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ScienceDirect

Dyes and Pigments 77 (2008) 437–440

DYES and PIGMENTS

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Photoelectrode characteristics of a perylene/phthalocyanine bilayer film in acetonitrile

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Received 31 May 2007; accepted 6 July 2007
Available online 22 July 2007

Abstract

An organic bilayer film, composed of 3,4,9,10-perylenetetracarboxyl-bisbenzimidazole (PTCBI, an n-type semiconductor) and metal-free phthalocyanine (H_2Pc, a p-type semiconductor), was employed as a photoelectrode in acetonitrile containing a I_3^-/I^- couple. The H_2Pc surface in the PTCBI/H_2Pc bilayer induces the oxidation of I^- through hole conduction, via a mechanism that involves the entire visible-light energy of <750 nm being available for carrier generation at the p/n interface, through which oxidation takes place at the solid/liquid interface. The typical photoanodic characteristics of the p/n bilayer in the organic solution phase are described in terms of voltammetry as well as action spectral measurements for photocurrents.

Keywords: Photoelectrode; Solid/liquid interface; Organic semiconductor; Phthalocyanine

1. Introduction

Considerable effort has been made to create a visible-light-induced photoenergy conversion system, currently aiming at uptaking wide visible-light energy into an efficient output [1]. Towards this, the use of organic dye is one of the most promising approaches. Organic dyes of hole/electron-conducting characters are often applied to photodevices in solid state, with which the combination of a p-type conducting material with an n-type conductor performs functions as dry type photodevices such as solar cells, field-effect transistors, and in electroluminescence applications [2]. However, there are few examples where organic materials having a layered structure are used as photodevices especially under wet conditions.

We recently reported that a solid/water interface in a p/n organic bilayer is capable of oxidation (or reduction) through photoconduction of the carriers (*i.e.*, holes/electrons) generated at the p/n interface [3–6], where wide visible-light energy at wavelengths of <750 nm is available for the photoinduced reaction at the above-mentioned interface. For example, when the organic bilayer of 3,4,9,10-perylenetetracarboxyl-bisbenzimidazole (PTCBI, an n-type semiconductor) and metal-free phthalocyanine (H_2Pc, a p-type semiconductor) was used as a photoelectrode in the water phase [3], the photoinduced oxidation of thiol was found to occur at the H_2Pc/water interface along with hole conduction through the H_2Pc layer (Scheme 1). In a dry state organic device, a thermal stress applied to a film as well as an increase in temperature during cell performance leads to a decrease in the photovoltaic characteristics [7,8]. However, in the water phase such an influence of heat is negligible because water is a medium capable of thermal absorption, thereby resulting in stable performance of the p/n organic film [6]. The stability of the film may also be ascribed to the characteristic that the consumption of carriers takes place efficiently at the solid/water interface. In order to investigate and accumulate fundamental knowledge on a solid/liquid interface that has potential characteristics, we investigated the photoelectrode characteristics of PTCBI/H_2Pc in an acetonitrile containing I_3^-/I^- couple.

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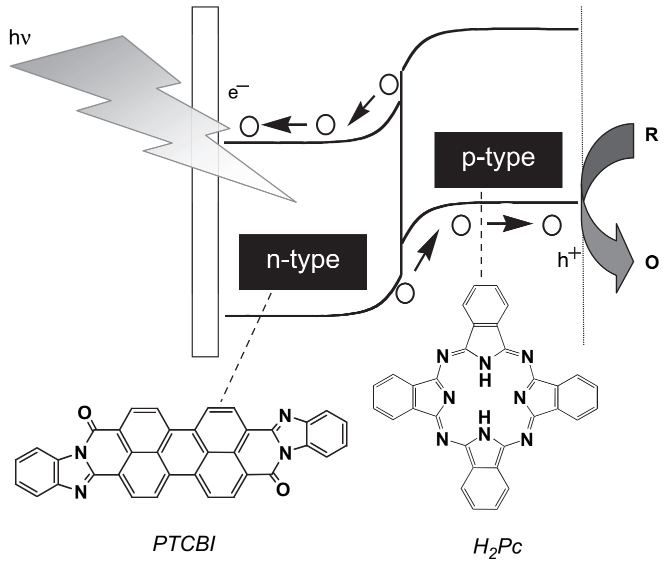
doi:10.1016/j.dyepig.2007.07.005



Scheme 1. Chemical structures of PTCBI and H_2Pc, and a schematic illustration for photoanodic reaction at H_2Pc/liquid interface.

