Electrochemical Preparation of Poly(3-thiopheneacetic acid) and Its n-Type Semiconductor Property

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3-Thiopheneacetic acid (3TA) was electrochemically oxidized and polymerized on indium tin oxide (ITO) electrodes in a 0.05 mol dm^{-3} tetrabutylammonium perchlorate (TBAP) acetonitrile solution; also, the photoelectrochemical properties of the resulting poly(3-thiopheneacetic acid) (P3TA) were studied. The film showed n-type semiconductor properties, although anion-doped conducting polymer prepared by electrochemical oxidation is generally of the p-type. An anodic photocurrent due to oxygen evolution from water was observed under white-light irradiation in a 0.1 mol dm^{-3} Na_2SO_4 aqueous solution. The anodic photocurrent density at 1.9 V vs. Ag/AgCl was 1.1 mA cm^{-2} and the flat-band potential of P3TA, estimated from the onset of an anodic photocurrent, was −0.1 V vs. Ag/AgCl. The band gap of P3TA was 2.4 eV, obtained from an $h\nu$ vs. $(h\nu \text{ PC})^{1/2}$ plot.

Thiophene is polymerized by electrochemical oxidation in nonaqueous electrolytes, producing polythiophene, which is a conducting and semiconducting polymer, as well as polyaniline and polypyrrole.[1—10] β-Substituted thiophene derivatives, such as 3-methylthiophene, were also electrochemically polymerized, forming a polymer.[3,11,12] 3-Thiopheneacetic acid (3TA) is also expected to be polymerizable into a conductive and semiconducting polymer by electrochemical oxidation. Functionalization of polythiophenes is one of the attractive applications of conducting polymer electrodes.[13] Photosensible, ionoselective, and chiral molecules can, for example, be used as functionalized groups. Poly(3-thiopheneacetic acid) (P3TA) is being considered for use in modified polymer electrodes, because several functionalized groups are introduced by chemical bonding with its carboxymethyl group ($-CH_2COOH$). Few studies have been made concerning the electrochemical polymerization of 3TA or the electrochemical properties of P3TA; however, the photoelectrochemical behavior of P3TA film electrodes remains to be clarified.

Waltman et al. studied the electropolymerization of thiophene derivatives having a β-substituent, such as methyl, bromo, dibromo, cyanomethyl (CN), carboxyl, and carboxymethyl groups, in a 0.1 mol dm^{-3} tetraethylammonium tetrafluoroborate (Et_4NBF_4) in an acetonitrile solution using a Pt electrode.[11] The results showed that the monomer oxidation potential strongly depended on the substituent and followed Hammett's rule. They concluded that P3TA was not obtained by the electrochemical polymerization of 3TA. Albery et al. reported on the electropolymerization of 3TA on a Pt disk electrode in a $LiClO_4$ acetonitrile solution.[14] The faradaic efficiency for such electropolymerization was remarkably low due to the high solubility of the resulting P3TA, with over 48% of the oxidative product being present in the electrolyte. They suggested that a high monomer concentration exceeding 0.2 mol dm^{-3} and a more positive potential are required to form a P3TA film, but did not study the photoelectrochemical properties of the P3TA film.

We electrochemically oxidized 3TA using ITO working electrodes in a 0.02 mol dm^{-3} monomer in acetonitrile. After P3TA thin films were formed, we studied their photoelectrochemical properties for the first time. Interestingly, P3TA thin films showed n-type semiconductor properties, although conducting and semiconducting polymers prepared by electrochemical oxidation are generally of the p-type.

Experimental

The electrolyte for electropolymerization was a 0.05 mol dm^{-3} tetrabutylammonium perchlorate (TBAP, Bu_4ClO_4) of an acetonitrile solution containing 0.02 mol dm^{-3} of 3TA. Reagent-grade TBAP (Fluka Chemical) and 3TA (Tokyo Kasei) were used without further purification. Acetonitrile (Wako Pure Chemical Industries, Ltd.) was dehydrated with molecular sieve 5A and then calcium hydride. ITO (Nihon Sheet Glass Co., 6 Ω/sq) and fluorine-doped SnO_2 (F-SnO_2, Asahi Glass Co., 8 Ω/sq) electrodes previously washed with hexane, acetone, and ethanol were used as the working electrode for electropolymerization. The apparent surface area of the working electrode was 1.4—2.9 cm^2. The reference electrode was an Ag |AgCl| saturated KCl (aq) separated from the electrolyte with a salt bridge containing KCl. A Pt plate electrode was used for the counter electrode.

