocurrent action spectra for both irradiation from the TCO side and from the Au side in TCO/TiO_2/P3HT+ZnTPP/Au with R=0.4 and the film thickness d=90 nm, and the absorption spectrum of the solid film on a glass substrate. To adjust the strength of incident light from TiO_2 side at the TiO_2/P3HT+ZnTPP interface and from Au side at the P3HT+ZnTPP/Au interface to be approximately the same, an Au deposited glass as the optical filter was placed in front of the TCO electrode side, while a TCO/TiO_2 glass was placed in front of the Au electrode side. Incident photon to current conversion efficiency, *IPCE,* was obtained for incident photon number onto each interface at the TiO_2/P3HT+ZnTPP and the Au/P3HT+ZnTPP. When monochromatic light was irradiated from the TiO_2, that is, the TCO electrode side, the action spectrum followed the absorption spectrum of P3HT+ZnTPP. While, when irradiated from the Au electrode side, rather lower photocurrent was observed due to the so-called optical filtering effect of the P3HT+ZnTPP blended solid film. This result indicates that the photocurrent generates inside of P3HT+ZnTPP near the TiO_2/P3HT+ZnTPP interface. Figure 5b shows the dependence of *IPCE* at 430 nm on the film thickness d of the organic solid, where *IPCE* at 430 nm is the *IPCE* value under irradiation of 430 nm monochromatic light showing maximum optical filtering effect. The *IPCE* at less than d=40 nm cannot be obtained because of the short-circuit of the cells. When irradiated from the both electrode sides, the *IPCE* at 430 nm increased with increasing the thickness up to 60 nm, and it decreased from more than 60 nm. The magnitude of the decrease was much larger under irradiation from the Au side compared to under irradiation from the TCO side because of the so-called optical filtering effect of the P3HT+ZnTPP blended solid. This exhibits that photons absorbed in the organic solid within 60 nm region from the TiO_2/organic solid interface more effectively administer to the photocurrent. Since

the migration length of excitons for organic semiconductors is typically less than 20 nm [1], the width of a potential gradient, namely a band bending in the organic solid under illumination is estimated to reach 40-60 nm from the TiO_2/organic solid interface. Since the open-circuit voltage was 0.50 V for the P3HT+ZnTPP cell, the average electric field in the depletion layer was about 1×10^5 V/cm. This zone functioned as an effective charge-separation site. That is, the photocurrent generation mechanism for the blended cells is different from that of Grätzel cells employing only a mono-layer of chemically adsorbed dye on a nano-porous TiO_2 photo-electrode [17, 18]. On the other hand, the photons absorbed in the remote organic solid above 60 nm from the TiO_2/P3HT+ZnTPP interface cannot contribute to the photocurrent generation because of the inactivation of the photo-produced excitons. After all, the photocurrent of the blended cells with the thickness of more than 60 nm decreased perhaps because of large electric resistance of the organic solid.

Effect of photo-induced charge transfer in blended solid. We previously reported that when a photo-induced hole-transfer occurred from the HOMO level of TPP to the valence band of P3HT in an Al/P3HT+TPP Schottky-barrier cell, the photovoltaic properties were improved [2, 4]. The ionization potentials I_p corresponding to HOMO levels of P3HT and porphyrin derivatives were estimated by photoelectron spectroscopy in air (PESA). The value of I_p =4.7 eV was obtained for the P3HT solid film, and the values of I_p =5.5-5.9 eV were obtained for the solid film of porphyrin derivatives. The energy difference between HOMO and LUMO was estimated from the longest wavelength edge of the absorption spectra of the solid films. Therefore the LUMO levels are calculated from the both values. The energy diagram is shown in Fig.6. According to the energy diagram, the photo-induced intermolecular hole-transfer from porphyrins to P3HT is thermodynamically possible in the blended solids. We propose the following explanation for the performance enhancement by blending porphyrin dyes in the TiO_2/P3HT/Au cell [2, 4]. The coulombic force between the photo-produced electron and hole is much smaller in the excited P3HT-TPP complex than in the excited P3HT or TPP molecule because of the longer distance between

them. Further, since the bottom energy of the conduction band of TiO_2 is about 4.2 eV, the photo-produced electrons in the TPPs having the electronic energy of 3.5-4.0 eV can be injected to the TiO_2 at the TiO_2/organic solid interface being a blocking contact. On the other hand, the organic solid/Au interface may be approximately an ohmic contact because the work function of the Au is 4.8 eV, the photo-produced holes transporting easily from the P3HT to the Au electrode. Such a factor increased the photocurrent.

