# Photoelectrochemical response of poly(3-hexylthiophene) and poly(2,3-diethylquinoxaline-5,8-diyl) in aqueous media

Keisuke Saito, Junpei Kuwabara, and Takaki Kanbara*

Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba 305-8573, Japan.
*Corresponding author. Tel.: +81-29-853-5066, fax: +81-29-853-4490,
E-mail address: kanbara@ims.tsukuba.ac.jp

**Abstract**

The photoelectrochemical properties of poly(3-hexylthiophene) (P3HT) and poly(2,3-diethylquinoxaline-5,8-diyl) (PDEQx) thin films on ITO (indium-tin oxide) electrodes were investigated in aqueous media. Photoirradiation of the P3HT-coated electrode resulted in cathodic photocurrents in the presence of methyl benzoylformate, whereas the PDEQx-coated electrode generated stable anodic photocurrents in the presence of 2-mercaptoethanol. The action spectra indicate that photoexcitations of the polymers cause photoelectrochemical reactions. The films of P3HT and PDEQx exhibit a typical photochemical response of p- and n-type semiconducting materials, respectively.

*Keywords*: conjugated polymers; photoelectrochemistry; organic semiconductors

## 1. Introduction

Since the discovery of photoinduced charge transfer in π conjugated polymers and $C_{60}$, polymer-based solar cells have attracted considerable attention.[1] There are many reports on photoelectrochemical solar energy conversion using polythiophene derivatives as p-type semiconducting material with $C_{60}$ derivatives as n-type semiconducting material.[1,2] The regioregular poly(3-hexylthiophene) (P3HT) has emerged as the most promising p-type semiconducting polymer in organic electronic devices owing to its high solubility and high hole carrier mobility.[3] In comparison with p-type polymers, the development of the n-type polymers has been still limited in terms of the number of reported examples and the semiconducting performance.[4-6] Nevertheless, the development of both kinds of semiconducting polymers is desired for the fabrication of the numerous electronic and optoelectronic devices including all-polymer solar cells.[7] Therefore, an investigation of photoelectrochemical properties of n-type polymers is an important subject as well as further developments of p-type polymers.

A photocatalytic property is one of the representative characteristics of semiconducting materials. In literatures, π conjugated polymers exhibit the photocatalytic properties for reductions of organic molecules[8,9] and a fixation of $CO_2$ on phenol.[10] For example, Yanagida et al. reported the photoreductions of ketones by poly(p-phenylene) as a heterogeneous photocatalyst, that result in the formation of the corresponding alcohol.[8] We also previously reported photocatalytic degradation of agrochemicals using poly(3-octylthiophene).[11] Owing to the different band gap and carrier mobility, n-type semiconducting polymers are likely to exhibit different photocatalytic properties from those of p-type semiconducting polymers. The characterization on the photocatalytic response of the polymers is expected to give valuable information for semiconducting properties such as photoexcitation behaviors, carrier mobility, and electron transfers. Since photoelectrochemical techniques enable us the quantitative analysis of the photocatalytic reaction at the polymers/water interface, the present work focuses on the photoelectrochemical characteristics of p- and n-types of semiconducting polymers, P3HT and poly(2,3-diethylquinoxaline-5,8-diyl) (PDEQx),[4] on ITO (= indium-tin oxide) electrodes in aqueous media. The organic-semiconducting-compound-based photoelectrodes have also been evaluated via photoelectrochemical techniques.[12,13] Since PDEQx is an electron acceptor and an electron-transporting material, PDEQx is evaluated as a typical n-type semiconducting polymers. We here report the photoelectrochemical properties of P3HT- and PDEQx-coated ITO electrodes in aqueous media.

<Structure of polymer>

## 2. Experimental

The regioregular P3HT was purchased form Aldrich Co. Ltd., and PDEQx was prepared by a method analogous to that in our previous reports.[4] The polymer-coated photoelectrodes were prepared by casting of the chloroform solution of P3HT and the formic acid solution of PDEQx on the ITO electrode, respectively. Thickness of the P3HT and PDEQx films were 185 and 160 nm, respectively, which were evaluated from atomic force microscope (AFM) observation using Nano Search Microscope SFT-3500 (Shimadzu Corp.). Electrochemical measurements were performed by ALS Model 1200A Electrochemical Analyzer (BAS Inc.). Photocurrent measurements were carried out using a three-electrode electrochemical cell in an aqueous solution at room temperature under nitrogen atmosphere containing 0.1 M KCl; HCl and NaOH solutions were added to adjust pH of the solution. The polymer-coated ITO glass electrode was used as the working electrode; a platinum wire electrode and a SCE (sat. KCl) electrodes were used as the counter and reference electrodes, respectively. The working electrode was irradiated with a 500W ultrahigh-pressure Hg lamp from the rear side of the electrodes. The area of the working electrode was 0.79 $cm^2$. The light-to-electricity conversion characteristics of the electrodes were obtained by a two-electrode system in the presence of the substrates ($1.0\times10^{-3}$ mol $dm^{-3}$). The action spectra were measured under irradiation with a monochromatic light from Xe lamp under fixed photon number ($5.4\times10^{15}$) by HSM-25ND Hyper Monolight (BUNKOUKEIKI Co., Ltd).