A two-compartment glass cell was used for electrolysis. Before electrolysis, the electrolyte was deaerated with bubbling N_2 gas for 15 min. Electropolymerization was conducted galvanostatically with a constant anodic current density of 10 mA cm^{-2} using a potentio/galvanostat (Hokuto HA-501) connected in series to a coulomb-ampere-hour meter (Hokuto HF-201). The charge passed for polymerization was 100 to 200 mC cm^{-2}. A voltammetric measurement was performed using an arbitrary function generator (Hokuto HB-105) and an *X*–*Y* recorder (Riken Denshi F-5C). The UV-visible absorption spectra of P3TA films were measured using a Shimadzu MPS-2000 and a UV-3101PC. The thickness of P3TA thin films were measured using an Alpha-Step 300 profiler (Tencor Instruments). SEM measurements of P3TA films were conducted with a Hitachi S-800. Photoelectrochemical measurements of P3TA films were performed in a glass cell having a quartz window in a 0.1 mol dm^{-3} Na_2SO_4 aqueous electrolyte. A high-pressure Hg lamp (400 W) was used as the light source.

Results and Discussion

Electrochemical Preparation of P3TA Films. We measured the cyclic voltammogram of the oxidation of 3TA (0.02 mol dm^{-3}) on an ITO electrode in a 0.05 mol dm^{-3} TBAP acetonitrile solution. The anodic current due to 3TA oxidation was observed from 1.8 V vs. Ag/AgCl, but no oxidation peak was seen, even at 2.4 V. A similar voltammogram was obtained for thiophene oxidation, indicating that the carboxymethyl group did not affect the oxidation potential of the thiophene ring. Waltman at al. reported that the oxidation potential of thiophene was 2.06 V vs. SSCE and that of 3TA was 1.94 V using a Pt electrode in 10^{-4} to 10^{-5} mol dm^{-3} of monomer acetonitrile solutions containing 0.1 mmol dm^{-3} Et_4NBF_4,[11] which agrees with our result. Albery et al. have reported that the oxidation potential of 3TA for electrochemical polymerization in 0.5 mol dm^{-3} monomer in 0.1 mol dm^{-3} $LiClO_4$ acetonitrile solution was 1.2 V vs. SCE, and shifted toward the positive with a potential sweep.[14] This difference in the 3TA oxidation potential is considered to be due to different monomer concentrations. They observed an anodic current onset in a low monomer concentration, 0.01 mol dm^{-3}, at a more positive potential compared to that in a high monomer concentration; also, because the anodic current drastically decreased with a potential sweep, they assumed that a monomer concentration exceeding 0.2 mol dm^{-3} was required for 3TA polymerization. In our study, the anodic current of polymerization also rapidly decreased with a positive potential sweep, and no oxidation current was observed finally, indicating that a high monomer concentration is needed to oxidize the monomer, and that the resulting polymer film has no electrochemical activity under a dark condition.

White transparent films were formed on ITO electrodes by the electrochemical oxidation of 3TA. A soluble polymer (deep purple) formed near to the electrode surface, suggesting a low faradaic efficiency for the polymer film formed on the electrode surface. The film was not uniform and was 0.1—0.2 μm thick. A typical SEM photograph of P3TA is shown in Fig. 1. This photograph shows P3TA with small 30—100 nm particles. The morphology of P3TA was similar to that of polythiophene, poly(3-bromothiophene), and poly(3-methylthiophene).[11] P3TA particles were, however, much smaller than those of other polythiophenes (2—5 μm). The P3TA film thickness and the particle size suggest that several particles of P3TA were deposited onto the ITO substrate.