The enhanced performance of the P3HT+metal-free porphyrin blended cells was approximately the same despite of the difference of the HOMO-LUMO levels. On the other hand, the performance for the P3HT+ZnTPP cell was further improved compared to for the P3HT+H_2tpp cell. The photo-induced intermolecular charge transfer may be relatively easy between P3HT and ZnTPP because a ground-state complex is produced in the blended solid. Since a new absorption peak was appeared at 765 nm in a concentrated chloroform solution containing 6×10^{-3} mol/dm^3 thiophene unit in P3HT and 2.4×10^{-3} mol/dm^3 ZnTPP, such a complex may be formed in the blended solid enhancing the photocurrent.

4. Conclusions

In the TiO_2/organic solid/Au sandwich-type cells, the photovoltaic properties were remarkably enhanced for the P3HT+ZnTPP blended cell compared to for the pure P3HT cell. This is because an effective photo-induced charge transfer occurred between the donor P3HT and the acceptor ZnTPP, accelerating the photo-charge separation in the depletion layer formed at the interface of TiO_2 and P3HT+ZnTPP. The depletion layer existed in the narrow region of 40-60 nm on the organic solid side, and the electric field was about 1×10^5 V/cm. That is, the blended solar cell in this work is not so-called a Grätzel cell being sensitized by mono-layer dyes chemically adsorbed on to a TiO_2 electrode, but rather the enhanced photovoltaic properties are attributable to the dye-sensitization of the regioregular polythiophene.

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Figure Captions.

Fig. 1 Chemical structures of polythiophene and porphyrins, and schematic structure of solar cell.

Fig. 2 AFM images of the TCO substrate (a) and the spin-coated TiO_2 film on the TCO substrate (b).

Fig. 3 Current-voltage characteristics of TiO_2/organic solid/Au sandwich-type solar cells with the P3HT+ZnTPP (R=0.4, d=60 nm) and P3HT+H_2TPP (R=0.1, d=70 nm) blended solids under illumination of AM1.5-100 mW/cm^2 and in the dark. R is molar ratio of TPP to thiophene unit in P3HT, and d is the film thickness of the blended solid.

Fig. 4 Mixing molar ratio R dependence of short-circuit photocurrent J_{sc} (a), open-circuit photovoltage V_{oc} (b), fill factor FF (c) and energy conversion efficiency η (d) under illumination AM1.5-100 mW/cm^2 for the P3HT+ZnTPP and P3HT+H_2TPP blend solar cells. The film thickness d of the blended solids was about 60 nm.

Fig. 5 Photocurrent action spectra (a) under TCO and Au side illuminations for the TCO/TiO_2/P3HT+ZnTPP/Au sandwich-type solar cell (R=0.4, d=90 nm), the absorption spectrum of the P3HT+ZnTPP blended solid (a), and the film thickness d dependence of $IPCE$ at 430 nm (b) for the TCO/TiO_2/P3HT+ZnTPP/Au sandwich-type solar cell (R=0.4).

Fig. 6 Schematic energy diagram for TCO/TiO_2/P3HT+ZnTPP/Au sandwich-type solar cell.