## 3. Results and Discussion

The photoelectrochemical characteristics of the polymer-coated electrodes were examined by voltammetry. Fig. 1(a) shows cyclic voltammograms (CVs) of the P3HT- and PDEQx-coated ITO electrodes in the presence of methyl benzoylformate under both photoirradiation and dark conditions. As shown in Fig. 1(a), high photocathodic current was observed for the P3HT-coated ITO electrode, whereas PDEQx showed no response. There was no photoelectrochemical response at the P3HT-coated ITO electrode in the absence of methyl benzoylformate. These phenomena indicate that the generation of photocathodic current is coupled with the formation of the photogenerated carrier originating in the charge separation at the P3HT/water interface. The formation of the carrier consequently leads to the reduction of methyl benzoylformate.[8] The photoelectrochemical reduction is reminiscent of ordinary photoelectrode behavior at a p-type semiconductor/liquid

interface of a Schottky junction.[14] The light-to-electricity conversion characteristics of the present P3HT-coated ITO electrode were obtained by a two-electrode system in the presence of methyl benzoylformate. The important values were as follows: $V_{oc}$, 0.33 V; $J_{sc}$ = 2.1 μAcm$^{-2}$; fill factor = 0.20.[15]

Fig. 1b shows photocathodic responses of the P3HT-coated ITO electrode upon photoirradiation at 0 V vs SCE bias; the transient photocathodic current initially appeared, and it then attained a steady state. The existence of the transient photocathodic current indicates that hole transport in the polymer film is faster than diffusion of methyl benzoylformate to the surface in aqueous media. Repeated photoexcitation of P3HT film did not lead to any decrease in the photocurrent. The photocurrent at the steady state increased linearly with increasing intensity of photoirradiation (Fig. 1c). The photocurrent also increased with increasing concentration of methyl benzoylformate (Fig. 1d). Then it began to saturate in the high-concentration region. These results suggest that the photoelectrochemical reduction is dominated by the charge transport at the P3HT/water interface.[13] A similar photocathodic response for the reduction of benzaldehyde was observed but the cathodic current (-0.98 μA) was lower than that of methyl benzoylformate (-11 μA) at the steady state.

<Fig. 1>

In contrast to the photocathodic response of the polymer-coated electrodes, we found that photoirradiation induces a photoanodic reaction at the PDEQx-coated ITO electrode/liquid interface. Fig. 2 shows the photoelectrochemical characteristics of the P3HT- and PDEQx-coated ITO electrodes in the presence of 2-mercaptoethanol under both photoirradiation and dark conditions. The photoirradiation of the PDEQx-coated ITO electrode resulted in an anodic current from the occurrence of the oxidation of 2-mercaptoethanol, which is characteristic of the n-type semiconductor-liquid interface,[16,17] whereas negligible photoelectrochemical response was observed for the P3HT-coated ITO electrode. The light-to-electricity conversion characteristics of the PDEQx-coated ITO electrode were as follows: $V_{oc}$, 0.52 V; $J_{sc}$ = 5.0 μAcm$^{-2}$; fill factor = 0.57. Photocurrent at ITO/PDEQx depends on the lighting intensity and a concentration of 2-mercaptoethanol (Fig. 2c and 2d). In terms of a substrate, an anodic current was observed in the presence of 2-mercaptoethanol (7.0 μA) and triethylamine (6.1 μA), whereas negligible anodic current was observed in the case of ethanol. The substrate dependence of photocurrent can be explained by the oxidation potential of the substrates.

The photoanodic responses of PDEQx exhibit no transient photocurrent (Fig. 2b) in contrast to P3HT showing the transient photocurrent before steady state under irradiation, as shown in Fig. 1b. The absence of transient photocurrent in PDEQx indicates that the rate-determining step is not the diffusion of the substrate components to the surface of the polymer. AFM observation indicates that the surface of the PDEQx film is much rougher than that of the P3HT film. Since the increase in roughness increases the surface area, PDEQx film has a larger surface area than that of P3HT film, which indicates the existence of a sufficient amount of the substrate for the anodic reaction on the surface.

Following sentence was removed.
"The carrier migration in the PDEQx film is likely to be a rate-determining step because the current linearly increased with the potential in CV (Fig. 2a)."

