Dependence of Band Offset and Open-Circuit Voltage on the Interfacial Interaction between TiO_2 and Carboxylated Polythiophenes

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The interface of planar TiO_2/polymer photovoltaic cells was modified with two carboxylated polythiophenes having different densities of carboxylic acid groups. Both of the interface modifiers increase the photocurrent of the cells but lower the open-circuit voltage. The work function of the TiO_2, measured using a Kelvin probe, increases with increasing density of carboxylic acid groups due to the formation of interfacial dipoles pointing toward the TiO_2 surface. The formation of interfacial dipoles results in a shift in the band offset at the TiO_2/polymer interface, which explains the decrease in the open-circuit voltage. This work demonstrates that care must be taken when using carboxylic acid side groups to attach polymers to titania surfaces in photovoltaic cells. If the density of attachment groups is just enough to attach the polymer, then the benefits of the interface modifier can be realized without substantially decreasing the open-circuit voltage.

An attractive approach for making low-cost photovoltaic (PV) cells is to use bulk heterojunctions, i.e., films containing two semiconductors interpenetrated at the sub-20-nm length scale, since charge carriers in these devices can be efficiently collected even if their exciton diffusion lengths and charge carrier mobilities are relatively low.[1−9] The interface between donor and acceptor is critical to the operation of bulk heterojunction PV cells since excitons are dissociated there, and recombination must be avoided. There are potentially many advantages of modifying the interface with a thin layer of molecules. To name just a few, one could design the layer to harvest excitons by resonance energy transfer,[10] prevent back electron transfer by providing an energetic and spatial barrier,[11] or adjust the band offset by creating a dipole layer.[12] Titania is a good acceptor semiconductor to use for studies of interface modification because it can be deposited as a solid or nanoporous film, and its surface can be modified easily with many organic molecules that have carboxylic acid groups. Once the interface modifier is attached, polymers can be cast over the structure without removing the modifier due to the large binding constant between carboxylic acid groups and titania.[12] Recently we reported on two novel polythiophenes with removable solubilizing side groups (Figure 1). These materials can be spin-cast and infiltrated into nanoporous films. When they are thermally treated at 210 °C, the side groups come off, leaving carboxylic acid groups that can attach to titania.[13] For polymer 1 (P1), all of the ester groups can be fully converted into carboxylic acid groups at 210 °C. For polymer 2 (P2), only 10% of the ester groups are tertiary groups that can be converted into carboxylic acid groups. The remaining 90% of the ester groups are secondary esters that remain stable at the same temperature of 210 °C. In this paper we show that a dipole layer forms at the polymer−titania interface, which introduces a band offset and lowers the open-circuit voltage of photovoltaic cells. This study points out that care must be taken when using acidic groups to modify polymer/oxide interfaces. Fortunately, the decrease in open-circuit voltage can be minimized by using a polymer with a small density of attachment sites to the titania.

Since donor−acceptor photovoltaic cells with flat layers are easier to understand and the purpose of this study is to understand how carboxylated polythiophenes at the interface affect device performance, we chose to cast films of polymer over smooth titania films. It is possible, however, to use nanoporous titania, which would enable more excitons to be harvested. Since both of the carboxylated polymers are insoluble in tetrahydrofuran (THF) at room temperature after the thermal treatment, regioregular poly(3-hexylthiophene) (P3HT) dissolved in THF can be spin-coated over the P1 or P2 layer without causing intermixing of the two different polymer layers. Fluorine-doped SnO_2 (FTO obtained from AFG Industries, Inc., 100 Ω/square) was used to construct FTO/TiO_2/P1 (or P2)/P3HT/Ag trilayer solar cells and also FTO/TiO_2/P3HT/Ag bilayer cells to serve as control devices (Figure 2a). The solid TiO_2 films were made using sol−gel methods as follows: 100 parts of ethanol, 2.5 parts of deionized water, 1 part of concentrated hydrochloric acid, and 10 parts of titanium tetraethoxide were mixed and kept under stirring for 0.5 h. The solution was spin-coated onto the substrate at 2500 rpm. The TiO_2 films were then calcined at 450 °C for 1 h leading to a film with a final thickness of approximately 50−70 nm. A polythiophene (P1 or P2) solution in THF was spin-cast onto the solid TiO_2 films, and the 5-nm-thick films were then treated

