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An Easy and Effective Method To Modulate Molecular Energy Level of Poly(3-alkylthiophene) for High- V_{oc} Polymer Solar Cells

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Polymeric photovoltaic devices have attracted much attention as potential large-area, flexible, and low-cost solar cells.^{1–4} Bulk heterojunction (BHJ) polymer solar cells (PSC) have been proved to be the most successful device structure. The active layer in this kind of device consists of an interpenetrating network formed by an electron donor material blended with an electron acceptor material. Short circuit current (J_{sc}), open circuit voltage (V_{oc}), and fill factor (FF) are three main parameters to characterize a BHJ PSC device. In order to get better J_{sc} , some narrower band gap polymers were synthesized and applied to the PSCs. For example, by using PSBTBT⁵ and PCPDTBT,⁶ two thiophene-based conjugated polymers with a band gap of around 1.5 eV, photon harvesting by the PSCs was improved greatly, and hence J_{sc} of ~ 15 mA/cm² has been achieved, which is much higher than that obtained from the poly(3-hexylthiophene) (P3HT)-based PSC device.⁷ Since V_{oc} of PSC is directly proportional to the difference between HOMO level of the electron donor material and LUMO level of the electron acceptor material,⁸ to improve V_{oc} by using deeper HOMO level electron donor material is another effective approach to getting high power conversion efficiency (PCE). For instance, PFDTBT,⁹ PSiFDBT,¹⁰ and PCDTBT¹¹ were used as electron donor materials in PSCs, and great improvement has been achieved in the recent years.

Soluble polythiophene derivatives (PTs) have attracted much attention in recent years due to their promising applications in electrochromics, biosensors, electrochemical supercapacitors, anticorrosion, polymer thin film transistors, and polymer light-emitting diodes (PLEDs). As active layer materials in polymer solar cells, polythiophenes exhibited very interesting properties. Poly(3-alkylthiophene)s are very important photovoltaic materials, in which regioregular poly(3-hexylthiophene) (rr-P3HT) is one of the most important photovoltaic materials and has attracted much attention in this field. Although photovoltaic performance of P3HT-based PSC devices can be improved effectively by different methods, such as adding additives,¹² slow growth, and annealing,⁷ the V_{oc} of P3HT-based devices is very low at 0.6 V, which limits further improvement of the PCE. For polythiophene-based devices, higher V_{oc} can be obtained by using electron acceptor materials with high LUMO level, like fullerene derivatives;¹³ however, for polythiophene/PCBM-based devices, the V_{oc} is only 0.6–0.65 V. Therefore, how to effectively improve V_{oc} of the device by molecular structure design of polythiophene is still an unsolved problem in this field.

When a conjugated polymer is substituted by a strong electron donating group, like alkoxy, its HOMO level will be elevated

effectively. For example, the HOMO level of regioregular poly(3-alkylthiophene) (rr-P3AT) is ca. -5.0 eV, and the HOMO level of regioregular poly(3-alkoxythiophene) (rr-P3AOT) is ca. -4.5 eV.¹⁴ As a result, the V_{oc} of the rr-P3AOT/PCBM-based PSC device is lower than 0.1 V, which is much lower than the V_{oc} of the rr-P3AT/PCBM-based device. This simple example provided us a clear hint and also an evident proof that if the electron donating effect from the side chains of P3AT can be reduced, the HOMO level of P3AT will be reduced and hence V_{oc} of the P3AT/PCBM-based PSC device will be improved. Since alkyl is still an electron donating group, one of the simplest ways to reduce the electron donating effect of side chains would be to reduce the number of alkyl side chains. Therefore, a new polythiophene, P3HDTTT as shown in Scheme 1, was designed. In P3HT, each thiophene unit has one alkyl side chain, while in P3HDTTT, there is only one alkyl side chain for three thiophene units. 2-Hexyl-decyl was used as substituent to keep good solubility of the polymer.