<Fig. 2>

Fig. 3 shows the action spectra of ITO/P3HT and ITO/PDEQx electrodes; they are in accord with the absorption spectra of P3HT and PDEQx in the film state, respectively. These results indicate that the generation of photocurrent is caused by the photoexcitation of these polymers. Fig. 4 shows schematic energy diagrams of the polymers and substrates. As was reported in our previous papers,[4] the ionization potential of PDEQx is higher than those of P3HT and the $RS^{\cdot}/RS^{-}$ couple; it appears that photoinduced oxidation power at the PDEQx/liquid interface is sufficient for thiol oxidation. In terms of the electron affinity of P3HT and PDEQx, methyl benzoylformate should have been reduced in both electrodes under light irradiation. However, PDEQx exhibited negligible photocathodic current for the reduction of methyl benzoylformate. This mismatch is probably due to Schottky junction at the n-type semiconductor/liquid interface, which is reminiscent of an ordinary n-type inorganic semiconductor.[16,17] Since PDEQx works as hole-blocking layers in the organic EL devices,[18] hole transport in PDEQx is unfavorable. The unfavorable hole transport ability should also contribute the low photocathodic current on PDEQx in addition to Schottky junction. PDEQx have been recognized as n-type semiconducting polymer, which serve as an electron acceptor and electron-transporting materials. This work coincides with the criteria; n-type semiconducting characteristics of PDEQx in terms of the photocatalytic response.

<Fig. 3>

<Fig. 4>

## 4. Conclusions

P3HT and PDEQx exhibited opposite photoelectrode characteristics at the polymer/water interface. The photoelectrode characteristics clearly represent p- and n-type semiconducting properties of the polymers. This work revealed semiconducting properties of n-type polymer which has not been well investigated in comparison with p-type semiconducting polymer. It is important that both types of polymers are evaluated by the same method for the development of the polymer-based semiconducting materials. The present methodology will provide a promising method for evaluating semiconducting polymers.

## Acknowledgement

We thank to Dr. *Takashi Fukuda* and Dr. *Daisuke Sakai* for the measurement of AFM image and helpful discussion. Dr. *Hidenobu Nakao* was acknowledged for the technical support of the electrochemical measurements. The authors are grateful to Prof *Takakazu Yamamoto* for helpful suggestion and discussion. This work was supported by Grant-in-Aid for Scientific Research (c) (20550105).

**References**

[1] S. Günes, H. Neugebauer, N.S. Sariciftci, Chem. Rev. 107 (2007) 1324-1338.

[2] H. Xin, F.S. Kim, S.A. Jenekhe, J. Am. Chem. Soc. 130 (2008) 5424-5425.

[3] J. Roncali, Macromol. Rapid Commun. 28 (2007) 1761-1775.

[4] T. Yamamoto, K. Sugiyama, T. Kushida, T. Inoue, T. Kanbara, J. Am. Chem. Soc. 118 (1996) 3930-3937.

[5] A. Babel, S.A. Jenekhe, J. Am. Chem. Soc. 125 (2003) 13656-13657.

[6] M.M. Durban, P.D. Kazarinoff, C.K. Luscombe, Macromolecules 43 (2010) 6348-6352.

[7] M.M. Alam, S.A. Jenekhe, Chem. Mater. 16 (2004) 4647-4656.

[8] T. Shibata, A. Kabumoto, T. Shiragami, O. Ishitani, C. Pac, S. Yanagida, J. Phys. Chem. 94 (1990) 2068-2076.

[9] S. Matsuoka, H. Fujii, T. Yamada, C. Pac, A. Ishida, S. Takamuku, M. Kusaba, N. Nakashima, S. Yanagida, J. Phys. Chem. 95 (1991) 5802-5808.

[10] T. Kawai, T. Kuwabara, K. Yoshino, J. Chem. Soc., Faraday Trans. 88 (1992) 2041-2046.

[11] C. Wen, K. Hasegawa, T. Kanbara, S. Kagaya, T. Yamamoto, J. Photochem. Photobiol. A: Chem. 133 (2000) 59-66.

[12] O. Inganäs, I. Lundström, J. Appl. Phys. 54 (1983) 4185-4192.

[13] T. Abe, S. Miyakushi, K. Nagai, T. Norimatsu, Phys. Chem. Chem. Phys. 10 (2008) 1562-1568.

[14] J.A. Turner, J. Chem. Educ. 60 (1983) 327-329.

[15]M. Kaneko, K. Takahashi, E. Tsuchida, J. Electroanal. Chem. 227 (1987) 255-258.

[16] M. S. Wrighton, J. Chem. Educ. 60 (1983) 877-881.

[17] M.A. Fox, Acc. Chem. Res. 16 (1983) 314-321.

[18] T. Fukuda, T. Kanbara, T. Yamamoto, K. Ishikawa, H. Takezoe, A. Fukuda, Appl. Phys. Lett. 68 (1996) 2346-2348.