The P3TA film obtained from a high monomer concentration (0.5 mol dm^{-3}) was bright blue under the oxidized condition.[14] No P3TA was formed under low concentrations of the monomer (10^{-4}—10^{-5} mol dm^{-3}), however.[11,14] In our study, soluble polymer formation was enhanced by increasing the monomer concentration. The formation of a soluble polymer and a low concentration of the monomer in the polymerization solution is considered to lead to a low degree of P3TA polymerization on ITO electrodes. In a control experiment, we measured the cyclic voltammogram in a positive direction using an ITO electrode in the absence of the monomer. No change was seen to the ITO electrode surface, suggesting that P3TA formed on the ITO electrode in the presence of the monomer.

Fig. 1. SEM photograph of P3TA electrochemically produced on an ITO electrode.

Absorption Spectra of P3TA Films. Figure 2 shows typical UV-visible absorption spectra of a produced P3TA film and monomer (3TA) in ethanol. The absorption maximum, λ_{max}, was observed at 230 nm in the absorption spectrum of 3TA. For P3TA film, two absorption peaks were observed at 340 and 450 nm. This red shift of λ_{max} suggests that the monomer was electrochemically oxidized and polymerized. Albery et al. reported that the λ_{max} of P3TA in DMA was observed at 410 nm.[14] The λ_{max} of thiophene was reported to be 231 nm, 301 nm for bithiophene, 350 nm for terthiophene, and 410 nm for polythiophene, indicating that λ_{max} shifts toward the red side with increasing the degree of polymerization.[15] It may be possible that the peak at 450 nm is derived from the P3TA absorption and that λ_{max} at 340 nm can be assigned to absorption with products of low polymerization. In addition, the absorption of the reductive polymer (nondoped) shifts toward the blue side compared to that of the oxidative condition.[10] Thus, the absorption at 340 nm may be attributable to nondoped P3TA. The ratio of the peak intensities suggests that nondoped P3TA was mainly

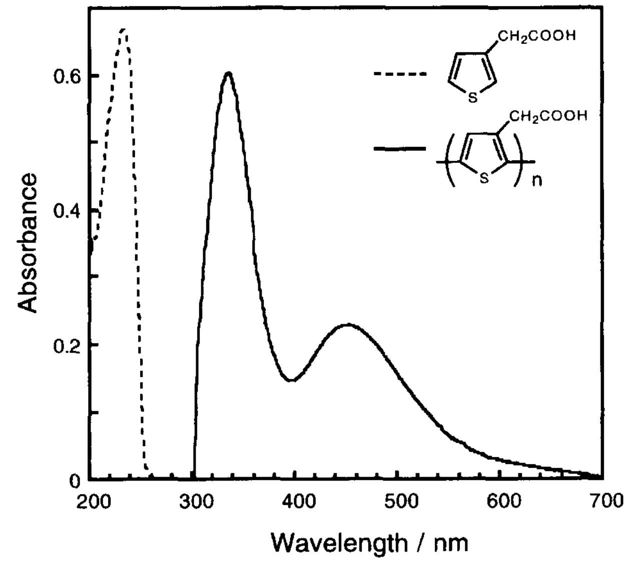

Fig. 2. Absorption spectra of P3TA film (solid line) and monomer (3TA) in EtOH (dotted line).

produced under our electropolymerization conditions. This may be attributable to the structure of 3TA having a carboxyl anion (COO^-) of the carboxymethyl group, because it acts as a dopant. The ratio of the peak intensities at 340 and 450 nm depended on the electropolymerization conditions, such as the electrolyte anion and the working electrode substrate.

The carboxymethyl group may be oxidized despite the thiophene ring. However, the 3TA oxidation potential was almost the same that of thiophene, as described above. In addition, the carboxyl group was reportedly not oxidized in the electropolymerization of 3-thiophenecarboxylic acid, since the oxidation potential followed Hammett's rule.[11] Given these results, the α-position of the thiophene ring would be oxidized preferentially, leading to polymer formation and no carboxymethyl group oxidation. To confirm P3TA formation, an FT-IR measurement of the film was conducted. Spectra showing the presence of the carboxymethyl group and conjugated polyheterocycles were not obtained, however, due to the low polymer concentration on the ITO electrode.