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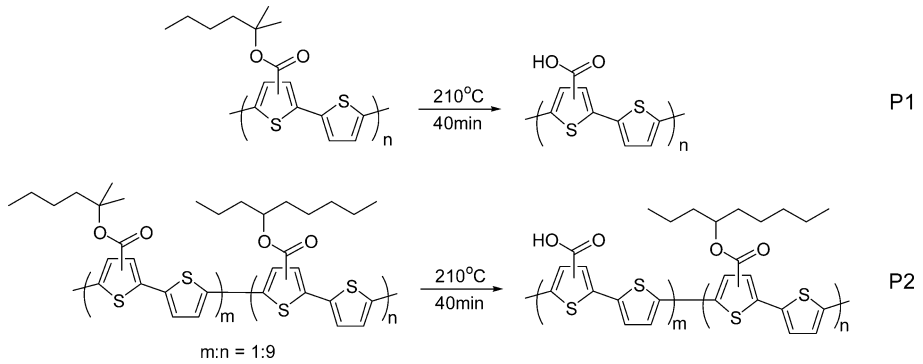

Figure 1. Chemical structures of the carboxylated polythiophenes.

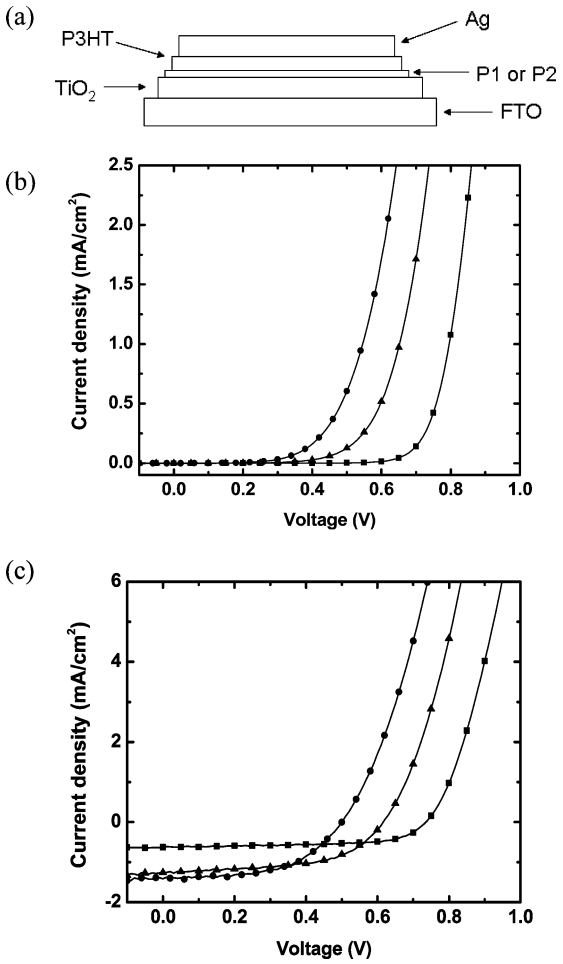

Figure 2. (a) Device structure of FTO/TiO_2/P1 (P2)/P3HT/Ag devices; device $I-V$ characteristics (b) in the dark and (c) under 30 mW/cm^2 monochromatic illumination at 514 nm. (FTO/TiO_2/P3HT/Ag, solid square; FTO/TiO_2/P1/P3HT/Ag, solid circle; FTO/TiO_2/P2/P3HT/Ag, solid triangle).

at 210 °C for 40 min. After the thermal treatment, another 50-nm-thick film of P3HT was spin-coated from THF solution. Finally, a 70-nm-thick Ag electrode was thermally evaporated onto the sample under 10^{-6} Torr. All devices were tested with 30 mW/cm^2 monochromatic illumination at 514 nm. In the following, P1 will be used as the example to illustrate the mechanism of our devices.