2. Experimental

PTCBI was prepared and purified according to a previously described method [9]. H_2Pc was purchased from Tokyo Kasei Kogyo Co. Ltd., and purified by sublimation in a vessel thermostated at 440 °C prior to use (*i.e.*, thermal control was conducted for the outside of the vessel). The purest grade reagents of iodine, potassium iodide, and acetonitrile (anhydrous) were purchased from Kanto Chemical Co. Inc. and used as available. The ITO-coated glass plate (resistance, 8 $\Omega\,cm^{-2}$; transmittance, >85%; ITO thickness, 174 nm) was obtained from Asahi Glass Co., Ltd.

The photoelectrode device was prepared by vapor deposition (degree of the vacuum, $<1.0\times10^{-3}$ Pa; deposition speed, 0.03 $nm\,s^{-1}$), and consisted of PTCBI coated on an ITO and H_2Pc coated on the top of the PTCBI (denoted as ITO/PTCBI/H_2Pc). During vapor deposition, the temperature at the ITO plate was not controlled. Absorption spectral measurement was conducted using a Hitachi U-2010 spectrophotometer. The resulting absorption spectra of both PTCBI and H_2Pc were identical to those reported earlier [10], and their absorption coefficients indicate the thickness of the film employed (*cf.*, the aggregation structure of the H_2Pc single layer can also be identified from the absorption spectrum; that is, the polymorph of H_2Pc was assignable to the alpha-phase, which is also supported by the findings of an earlier study [11]). Since the additivity of the absorption coefficients is considered to be held on the visible-light absorption spectrum of the bilayer, the two unknown parameters of each thickness were estimated by solving simultaneous equations on absorbance at two distinct wavelengths.

An electrochemical glass cell was equipped with the modified ITO working electrode (effective area, 1 cm^2), a spiral Pt counter electrode, and an Ag/AgCl (in saturated KCl electrolyte) reference electrode in an acetonitrile containing I_3^-/I^- couple . As for the electrolyte solution, a mixture solution of I_2 (0.3 mmol dm^{-3}) and KI (6.0 mmol dm^{-3}) was prepared. I_2 usually forms complex with I^- into I_3^-. According to the following equilibrium constant ($K = [I_3^-]/([I_2][I^-]) = 10^{6.2}$ [12]), the I_3^- and I^- concentrations were estimated as 0.3 mmol dm^{-3} and 5.7 mmol dm^{-3}, respectively (*i.e.*, there was no presence of the non-complexed I_2 under the present conditions). The entire photoelectrochemical study was conducted using a potentiostat (Hokuto Denko, HA-301) with a function generator (Hokuto Denko, HB-104), a coulomb meter (Hokuto Denko, HF-201), and an X-Y recorder (GRAPHTEC, WX-4000) under illumination and run in an Ar atmosphere. A halogen lamp (light intensity, ca. 70 $mW\,cm^{-2}$) was used as a light source under typical conditions. When measuring the action spectrum for photocurrent, a halogen lamp was used as a light source in combination with a monochromator (Soma optics, Ltd., S-10). The light intensity was measured using a power meter (type 2A from OPHIR JAPAN, LTD.). The incident photon-to-current conversion efficiency (denoted as *IPCE*) was calculated according to the conventional procedure [3–5]. In the present study, the effect of the reflection of the incident light from the glass surface was not considered (*i.e.*, the light intensity was not corrected).

3. Results and discussion

The measurement of cyclic voltammogram (CV) at ITO/PTCBI/H_2Pc was conducted in acetonitrile containing I_3^-/I^- couple. Fig. 1 shows CV under illumination (a), in comparison to that in the dark (b). When measuring the CV by a potential scan starting from −0.4 V (vs. Ag/AgCl), the generation of a photoanodic current due to the I^- oxidation was found to take place at the H_2Pc/liquid interface. This evidently differs from the ordinary photoelectrode characteristics at a p-type semiconductor/liquid interface of the Schottky junction. In