The polymer P3HDTTT was synthesized by the route as shown in Scheme 1. The dibromo monomer, compound **3**, was prepared by the same procedure as 2,5-dibromo-3-hexylthiophene,¹⁵ and the 5,5'-bis(trimethyltin)-2,2-bithiophene, compound **1**, was synthesized by the reported method for other kinds of bis(trimethyltin) compounds¹⁶ and purified by recrystallization from methanol. The polymer was prepared through a typical Stille coupling reaction under the reported conditions¹⁶ and purified by preparation GPC column, and a yield of $\sim 40\%$ was obtained. The analytical data of the polymer are as follows: ¹H NMR (CDCl₃, 400 MHz): 6.9–7.2 (5H), 2.9 (2H), 1.30–1.0 (25H), 0.9–0.7 (6H). Elemental analysis: Calculated for (C₂₈H₃₈S₃): C, 71.43; H, 8.14. Found: C, 70.45; H, 8.3. The polymer exhibited excellent solubility in commonly used solvents, such as tetrahydrofuran, chloroform, chlorobenzene, methylene chloride, toluene, etc. The weight-average molecular weight and polydispersity index were estimated as 18.9K and 1.8, respectively, using GPC (polystyrene standards, chloroform as eluent under 40 °C). TGA showed excellent thermal stability with an onset of decomposition temperature under ambient atmosphere at 380 °C, which is similar to that of other kinds of P3ATs.¹⁷

The absorption spectrum of P3HDTTT is shown in Figure 1a. In order to make clear comparison, the absorption spectrum of P3HT is also shown in the figure. It is very clear that the absorption edge of P3HDTTT at longer wavelength is at 650 nm, corresponding to an optical band gap of 1.9 eV, which is almost same as that of P3HT. The absorption peak position of P3HDTTT is at 537 nm, which is very similar to P3HT. These results indicate that, as a photovoltaic material, the optical properties of P3HDTTT are comparable to P3HT.

Electrochemical cyclic voltammetry (CV) was performed to determine the HOMO and the LUMO energy levels of the conjugated polymers.¹⁸ Figure 1b shows the cyclic voltammograms of P3HDTTT and P3HT films on Pt electrode in 0.1 mol/L Bu₄NPF₆, CH₃CN solution. These two polymers exhibited well reversible p-doping processes. As shown, the onset oxidation potentials (ϕ_{ox}) of P3HDTTT and P3HT are ca. -0.50 and -0.10 V, respectively. Since the potential of Fc/Fc⁺ is -4.8 eV below vacuum level, the HOMO levels of P3HDTTT and P3HT are calculated to be -5.3 and -4.9 eV, respectively. It is very clear that the HOMO level of P3HDTTT is 0.4 eV lower than P3HT. Therefore, for the P3HDTTT/PCBM-based PSC device, a V_{oc} higher than the P3HT/PCBM-based device can be expected.

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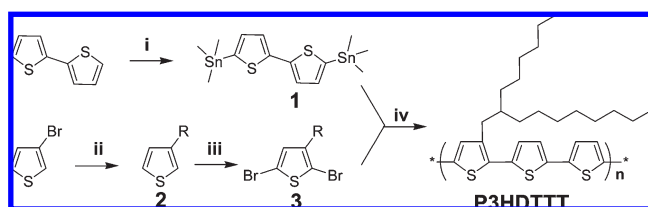
The photovoltaic device with a structure of ITO/PEDOT–PSS/P3HDTTT:PCBM/Ca/Al was fabricated. After spin-coating a 30 nm layer of poly(3,4-ethylene dioxythiophene):poly(styrenesulfonate) onto a precleaned indium–tin oxide (ITO)-coated glass substrate, the polymer/PCBM blend solution was spin-coated. The devices were completed by evaporating Ca/Al metal electrodes with area of 10 mm² defined by masks. The D/A weight ratio of the active layer is 1:1 (P3HDTTT/PCBM). A typical concentration of the blend solution used in this study for spin-coating active layer was 10 mg/mL, and chlorobenzene was used as solvent; there was no annealing process needed. The thickness of the active layer was ~80 nm. For comparison, the P3HT/PCBM-based device was fabricated under the same conditions. Figure 2a shows the *I*–*V* curves of P3HDTTT/PCBM- and P3HT/PCBM-based PSC devices under illumination of AM1.5G (100 mW/cm²). The *V*_{oc} of the P3HDTTT/PCBM-based device reached 0.82 V, which is ~0.2 V higher than the

P3HT/PCBM-based device. The fill factor of the P3HDTTT/PCBM-based device was 0.66, which is higher than the P3HT/PCBM-based device under the same conditions; this number is also very close to the best FF of the P3HT/PCBM-based device fabricated by the slow-growth method.