When the devices are illuminated, excitons are generated directly in the P1 layer, or more likely, they are generated in the P3HT layer and subsequently diffuse to the P1 layer or decay. Once the excitons in the P1 layer reach the TiO_2 interface, they are dissociated into conduction-band electrons in TiO_2 and holes in P1. Since P1 has a larger ionization energy than P3HT (5.3 vs 5.0 eV measured with cyclic voltammetry), holes are transferred from the P1 layer to P3HT and eventually are collected at the Ag electrode. The device with a 5-nm P1 layer had a short-circuit current density (J_{sc}) that was slightly more than twice that of the control device without P1 (Table 2 and Figure 2c). The increased J_{sc} can be attributed at least partly to the larger optical absorption coefficient of P1, which is a consequence of the P1 not having insulating side groups after thermal conversion. Unfortunately the improvement of device performance due to the increase of photocurrent was partially canceled out by the lowering of the open-circuit voltage (V_{oc}) of the device. As a result, the overall device power efficiency with P1 was only 30% higher than the control device. We found that the reduction of V_{oc} was dependent on the density of activated acidic groups. For example, the density of carboxylic groups of P2 is only 10% of that of P1, and the device with a 5-nm P2 layer has a larger V_{oc} (0.62 V) than the device with a 5-nm P1 layer (0.50 V) while nearly maintaining the same photocurrent. The reduced loss of device V_{oc} with P2 layer leads to a 50% increase of power efficiency compared to the control device.

To understand why the open-circuit voltage of the diodes changes when the titania surface is modified by P1 and P2, we measured the work function of modified TiO_2 films with a KP6500 McAllister Kelvin probe using an off−null configuration. Since the work function of TiO_2 is the energy difference between the Fermi level (E_F) and the local vacuum level (E_l), any shift of E_l should lead to a change of the effective work function of TiO_2.[14−21] The approximately 50-nm-thick TiO_2 films were all made from the same batch and were annealed at 210 °C for 40 min even if they were not coated with polymer to ensure the same thermal history. The measurements were carried out in a nitrogen atmosphere to prevent doping of the polymer and alteration of the surface states of the TiO_2. The Kelvin probe was calibrated with an Au reference sample whose work function was measured with ultraviolet photoelectron spectroscopy to be 5.21 eV. Table 1 shows the work function of each sample. The work functions of the TiO_2 films are increased by 0.22 and 0.06 eV by a 5-nm-thick P1 layer or P2 layer, respectively. Since both P1 and P2 have carboxylic acid groups in the polymer chain, a layer of interfacial dipoles can be formed between TiO_2 and the polymer due to acid−base interactions (Figure 3a). The interfacial dipole layer changes the electrostatic potential energy across the interface, which depends on the concentration of the acid and in turn also affects the equilibrium of the acid−base interaction. As a result, the conduction-band level (E_{CB}) of TiO_2 shifts downward by 60 meV at room temperature when the pH of the surrounding medium decreases by one unit, following the Nernst equation.[22−24]

TABLE 1: Kelvin Probe Measurements of the Work Function of Several Films[a]

sample	FTO	FTO/TiO_2	FTO/TiO_2/P3HT	FTO/TiO_2/P1	FTO/TiO_2/P2
work function (eV)	4.91 ± 0.01	4.51 ± 0.02	4.45 ± 0.01	4.73 ± 0.01	4.57 ± 0.01

[a] The thicknesses of the TiO_2, P3HT, P1, and P2 are 50, 5, 5, and 5 nm, respectively.

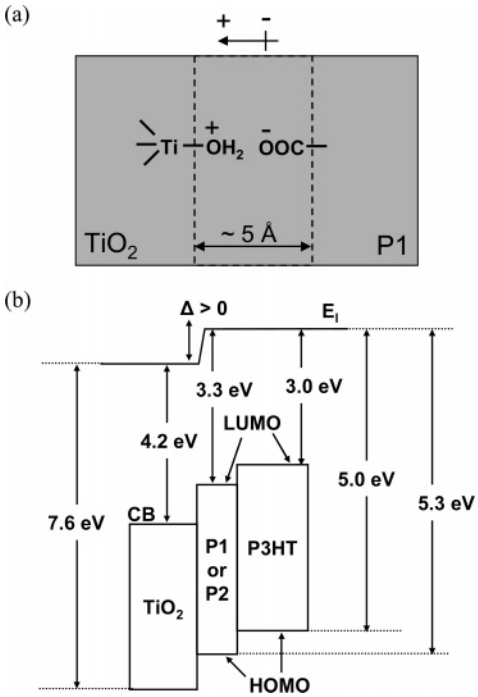

Figure 3. (a) Schematic of the formation of the dipole layer at the TiO_2/P1 interface due to acid−base interaction and (b) the flat-band energy diagram of the TiO_2/polymer structure. E_l, HOMO, LUMO, and CB stand for the local vacuum level, highest occupied molecular orbital, lowest unoccupied molecular orbital, and conduction band, respectively.