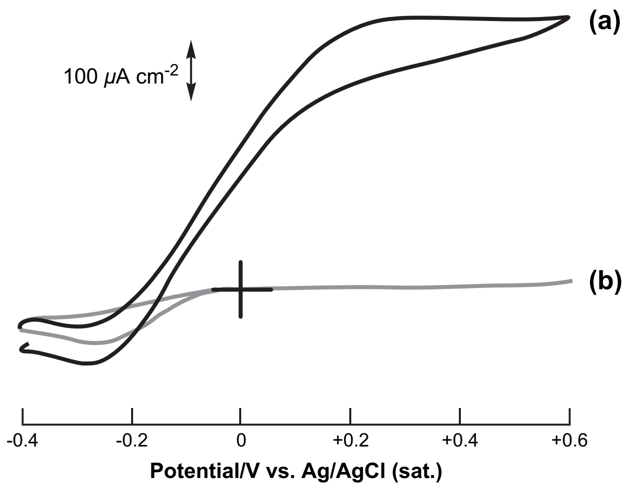


Fig. 1. CV at ITO/PTCBI/H_2Pc (a, illuminated; b, in the dark); electrolyte, 5.7×10^{-3} mol dm^{-3} (I^-) + 3.0×10^{-4} mol dm^{-3} (I_3^-); scan rate, 20 $mV\,s^{-1}$; film thickness (for a and b), 300 nm (PTCBI)/100 nm (H_2Pc).

addition, irrespective of illumination, a cathodic response most probably due to the I_3^- reduction appears at around −0.2 to −0.3 V. Those cathodic characteristics are discussed later.

The CV measurements were also conducted for an ITO coated with a single layer of PTCBI (denoted as ITO/PTCBI) under illumination (Fig. 2(a)) and in the dark (Fig. 2(b)). As expected, a photoanodic current occurred at the interface of the PTCBI/liquid. The thickness of the PTCBI layer in the ITO/PTCBI was consistent with that in the ITO/PTCBI/H_2Pc. However, comparing Fig. 2(a) with Fig. 1(a), it appears that the H_2Pc/liquid interface in the bilayer exhibits the more efficient characteristics; in other words, the photoinduced oxidation of I^- is kinetically fast in the bilayer. Considering that the PTCBI/H_2Pc bilayer is a photovoltaic material [10,13–15], the photoanodic current occurring at the H_2Pc/liquid interface can originate in the photophysical character of the p/n heterojunction, which takes place along with hole conduction by the H_2Pc layer.

A cathodic response was also observed at the PTCBI/liquid interface (see Fig. 2(a) and (b)), similar to that in the ITO/PTCBI/H_2Pc. These voltammetric results may indicate the presence of pin-holes in the H_2Pc layer of the bilayer; the electrochemical reduction of I_3^- can occur at the PTCBI surface particularly in the dark. When applying a potential of <0 V to the ITO/PTCBI (*cf.*, the energy level for the conduction band of PTCBI (*vide infra*) was assumed to be ca. +0.1 V (vs. Ag/AgCl)), an electron can be injected into the conduction band of PTCBI, thereby resulting in the I_3^- reduction (*cf.*, in acetonitrile, the potential of Ag/AgCl electrode (inner electrolyte, saturated KCl solution) was −0.068 V (vs. SCE). A formal potential for I_3^- (0.03 mol dm^{-3})/I^- (0.27 mol dm^{-3}) couple in acetonitrile has been reported to be +0.200 V (vs. SCE) [16,17], which is equal to +0.268 V (vs. Ag/AgCl). E° for I_3^-/I^- couple in acetonitrile was calculated according to the Nernst's equation, and consequently, the formal potential for I_3^- (0.3 mmol dm^{-3})/I^- (5.7 mmol dm^{-3}) couple was estimated to be ca. +0.36 V (vs. Ag/AgCl)). Moreover, the cathodic reaction may be enhanced under that applied potential condition of irradiation since the photogenerated electron carrier part moves to the PTCBI/liquid interface at which band bending is essentially reduced. Similar to the cathodic reaction at the n-type semiconductor, an anodic reaction (dark reaction) at p-type semiconductor (*e.g.*, single layer of zinc phthalocyanine) has also been reported [18].

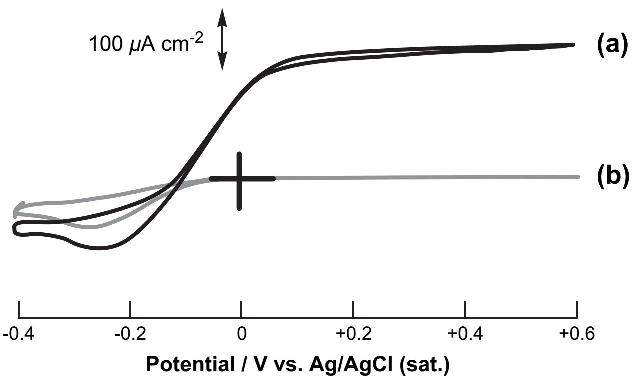


Fig. 2. CV at ITO/PTCBI (a, illuminated; b, in the dark); electrolyte, 5.7×10^{-3} mol dm^{-3} (I^-) + 3.0×10^{-4} mol dm^{-3} (I_3^-); scan rate, 20 mV s^{-1}; film thickness (for a and b), 300 nm (PTCBI).