Captions to figures

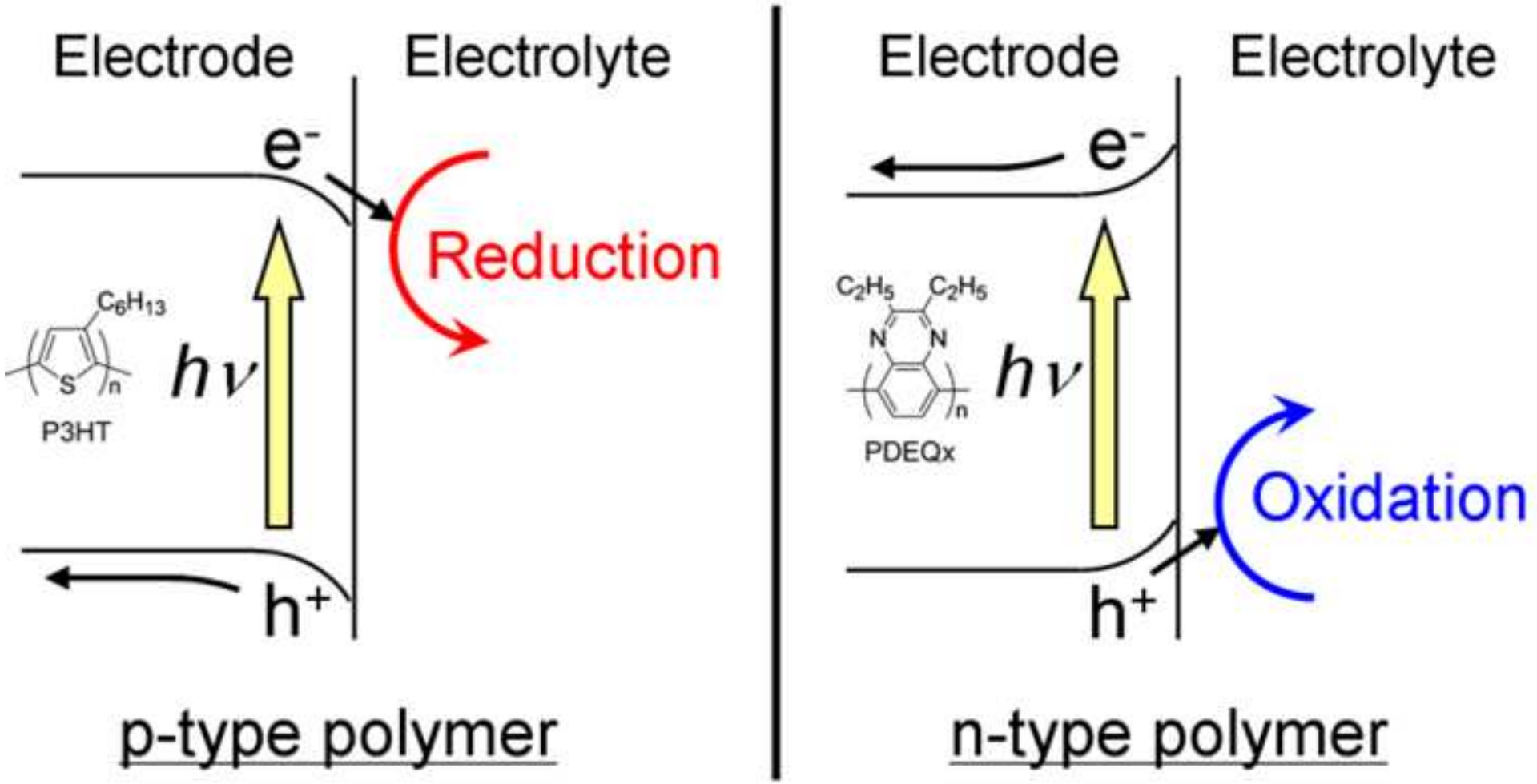
**Fig. 1.** (a) Cyclic voltammograms at (I) ITO/P3HT under illumination, (II) ITO/P3HT in the dark, (III) ITO/PDEQx under illumination, and (IV) a bare ITO under illumination. Conditions, aqueous KCl electrolyte with methyl benzoylformate ($1.0\times10^{-3}$ mol $dm^{-3}$; pH ≈ 6); scan rate, 20 mV $s^{-1}$; light intensity, *ca.* 100 mW $cm^{-2}$; Electrode area, 0.79 $cm^2$. (b) Typical current changes by switching on and off of illumination on (I) ITO/P3HT, (II) ITO/PDEQx, and (III) a bare ITO. Applied potential is 0 V vs. SCE. (c) Dependence of photocurrent on the lighting intensity. (d) Dependence of photocurrent on the concentration of methyl benzoylformate.

**Fig. 2.** (a) Cyclic voltammograms at (I) ITO/PDEQx under illumination, (II) ITO/PDEQx in the dark, (III) ITO/P3HT under illumination, and (IV) a bare ITO under illumination. Conditions, aqueous NaOH electrolyte with 2-mercaptoethanol ($1.0\times10^{-3}$ mol $dm^{-3}$; pH ≈ 10); Scan rate, 20 mV $s^{-1}$; Light intensity, *ca.* 100 mW $cm^{-2}$; Electrode area, 0.79 $cm^2$. (b) Typical current changes by switching on and off of illumination on (I) ITO/PDEQx, (II) ITO/P3HT, and (III) a bare ITO. Applied potential is 0.22 V vs. SCE. (c) Dependence of photocurrent on the lighting intensity. (d) Dependence of photocurrent on the concentration of 2-mercaptoethanol concentration.