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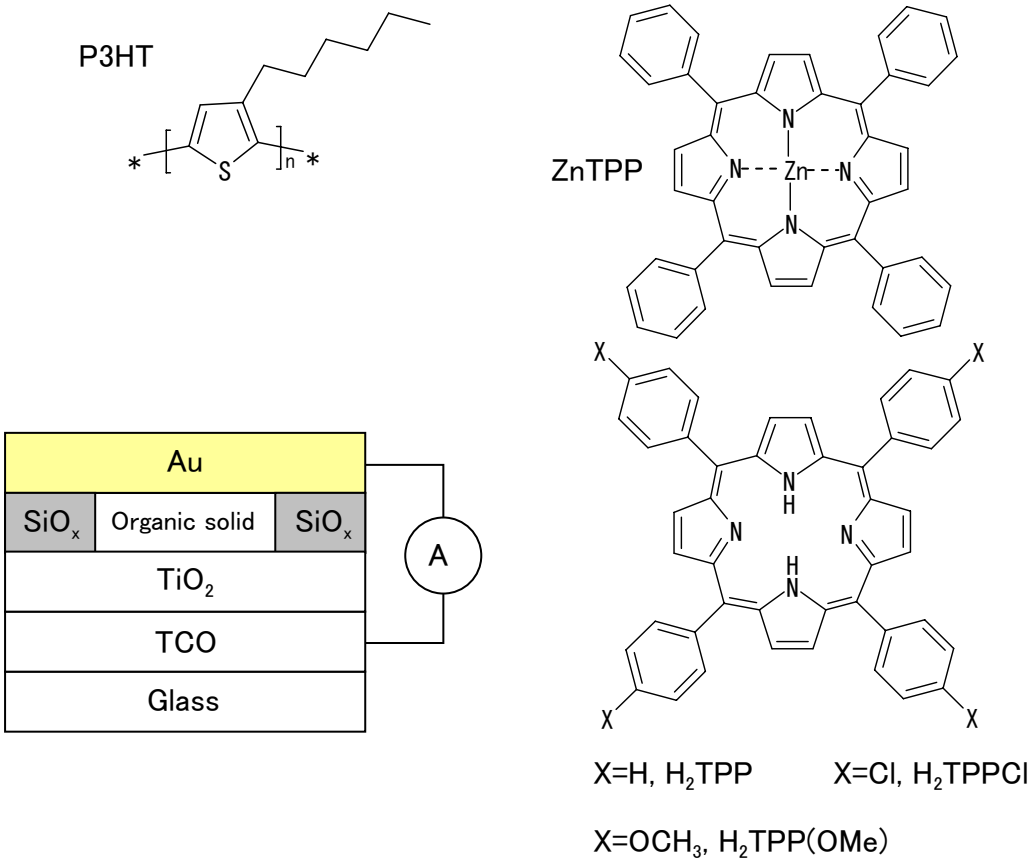
Table 1 Performance of TCO/Organic solid/Au sandwich-type solar cells under illumination of AM1.5-100mW/cm^2.

Organic solid	R	J_{SC} / mA cm^{-2}	V_{OC} / V	FF	η / %
P3HT	0	0.34	0.24	0.31	0.025
P3HT+ZnTPP	0.4	1.11	0.50	0.48	0.26
P3HT+H_2TPP	0.1	0.68	0.34	0.48	0.11
P3HT+H_2TPP(OMe)	0.2	0.70	0.59	0.27	0.11
P3HT+H_2TPPCl	0.5	0.45	0.55	0.32	0.08



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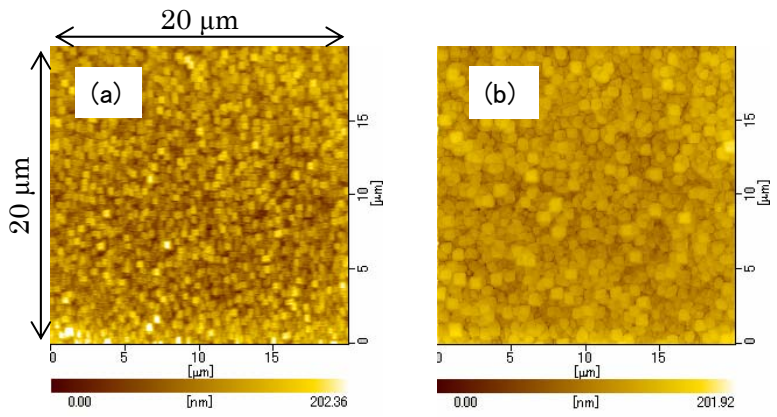

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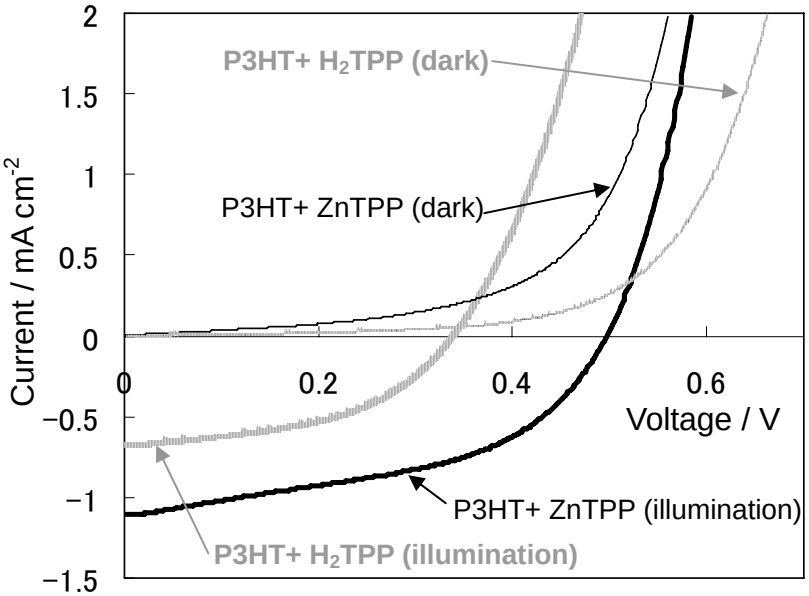