Photoelectrochemical Property of P3TA Films. We measured current–potential curves for a P3TA/ITO electrode prepared in a TBAP acetonitrile solution under dark and white light irradiation in a 0.1 mol dm^{-3} Na_2SO_4 aqueous solution (Fig. 3). In the dark, no cathodic or anodic currents were observed at −0.8 to 1.8 V vs. Ag/AgCl. Note that the anodic current increases drastically with a potential sweep in the positive direction to 2.0 V vs. Ag/AgCl under irradiation, while no cathodic photocurrent was observed (Fig. 3). This indicates that the P3TA film is an n-type semiconductor. The anodic photocurrent density at 1.9 V was 1.1 mA cm^{-2}, and no limited current density was observed. This photocurrent would be due to oxygen evolution by water oxidation, since no redox ions were contained in the electrolyte. No decrease in the photocurrent was observed with several potential sweeps, indicating the stability of the P3TA film under irradiation, and no degradation of P3TA. The onset potential of the anodic photocurrent (shown in the inset of Fig. 3) close to the flat band potential of P3TA was −0.1 V vs. Ag/AgCl. Generally, anion-doped polymers, such as polypyrrole and poly(3-methylthiophene), obtained by anodic electropolymerization, are p-type semiconductors.[16—21] Aizawa et al. reported that cation-doped polythiophene is an n-type semiconductor.[18,19] It is suggested that nondoped P3TA was mainly produced in our study, as described above. This may be a factor involved in the fact that the prepared P3TA showed properties different from those of an anion-doped polymer. Note that P3TA prepared by electrochemical oxidation is an n-type semiconductor and is stable under irradiation and oxidation.

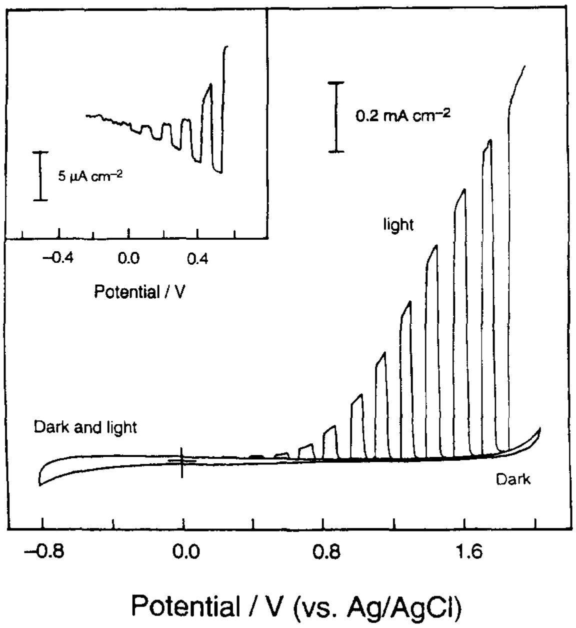

Fig. 3. Photocurrent-potential curve for a P3TA/ITO electrode in a 0.1 mol dm^{-3} Na_2SO_4 aqueous solution. Light source: 400 W Hg lamp. Scan rate: 100 mV s^{-1}. Inset: Photocurrent onset potential.

The effects of anions in the electrolyte under electropolymerization and the transparent conducting electrode on the photoelectrochemical property of P3TA films are given in Table 1. The photocurrent density strongly depends on the anions and the transparent conducting electrode. The an-

Table 1. Photoelectrochemical Properties of P3TA Films

Electrode	Anion	Photocurrent density[a) μA cm^{-2}
ITO	—	1.7
P3TA/ITO	ClO_4^-	670
P3TA/ITO	BF_4^-	7.1
P3TA/F-SnO_2	ClO_4^-	36

Conditions: electrolyte, 0.1 mol dm^{-3} Na_2SO_4 aqueous solution; irradiated light, white light (> 250 nm); electrode surface area, 1.4—2.9 cm^2. a) Anodic photocurrent density at 1.5 V vs. Ag/AgCl.