In order to determine the origin of the photocurrent generated at the ITO/PTCBI/H_2Pc, the action spectrum for the photoanodic current was measured. The action spectral measurement was conducted in terms of the irradiation direction on incident light. When irradiating a monochromatic light from the PTCBI side (Fig. 3(a)), the resulting action spectrum was in accordance with the absorption spectrum of PTCBI (solid line in Fig. 3(a)) rather than that of the bilayer employed (Fig. 3(b)). The photocurrent generation can be induced on a wide visible-light absorption of <750 nm. Furthermore, the action spectrum of the ITO/PTCBI/H_2Pc (○ in Fig. 3(a)) was also compared with that of the ITO/PTCBI (△ in Fig. 3(a)). Although a similar thickness of the PTCBI layer was employed in each case, the larger spectrum was confirmed to occur in the former, which also supports the more efficient CV characteristics in the bilayer (*vide supra*). In the case of monochromatic light irradiation from the H_2Pc side, the resulting action spectrum was consistent with the transmittance spectrum of H_2Pc (Fig. 4), meaning little contribution of the H_2Pc absorption to the photocurrent generation. This indicates that the present photoanodic current is induced on a broad visible-light absorption by only the PTCBI.

A mechanism with photocurrent generation at ITO/PTCBI/H_2Pc can be suggested as follows. According to the studies on quenching of PTCBI photoluminescence [19] and laser ablation [20,21], charge separation in the PTCBI/H_2Pc bilayer may be possible only by the absorption of PTCBI (Eq. (1)):

$$\mathrm{PTCBI^{*}{-}H_2Pc} \rightarrow \mathrm{PTCBI^{-}{-}H_2Pc^{+}} \quad (1)$$

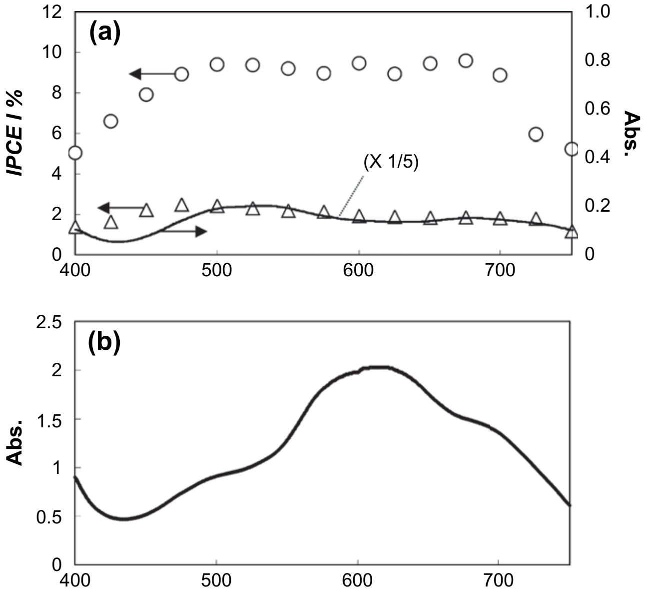


Fig. 3. (a) Action spectra for the photocurrent generated at ITO/PTCBI/H_2Pc (○) and ITO/PTCBI (△), and absorption spectrum of the single-layered PTCBI (320 nm, solid line); film thickness (○), 300 nm (PTCBI)/100 nm (H_2Pc); film thickness (△), 300 nm (PTCBI); electrolyte, 5.7×10^{-3} mol dm^{-3} (I^-) + 3.0×10^{-4} mol dm^{-3} (I_3^-); applied potential, +0.3 V (vs. Ag/AgCl); irradiation direction, PTCBI side. (b) Absorption spectrum of the PTCBI/H_2Pc bilayer employed.