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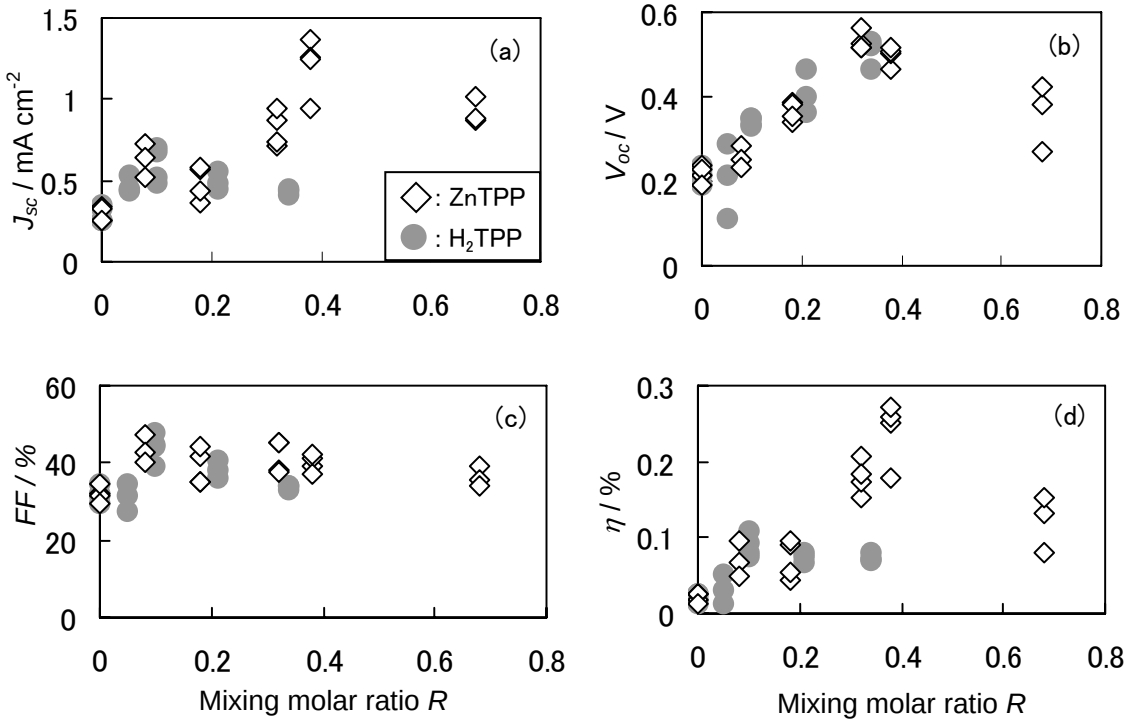