**Fig. 3.** (a) Action spectra for photocurrent generated at ITO/P3HT and ITO/PDEQx. Electrode area, 0.79 $cm^2$. Conditions for P3HT, aqueous KCl electrolyte with methyl benzoylformate ($2.0\times10^{-3}$ mol $dm^{-3}$; pH ≈ 6); Applied potential, 0 V vs. SCE; Photon number, *ca.* $5.4\times10^{15}$. Conditions for PDEQx, aqueous NaOH electrolyte with 2-mercaptoethanol ($2.0\times10^{-3}$ mol $dm^{-3}$; pH ≈ 11); Applied potential, 0.22 V vs. SCE; Photon number, $5.4\times10^{15}$. (b) Absorption spectra of P3HT and PDEQx in the film state.

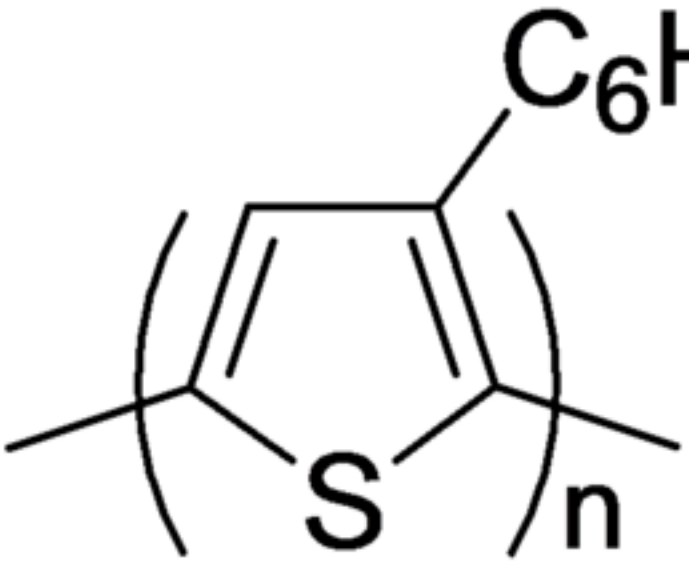
**Fig. 4.** A schematic energy diagram for polymers and substrates. $E_{VB}$ and $E_{CB}$ denote the energy levels of the valence and conduction bands, respectively. The energy levels of substrates were obtained from oxidation and reduction potentials according to SHE = 4.4 eV.