odic photocurrent density for P3TA polymerized in a 0.1 mol dm^{-3} Bu_4NBF_4 acetonitrile solution on an ITO electrode was remarkably small (7.1 μA cm^{-2} at 1.5 V) compared to that for a P3TA/ITO electrode prepared in a Bu_4ClO_4 solution: 670 μA cm^{-2} at 1.5 V. The photocurrent density for P3TA formed on a fluorine-doped SnO_2 electrode (F-SnO_2) was 36 μA cm^{-2} at 1.5 V. These results indicate that the polymerization conditions, such as anion types and working electrode substrates, greatly influence the produced P3TA properties, such as the dopant (anion) concentration, structure, and degree of polymerization. In the absence of P3TA, the photocurrent density for an ITO electrode at 1.5 V was only 1.7 μA cm^{-2} (Table 1). Moreover, the onset of the oxygen evolution current on an ITO electrode under a dark condition was observed at 2.0 V. These results suggest that oxygen evolution occurred on the P3TA film, and that P3TA has photocatalytic activity of water oxidation to form oxygen.

The photocurrent action spectrum obtained for a P3TA film is shown in Fig. 4. The anodic photocurrent was observed from 200 to 500 nm, and its spectrum agrees with the absorption spectra of P3TA film (Fig. 4). We therefore concluded that the photocurrent is caused by P3TA absorption. Figure 5 shows the relationship between the photon energy, $h\nu$, and $(h\nu \times PC)^{1/2}$, where PC represents the photocurrent density in arbitrary units, determining the band-gap energy (E_g) of P3TA. This plot indicates that the E_g of P3TA is approximately 2.4 eV. From an E_g of 2.4 eV, the valence band of P3TA is located to near 2.3 V vs. Ag/AgCl because the flat band potential of P3TA is close to −0.1 V. Since the oxidation potential of H_2O to O_2 is approximately 0.6 V vs. Ag/AgCl at pH = 7, the energy level of the valence band of P3TA is sufficiently positive to produce oxygen from water photoelectrochemically. To our knowledge, no report has treated oxygen formation by water oxidation on n-type polymer photoelectrodes; thus, our results suggest the possibility of new applications for polymer electrodes.

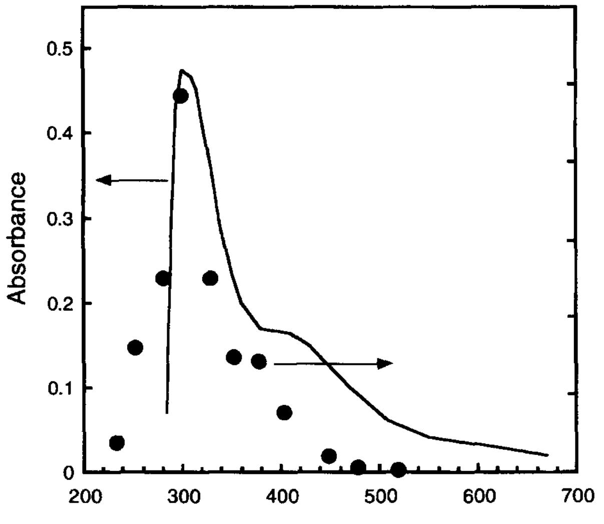

Fig. 4. Photocurrent action spectrum obtained for a P3TA/ITO electrode in a 0.1 mol dm^{-3} Na_2SO_4 aqueous solution.

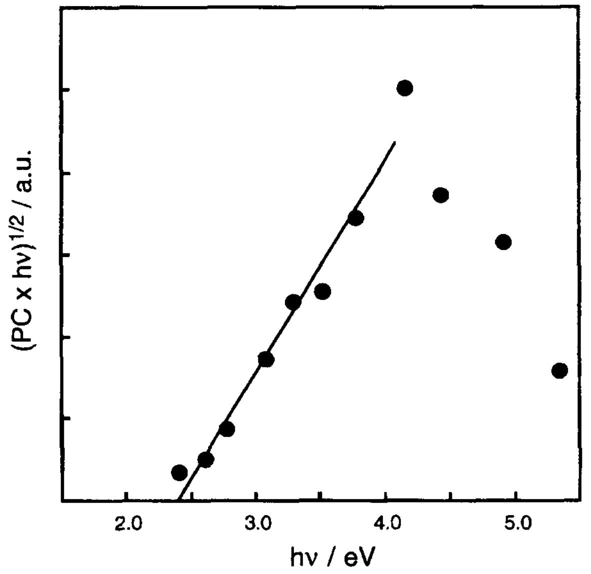

Fig. 5. $h\nu$ vs. $(h\nu\ PC)^{1/2}$ plot to determine band gap energy.