For this study we assume the dissociation constant (K_a) of P1 to be similar to that of 3-thiophenecarboxylic acid ($10^{-4.1}$ M^{-1}).[25] The density of P1 was measured to be 1.4 g/cm^3 using X-ray reflectometry;[13] the molecular weight of each repeating unit is 208 g/mol. The concentration of the carboxylic acid groups is calculated to be 7 M, and the pH of P1 is therefore given by the following equation

$$\mathrm{pH} = -\log [\mathrm{H}^+] = -\log \sqrt{K_a C_{\mathrm{acid}}} = 1.6 \qquad (1)$$

Assuming the isoelectric point of TiO_2 to be 5,[26] we calculate the shift of the vacuum level to be 0.20 eV, which is close to the measured value (0.22 eV).

For the P2 polymer, the acid concentration is reduced by about a factor of 10 compared to P1, and the shift of the vacuum level of TiO_2 should also decrease, which is observed in our measurement. From eq 1, since the concentration of the carboxylic acid groups is approximately 0.4 M, the calculated vacuum level shift should be 0.16 eV, in contrast to the measured value of 0.06 eV. The difference between the calculation and the measurement can be attributed to several factors. First, Raza et al. have reported that there is a very weak binding interaction between thiophene and TiO_2,[27] which could be due to the weak polarization of π-electrons of the thiophene ring by TiO_2 or partial alignment of the weak dipole of the thiophene ring. We have found that the work function of TiO_2 films treated with 5 nm of P3HT was reduced by 0.06 eV compared to that of the untreated TiO_2 sample, which could be due to this effect. Similarly, since most of the units of the P2 polymer do not have carboxylic acid groups, it is possible that the interaction between these thiophene groups and TiO_2 creates an interface dipole layer that shifts the E_l of TiO_2 in the opposite direction compared to the acid−base interactions. Second, the strength of the acid−base interaction is dependent on the dielectric constant of the medium. Since P2 polymer still retains 90% of the nonconjugated side groups after thermal treatment, it is expected to have a smaller dielectric constant than the P1 polymer. Therefore, the acid−base interaction could be weaker in the P2 polymer. Third, while in aqueous solution, the adsorbed protons on the TiO_2 surface are supplied by the bulk solution. For a thin polymer film on a TiO_2 surface, the adsorption of protons on a TiO_2 surface could decrease the local proton chemical potential of the polymer, which could lead to deviation from the Nernst equation. This effect is more dramatic for the P2 polymer, because the density of carboxylic acid groups is much smaller than that of the P1 polymer.

To attribute the change of work function of the TiO_2 films to the formation of an interfacial dipole layer between TiO_2 and the polymers, it was important to rule out the possibility of band bending in the polymer due to the formation of a depletion layer. Furthermore, if a depletion region near the surface of a TiO_2 film exists due to the presence of surface states, the deposition of a thin polymer layer should not change the band bending inside the TiO_2 film significantly. To avoid these two effects, it is necessary to reduce the doping level of the polymer and also use a thin layer of polymer for the Kelvin probe measurements. We used Soxhlet extraction to remove the residual impurities in the polymer to reduce the carrier concentration in the P3HT due to unintentional doping.[28] We also used only 5-nm-thick polymer P1 or P2 layers for all of the measurements. In addition, both the deposition of polymer films and the Kelvin probe measurement were carried out in a nitrogen atmosphere to minimize the oxidation of the polymer by air. To estimate the carrier concentration of P3HT, we made ITO/PEDOT:PSS/P3HT/Ag hole-only diodes. From the ohmic to space−charge-limited current transition, an upper limit of intrinsic carrier concentration of 2×10^{16} cm^{-3} was calculated. Sirringhaus et al. have shown that when carefully processed the residual doping level of polythiophene can be reduced below 5×10^{15} cm^{-3},[29] which is close to our measurement. If the bulk carrier concentration and the dielectric constant of the polymers are assumed to be 2×10^{16} cm^{-3} and 4 respectively, then the calculated Debye length is 17 nm, which is considerably larger than the thickness of the polymer film. Using Poisson's equation, we estimate the band bending across the 5-nm polymer to be about 1 meV, and therefore our assumption of a flat band inside the polymer film is justified.