**Graphical Abstract**

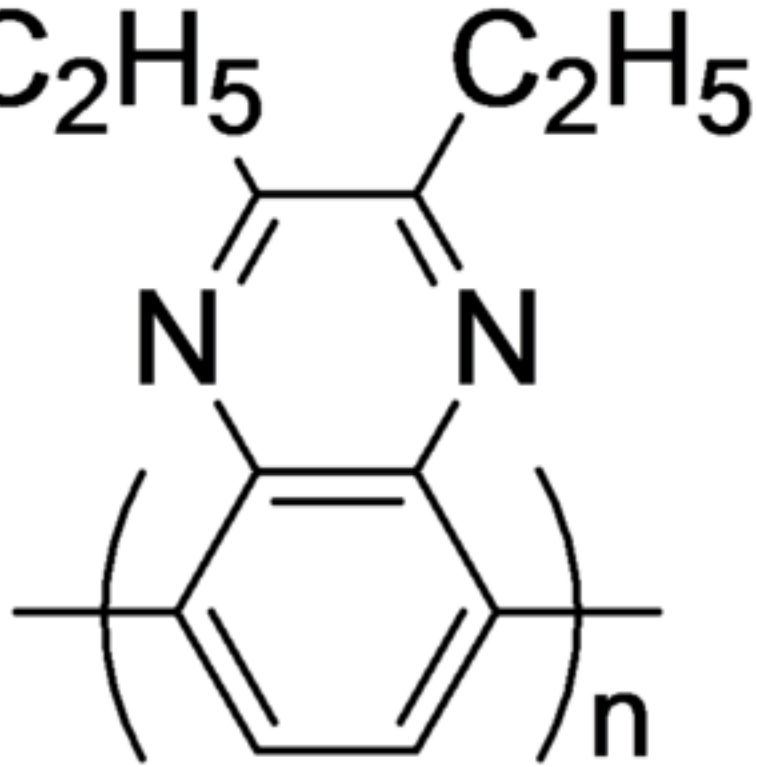


**Structure of polymer**

**Click here to download high resolution image**




P3HT




PDEQx

Figure 1