Electrochemical Behavior of P3TA in Redox Solutions. Cyclic voltammograms for (a) ITO and (b) P3TA/ITO electrodes in a 0.1 mol dm^{-3} Na_2SO_4 aqueous solution containing 50 mmol dm^{-3} of $FeSO_4$ under a dark condition are given in Fig. 6. The peaks derived from Fe^{2+} oxidation and Fe^{3+} reduction are observed at 1.60 V and −0.14 V vs. Ag/AgCl, respectively, for an ITO electrode (Fig. 6a); the difference between the oxidation and reduction peaks, ΔE, is 1.74 V ($E_{1/2}$ = 0.73 V). The Fe^{2+}/Fe^{3+} redox reac-

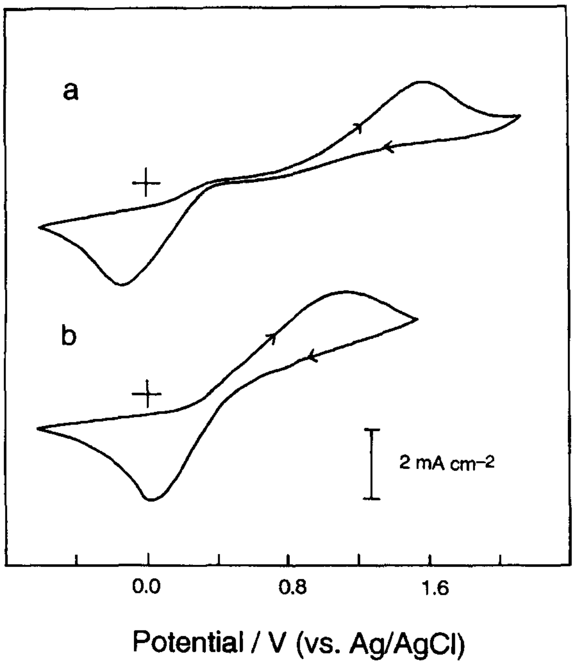

Fig. 6. Cyclic voltammograms in 0.1 mol dm^{-3} Na_2SO_4 aqueous solution containing 50 mmol dm^{-3} of $FeSO_4$ under dark condition: (a) ITO electrode; (b) P3TA/ITO electrode. Scan rate: 100 mV s^{-1}.

tion also occurs on a P3TA/ITO electrode, even under a dark condition (Fig. 5b), and no change in the voltammograms was observed under dark and light irradiation conditions, indicating that P3TA did not show the n-type semiconductor behavior in the Fe^{2+}/Fe^{3+} redox solution. As mentioned above, the P3TA film is electrochemically inactive toward further oxidation in a monomer solution, indicating its low conductivity and electrocatalytic activity. In addition, P3TA is not uniform on ITO electrodes. Given these results, the Fe^{2+}/Fe^{3+} redox reaction appears to occur inside P3TA film, i.e., on the ITO electrode surface. The thickness of the P3TA film and the P3TA particle size suggest that Fe^{2+} and Fe^{3+} ions easily contact the ITO electrode.

The peak of Fe^{2+} oxidation on a P3TA/ITO electrode is 1.14 V and that of Fe^{3+} reduction is 0.02 V. ΔE is 1.12 V ($E_{1/2}$ = 0.56 V), and decreases from 1.74 to 1.12 V and $E_{1/2}$ shifts toward a positive potential from 0.73 to 0.56 V due to a P3TA coating on an ITO electrode. The electrocatalytic activity for the Fe^{2+}/Fe^{3+} redox reaction thus increases in the presence of P3TA. No change was seen in the electrochemical behavior of the P3TA electrode compared to an ITO electrode in $Fe(CN)_6{}^{2+}/Fe(CN)_6{}^{3+}$ and I^-/I_2 redox solutions, however. We therefore concluded that P3TA has poor electrocatalytic activity for redox reactions, and that these redox reactions also occur on the ITO electrode surface.