For most n-type metal oxide semiconductors, such as TiO_2, there usually exists a certain concentration of surface states acting as electron-accepting states.[30,31] The electron transfer from the bulk to the surface creates a depletion layer and band bending near the surface, the degree of which is characterized by the surface voltage (V_s). When a thin layer of p-type conjugated polymer is deposited onto the n-type TiO_2, the mobile carriers of the polymer (holes) are completely depleted, and the negatively charged dopant inside the polymer film increases the overall surface charge density and the band bending inside TiO_2. The maximum differential band bending in TiO_2

induced by a 5-nm polymer film can be calculated using the following equations

$$Q_{ss} = -(2\epsilon\epsilon_0 n_b q)^{1/2}(|V_s| - kT/q)^{1/2} \quad (2.a)$$

and thus

$$\delta V_s = -(\epsilon\epsilon_0 n_b q/2)^{-1/2}(|V_s| - kT/q)^{1/2}\delta Q_{ss} \quad (2.b)$$

where Q_{ss} is the surface charge density of negatively charged surface states, ϵ is the dielectric constant of TiO_2, and V_s is the surface voltage, i.e., the band bending inside TiO_2 due to surface states. With a bulk carrier concentration, dielectric constant, and surface voltage[32] of 1×10^{17} cm^{-3}, 130,[33] and 0.2−0.3 V (from surface photovoltage measurement), the estimated differential surface charge density and differential band bending of TiO_2 due to a 5-nm-thick polymer film with a doping level of 2×10^{16} cm^{-3} are approximately 1×10^{10} cm^{-2} (1.6×10^{-9} C/cm^{-2}) and 3 mV, respectively. The small change of surface voltage of TiO_2 induced by the polymer layer is due to the small thickness and low residual doping level of the polymer film. Therefore, the change of surface voltage of TiO_2 due to a 5-nm polymer layer is within the experimental error (∼10 mV) and can be safely neglected. As a result, if the surface states of the TiO_2 film are not affected by the presence of the polymer film, the change of work functions of TiO_2 films treated with different polymers is a direct measure of the shift of E_l across the TiO_2/polymer interface.

It is important to note that the pK_a and isoelectric point are both measured in aqueous solutions, and great care has to be taken when applying the parameters measured in aqueous solution to the solid medium. The P1 polymer also has a permanent dipole moment, since the thiophene ring is an electron-donating group and the carboxylic group is an electron-withdrawing group. The alignment of the P1 molecules can create an additional interface dipole and change the work function of TiO_2. The dipole moment of P1 may also be modified upon adsorption onto TiO_2. Furthermore, the coverage of the TiO_2 surface with the carboxylated polymers and the interfacial interaction could change the density and the energy level of the surface states, which, in turn, could change the surface voltage and hence the work function of the TiO_2 film. These effects are under study at present.

After taking into account the shift of vacuum level (Δ) due to interfacial dipoles, the flat-band energy diagram of the devices can be drawn (Figure 3b). The shift of the vacuum level at the polymer−titania interface occurs over a few angstroms and therefore is represented by a sharp step transition in the energy diagram. From the conventions of surface science, the shift of the vacuum level is defined to be positive when the vacuum level is shifted upward across the TiO_2/polymer interface (since the electrostatic potential energy of the negatively charged electron increases).[14,17]

We compare the shift of the vacuum level with three different parameters that we can extrapolate from the device characteristics (Table 2 and Figures 2b and 2c). First, the shift of E_l directly changes the applied voltage needed to reach the flat-band condition, which is equal to the built-in voltage (V_{bi}) of the device. Mihailetchi et al. proposed that V_{bi} can be extrapolated from the device $I-V$ curve under illumination and approximately corresponds to the voltage at which the device photocurrent density is zero.[34,35] At a given voltage, the device photocurrent density is approximately equal to the difference between the current densities in the dark and under illumination. When the applied voltage is equal to V_{bi}, the built-in field vanishes, and the geminate pairs formed after exciton dissociation cannot be separated, leading to zero photocurrent. Second, the shift of the vacuum level also affects the dark $I-V$ characteristics. Since TiO_2 is a hole-blocking layer and the conjugated polymer is an electron-blocking layer, under forward bias there is only an electron current in TiO_2 ($J^e_{TiO_2}$) and a hole current in the polymer layer (J^h_{P3HT}), both of which are equal to the device dark current (J_{dark}). At the TiO_2/polymer interface, electrons and holes recombine with each other. The recombination current ($J^{rec}_{TiO_2/P3HT}$) is also equal to the device dark current at steady state. The overall relation is given by eq 3

$$J_{dark} = J^e_{TiO_2} = J^h_{P3HT} = J^{rec}_{TiO_2/P3HT} \quad (3)$$

The recombination current depends on the carrier concentrations, which in turn are determined by the quasi-Fermi levels of the charge carriers. The shift of the vacuum level changes the band offset and therefore the applied voltage required for the accumulation of a given concentration of charge carrier. We compare the shift of the vacuum level and the applied voltage needed to give rise to a dark current density of 2 mA/cm^2 and denote it as V_1. The choice of dark current density is somewhat arbitrary but does not affect the validity of our discussion.[36] Third, since the shift of the vacuum level changes both the band offset and the built-in potential and therefore affects the device V_{oc}, we also analyze the dependence of V_{oc} on the shift of E_l.[37]