Click here to download high resolution image

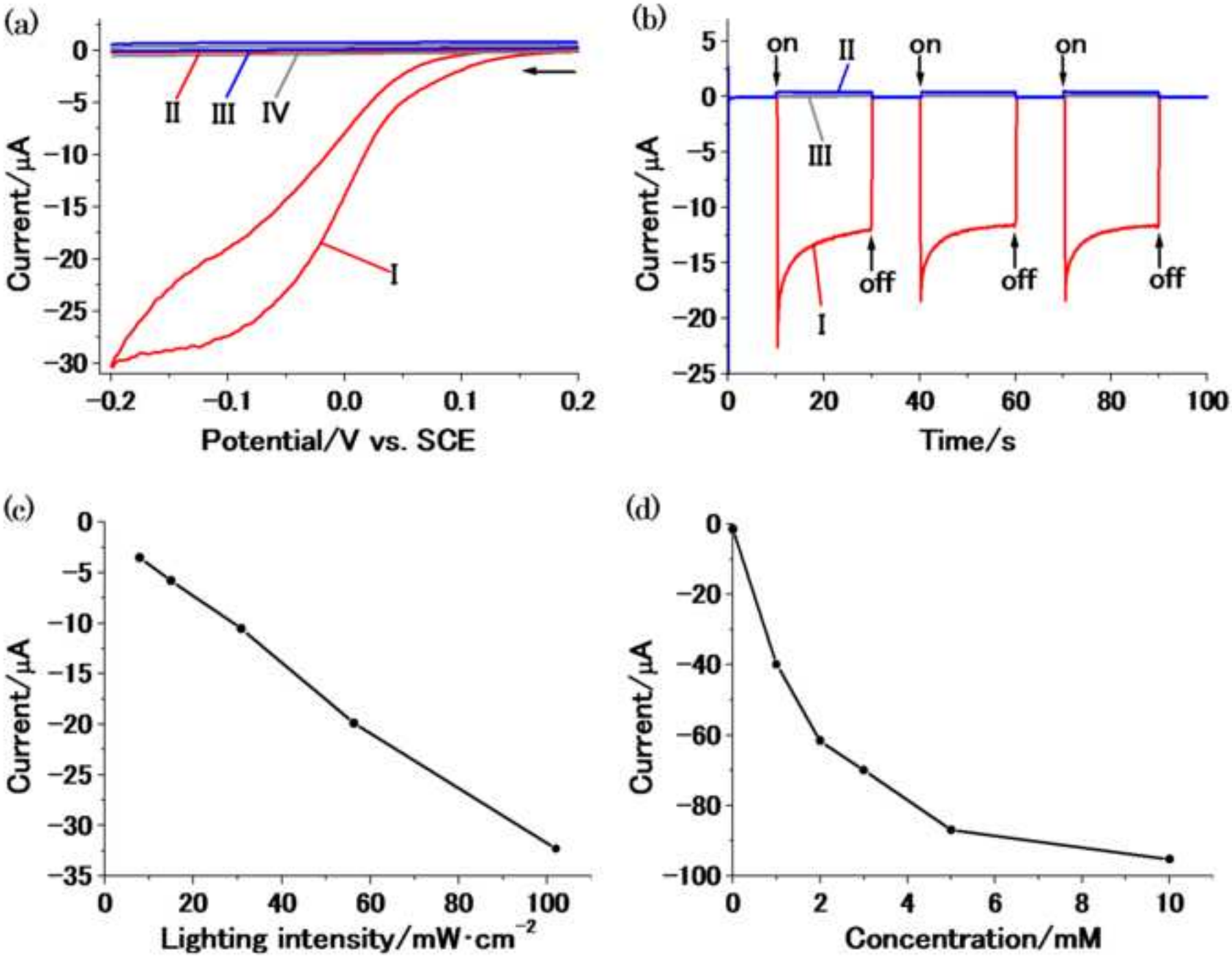


Figure 2

Click here to download high resolution image

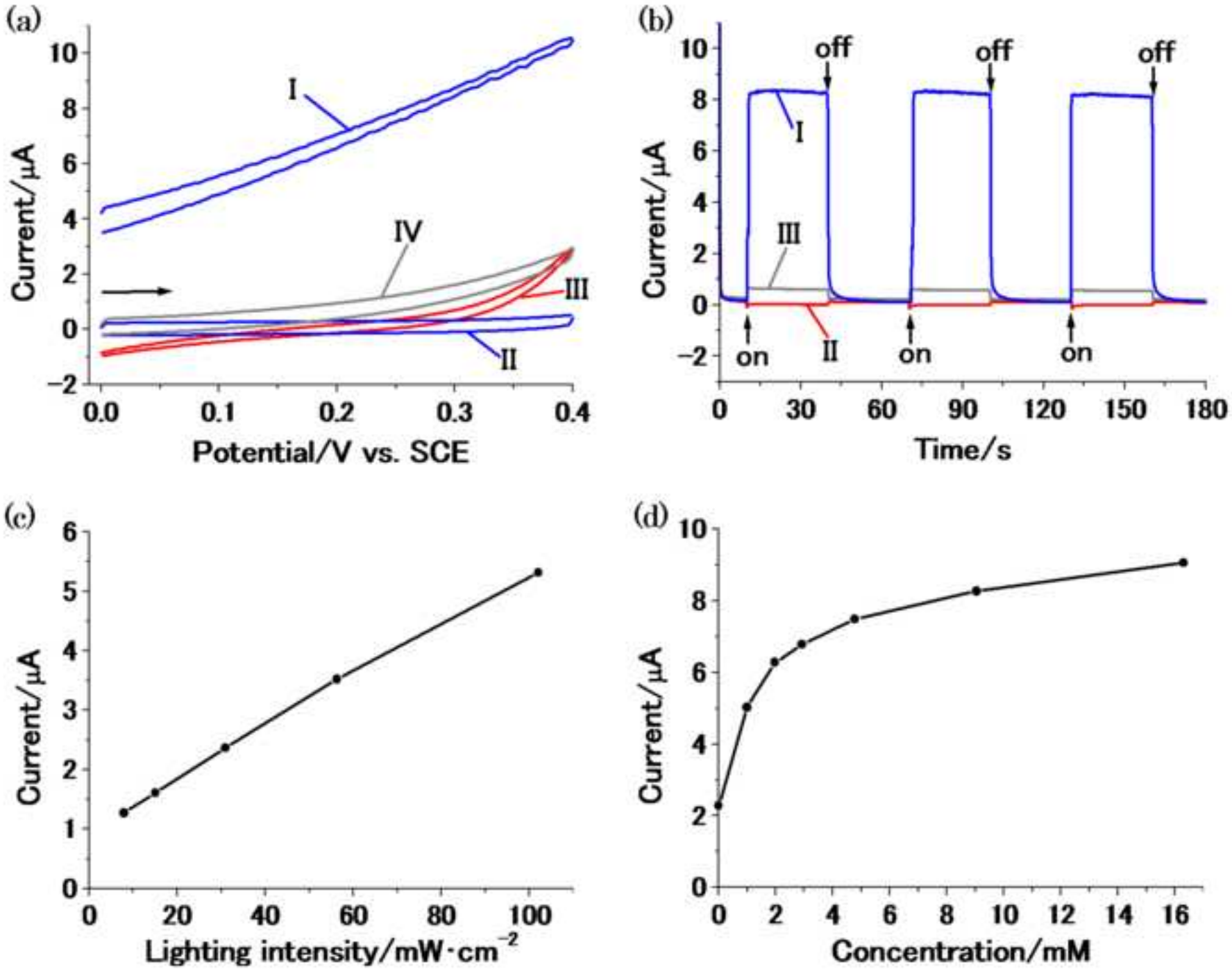


Figure 3