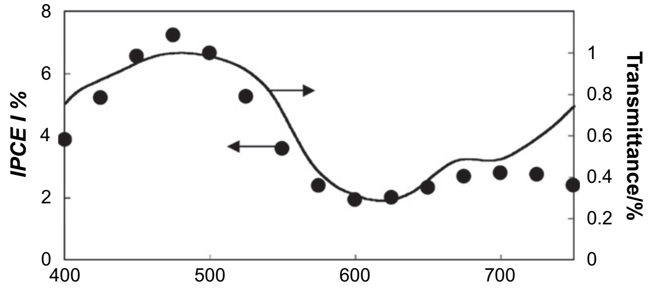


Fig. 4. Action spectrum for the photocurrent generated at ITO/PTCBI/H_2Pc (●), and transmittance spectrum of H_2Pc (80 nm, solid line); film thickness, 320 nm (PTCBI)/80 nm (H_2Pc); electrolyte, 5.7×10^{-3} mol dm^{-3} (I^-) + 3.0×10^{-4} mol dm^{-3} (I_3^-); applied potential, +0.3 V (vs. Ag/AgCl); irradiation direction, H_2Pc side.

where PTCBI* is an exciton of PTCBI. The previous findings may also be supported by the evidence that the photocurrent is generated at around 500 nm where there is no absorption of H_2Pc (*vide supra*). After the charge separation at the p/n interface, the photogenerated carriers of $PTCBI^-$ and H_2Pc^+ can migrate in each layer. The conduction through the H_2Pc layer in the bilayer can be associated with the photogeneration of H_2Pc^+ acting as a hole carrier, thus leading to an oxidation at the H_2Pc/liquid interface (Eq. (2)):

$$2H_2Pc^+ + 3I^- \rightarrow 2H_2Pc + I_3^- \tag{2}$$

Fig. 5 represents a schematic energy diagram for oxidation at ITO/PTCBI/H_2Pc. Considering the energy levels for ITO [22], PTCBI [22], H_2Pc [23], and I_3^-/I^- couple (*vide supra*), it appears that the oxidative power photogenerated at the H_2Pc/liquid interface is capable of I^- oxidation.

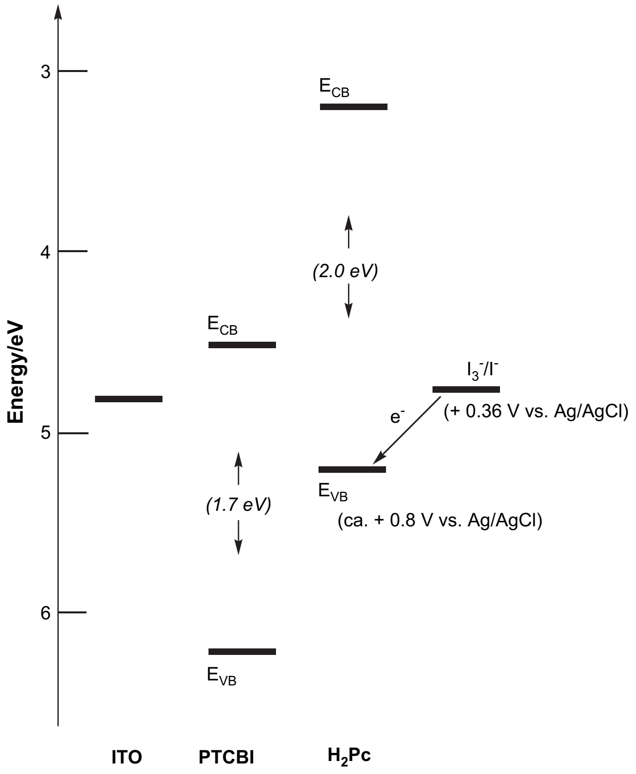


Fig. 5. A schematic energy diagram for oxidation at the H_2Pc/liquid interface. E_{VB} and E_{CB} denote the energy levels of the valence and conduction bands, respectively. The oxidation potential of H_2Pc in acetonitrile was measured in this work by means of voltammetry.

In the photoelectrode system of p/n organic bilayer film, photoinduced oxidation takes place at the exterior (solid/liquid interface) along with hole conduction through a p-type conducting layer, which is concerted with the photogeneration of carriers at the interior (p/n interface). The PTCBI/H_2Pc bilayer creates an advanced photofunctional interface that is responsive to the entire visible-light energy of < 750 nm. The photoelectrode characteristics of the PTCBI/H_2Pc are independent of the kinds of the electrolyte solution phase. Therefore, such a p/n organic bilayer device is extensively and practically applicable to various types of reaction, and its application is expected to reveal new aspects of photoelectrochemical research and technology.

Acknowledgments

This work was partially supported by a Grant-in-Aid for Scientific Research (no. 17750118 (T. A.)) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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