Conclusions

3-Thiopheneacetic acid (3TA) was electrochemically oxidized on ITO electrodes in a 0.05 mol dm^{-3} Bu_4NClO_4 acetonitrile solution at a 0.02 mol dm^{-3} monomer concentration. The λ_{max} of poly(3-thiopheneacetic acid) (P3TA) was observed at 340 and 450 nm, suggesting a low degree of polymerization and/or predominant nondoped P3TA formation. P3TA films behaved as n-type semiconductor electrodes. The anodic photocurrent due to oxygen evolution from water was observed under white-light irradiation in a 0.1 mol dm^{-3} Na_2SO_4 aqueous solution (1.1 mA cm^{-2} at 1.9 V vs. Ag/AgCl). The action spectrum of the photocurrent and absorption spectra indicate that photocurrent is derived from photon absorption with P3TA. The flat-band potential of P3TA, estimated from the onset of anodic photocurrent, was −0.1 V vs. Ag/AgCl. The band-gap of P3TA was 2.4 eV, obtained from the $h\nu$ vs. $(h\nu\ PC)^{1/2}$ plot. P3TA film did not show the n-type semiconductor behavior in redox solutions, such as Fe^{2+}/Fe^{3+}, and has a poor electrocatalytic activity for redox reactions.

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References

1 A. F. Diaz, *Chem. Scr.*, **17**, 142 (1981).

2 G. Tourillon and F. Garnier, *J. Electroanal. Chem.*, **135**, 173 (1982).

3 G. Tourillon and F. Garnier, *J. Phys. Chem.*, **87**, 2289 (1983).

4 J. H. Kaufman, T.-C. Chung, A. J. Heeger, and F. Wudl, *J. Electrochem. Soc.*, **131**, 2092 (1984).

5 G. K. Chandlar and D. Pletcher, *Rep. Electrochem. (Spec. Period.)*, **10**, 117 (1985).

6 A. J. Downard and D. Pletcher, *J. Electroanal. Chem.*, **206**, 147 (1986).

7 R. J. Waltman and J. Bargon, *Can. J. Chem.*, **64**, 76 (1986).

8 A. F. Diaz and J. C. Lacroix, *New J. Chem.*, **12**, 171 (1988).

9 Z. Adamcova and L. Dempirova, *Prog. Org. Coat.*, **16**, 295 (1989).

10 J. Roncali, *Chem. Rev.*, **92**, 711 (1992).

11 R. J. Waltman, J. Bargon, and A. F. Diaz, *J. Phys. Chem.*, **87**, 1459 (1983).

12 F. Garnier, G. Tourillon, M. Gazard, and J. C. Dubois, *J. Electroanal. Chem.*, **148**, 299 (1983).

13 J. Roncali, R. Garreau, D. Delabouglise, F. Garnier, and M. Lemaire, *Synth. Met.*, **28**, C341 (1989).

14 W. J. Albery, L. Fengbin, and A. R. Mount, *J. Electroanal. Chem.*, **310**, 239 (1991).

15 A. F. Diaz, J. Crowley, J. Bargon, G. P. Gardini, and J. B. Torrance, *J. Electroanal. Chem.*, **121**, 355 (1981).

16 T. Kenmochi, E. Tsuchida, M. Kaneko, and A. Yamada, *Electrochim. Acta*, **30**, 1405 (1985).

17 M. Kaneko, K. Okuzumi, and A. Yamada, *J. Electroanal. Chem.*, **183**, 407 (1985).

18 M. Aizawa, T. Yamada, H. Shinohara, K. Akagi, and H. Shirakawa, *J. Chem. Soc., Chem. Commun.*, **1986**, 1315.

19 M. Aizawa and H. Shinohara, *Synth. Met.*, **18**, 711 (1987).

20 S. Glenis and A. J. Frank, *Synth. Met.*, **28**, C681 (1989).

21 A. J. Frank, S. Glenis, and A. J. Nelson, *J. Phys. Chem.*, **93**, 3818 (1989).