Click here to download high resolution image

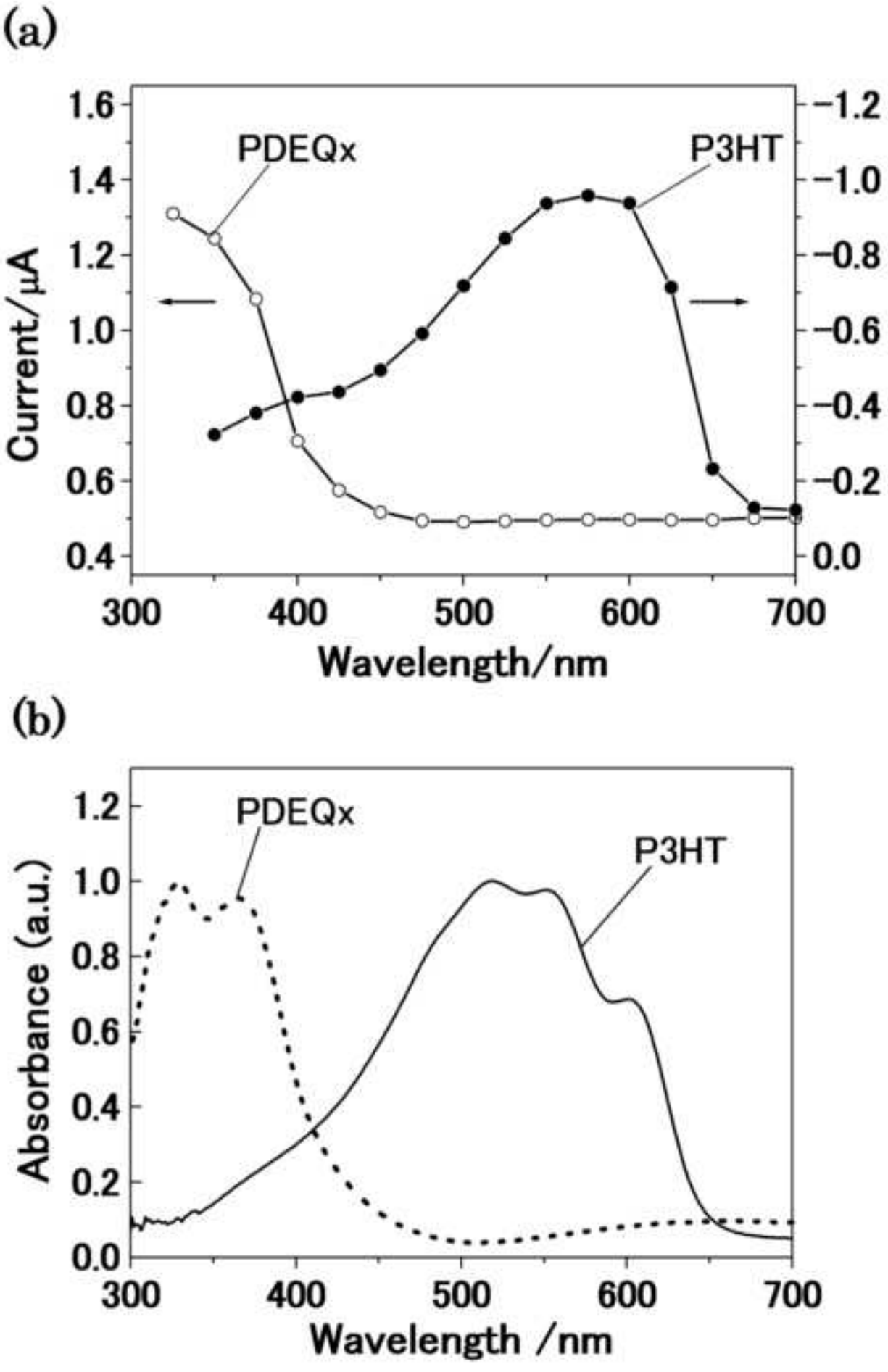
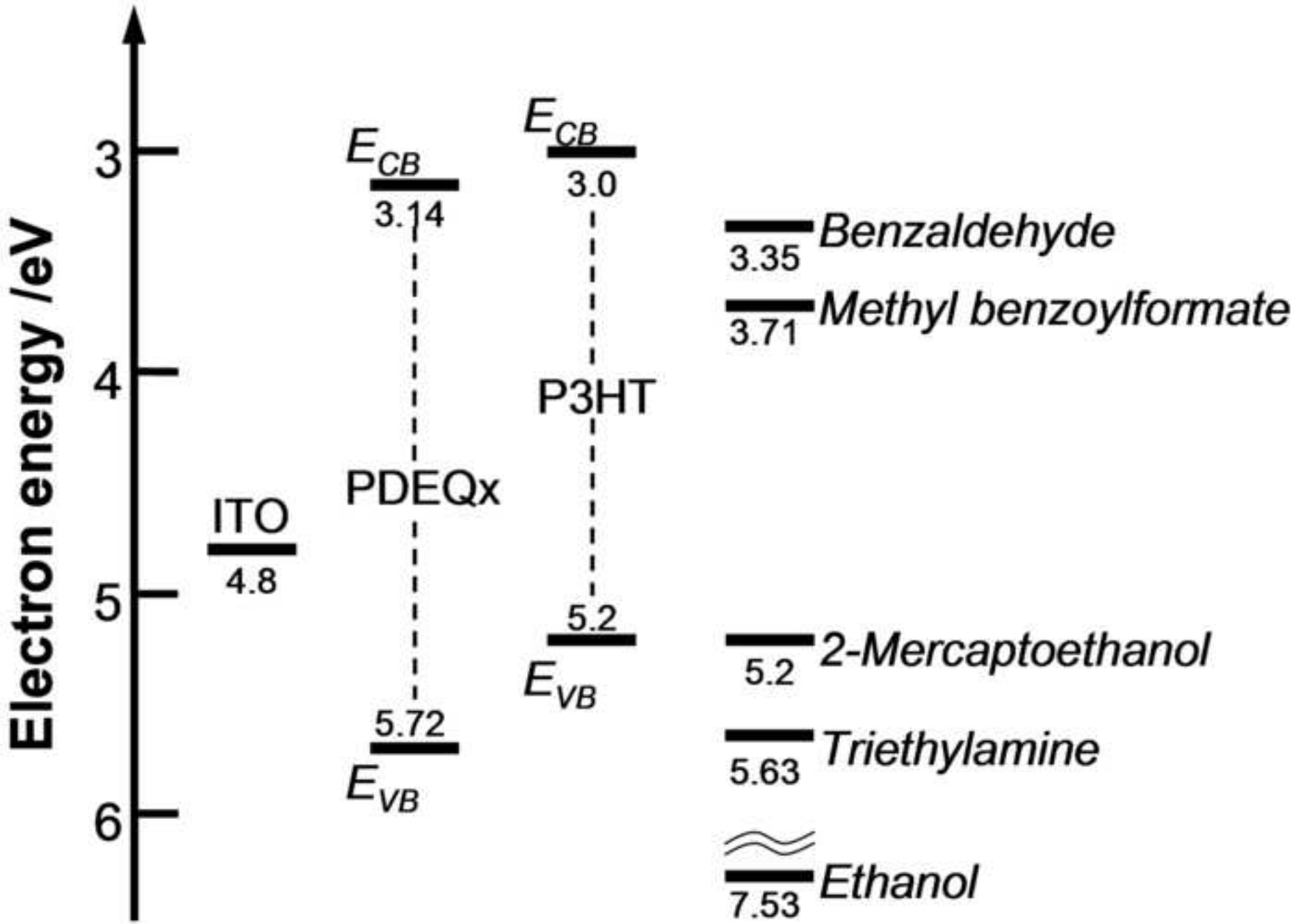


Figure 4

Click here to download high resolution image