The comparison between the shift of the vacuum level and the three different parameters is given in Figure 4. A linear inverse correlation between Δ and all three parameters can be clearly seen from the comparison. We propose that the formation of an interfacial dipole layer due to acid−base interaction gives rise to the shift of local vacuum level and reduces the band offset $I_{P3HT} - A_{TiO_2} - \Delta$. The reduction of band offset is manifested by the decrease in the device built-in voltage, the decrease in the applied voltage required for the accumulation of certain concentrations of charge carriers, and correspondingly a given dark current density. The shift of the local vacuum level

TABLE 2: Device Characteristics of Three Different Samples[a]

device	J_{sc} (mA/cm^2)	V_{oc} (V)	FF[b]
FTO/TiO_2/P3HT/Ag	0.63	0.73	0.64
FTO/TiO_2/P2/P3HT/Ag	1.26	0.62	0.56
FTO/TiO_2/P1/P3HT/Ag	1.41	0.50	0.54

[a] All devices are tested with 30 mW/cm^2 monochromatic illumination at 514 nm. [b] FF is defined as the ratio between the maximum device power density and the product of J_{sc} and V_{oc}.

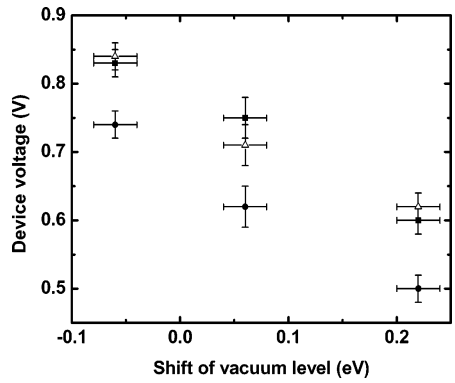

Figure 4. Comparison between the shift of vacuum level (Δ) and three different parameters of the devices. Device built-in voltage (V_{bi}), solid square; external applied voltage at 2 mA/cm^2 of dark current density (V_1), open triangle; open-circuit voltage (V_{oc}), solid circle.

also provides a stronger driving force for electron transfer from the conjugated polymer to TiO_2, which could contribute to the increase in device photocurrent. On the other hand, the shift of the local vacuum level and band offset inevitably lead to a greater energy loss, which, combined with the decrease of device built-in potential, reduces the device V_{oc} that can be achieved under normal conditions.

In summary, we have shown that the band offset between TiO_2 and conjugated polymers is affected by the acid−base interaction between TiO_2 and carboxylated polythiophenes. The resulting reduction of band offset between the conduction band of TiO_2 and the highest occupied molecular orbital of the polymer leads to reduced V_{oc} and can be controlled by changing the concentration of carboxylic acid groups of the polymer.

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(36) When we compared the dark I−V characteristics of different devices, it is important to take into account the device series resistance. At least, the potential drop due to series resistance should not vary significantly among different devices, which can originate from variations of device area, the thickness of TiO_2 and polymer, substrate resistance, and the metal/semiconductor contact resistance. Therefore, we compared the applied voltage at a small current density of 2 mA/cm^2 (∼100 μA for a 5 mm^2 device area) for different devices. At this device current, the variation of potential drop in the substrate for different devices is less than 5 mV. The variation of potential drop in P3HT due to 20% variation of P3HT thickness is about 20 mV. The potential drop inside TiO_2 due to space−charge effects is less than that of polymer because TiO_2 has a larger mobility, doping level, and dielectric constant. Furthermore, we assume both FTO/TiO_2 and Ag/P3HT contacts are ohmic.

(37) We tested the devices with 30 mW/cm^2 monochromatic illumination at 514 nm to avoid direct optical excitation of surface states of TiO_2. Our surface photovoltage measurement shows that the surface voltage of TiO_2 remains unchanged when illuminated with 514-nm optical excitation.