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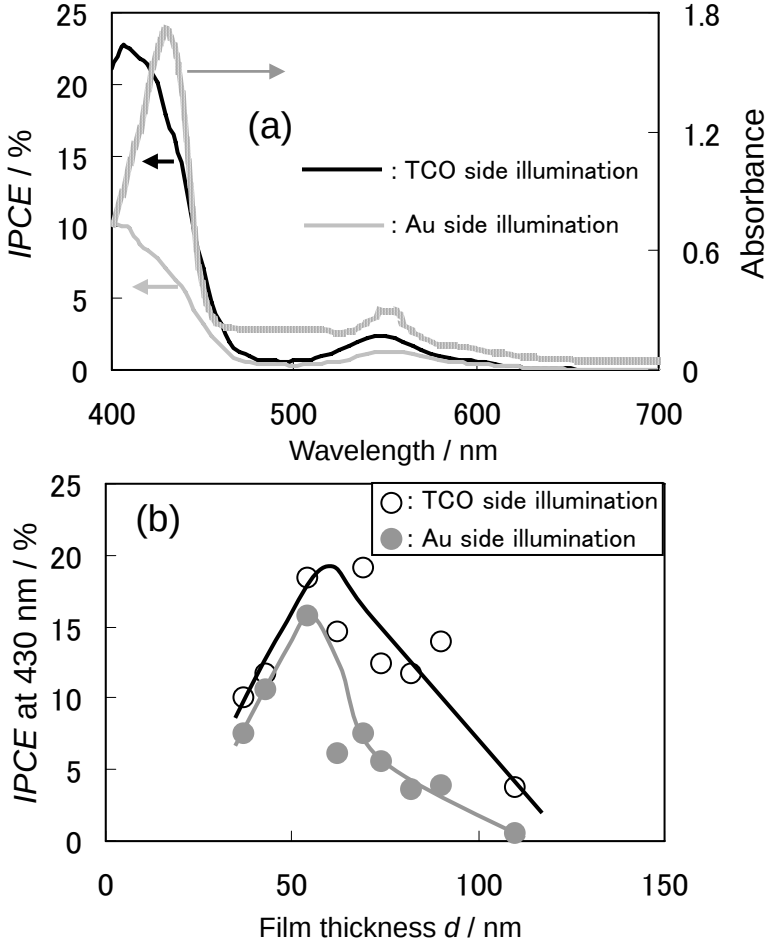

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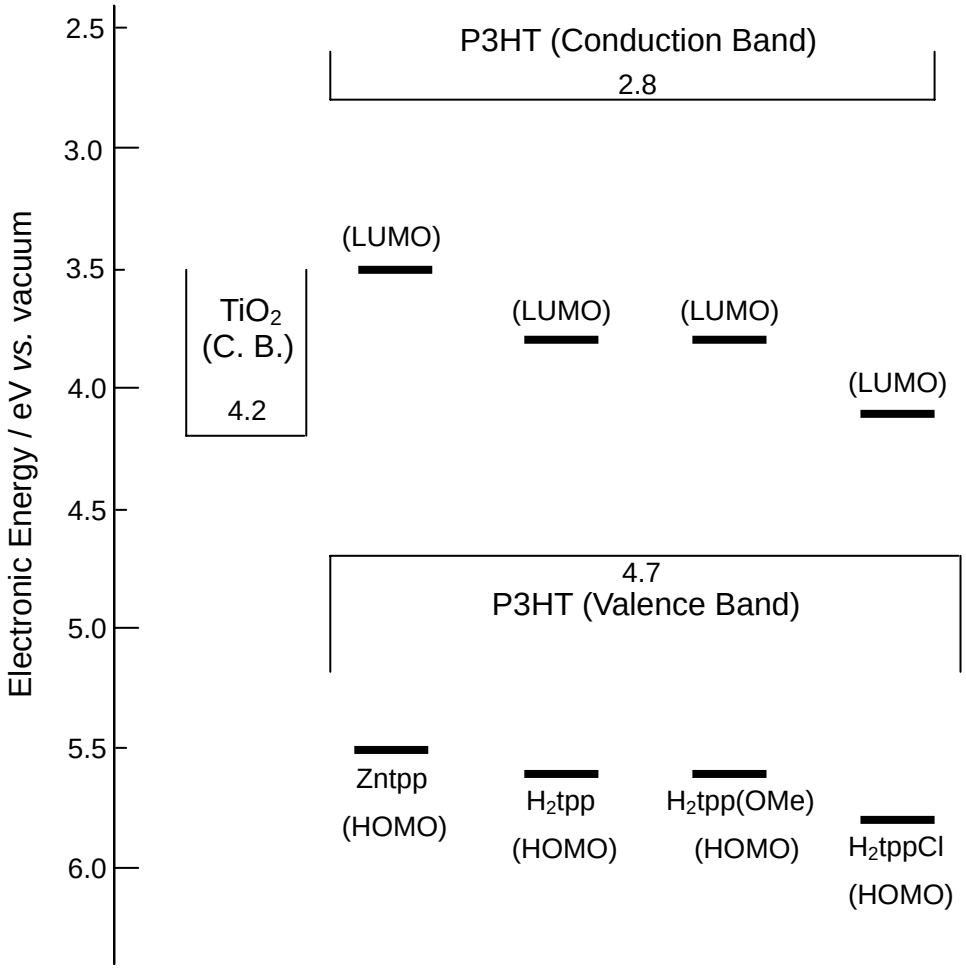

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