As listed in Table 1, the *J*_{sc} of the P3HDTTT/PCBM-based device is 6.33 mA/cm², which is higher than the P3HT/PCBM-based device under the same conditions, but it is much lower than the best *J*_{sc} of the P3HT/PCBM-based device fabricated by the slow-growth method.⁷ After measuring the *I*–*V* curve, the device was encapsulated in glovebox, and the external quantum efficiency (EQE) of devices were measured in air. The EQE curve of the P3HDTTT/PCBM-based device is shown in Figure 2b. The device exhibits a response range covering 650 to 350 nm, with a maximum EQE of 36% at 520 nm. As reported, the maximum EQE of the P3HT/PCBM-based device fabricated by the slow-growth method reached over 60%.⁷ If the EQE of the P3HDTTT/PCBM-based device can be improved to this value, a *J*_{sc} of ~10 mA/cm² can be achieved. That is to say, a PCE of around 5–6% would be highly expected by using this material.

As known, the morphology of the P3HT/PCBM blend as well as PCE of the P3HT/PCBM-based device are very susceptible to the fabrication process. For example, in the P3HT/PCBM-based photovoltaic system, by using slow growth, annealing, and adding additives, great improvements of the PCE, from ~1.6% to ~4%,^{7,12} were observed and well reported. In our initial testing, different fabrication processes/technology, like annealing, slow growth, and adding additives, were tried to improve the PCE of this new polythiophene-based PSC device, but we have not found an effective method to improve the PCE, and we are still working on it to explore the full potential of this new material.

Scheme 1. Synthesis Route of the Polymer P3HDTTT^a



^a Conditions: (i) butyllithium, THF, ambient temperature for 2 h; then trimethyltin chloride, ambient temperature for 1 h; (ii) 2-hexyldecyl magnesium bromide, Ni(dppp)Cl₂, THF, refluxing overnight; (iii) *N*-bromosuccinimide, chloroform, refluxing for 2 h; (iv) Pd(PPh₃)₄, toluene, refluxing for 24 h.

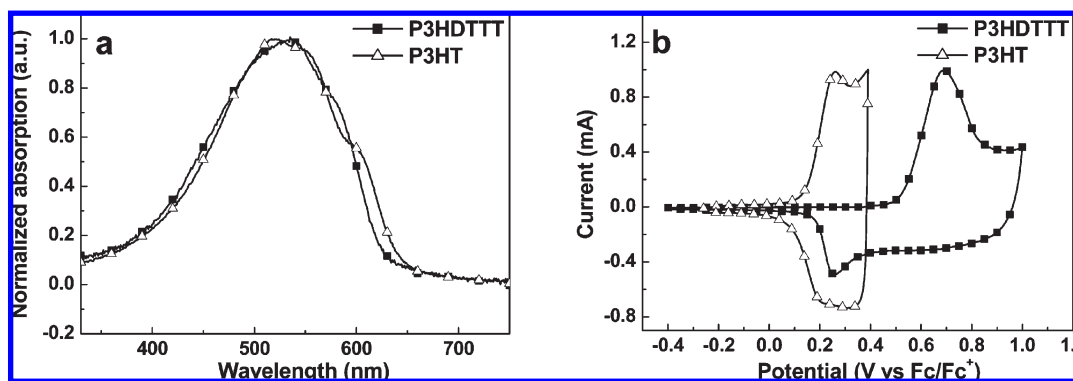


Figure 1. (a) Absorption spectra of P3HDTTT and P3HT films. (b) p-Doping/dedoping processes of the voltammograms of P3HDTTT and P3HT thin films in 0.1 mol/L [Bu₄N]PF₆–acetonitrile solution, with a scan rate of 50 mV/s.

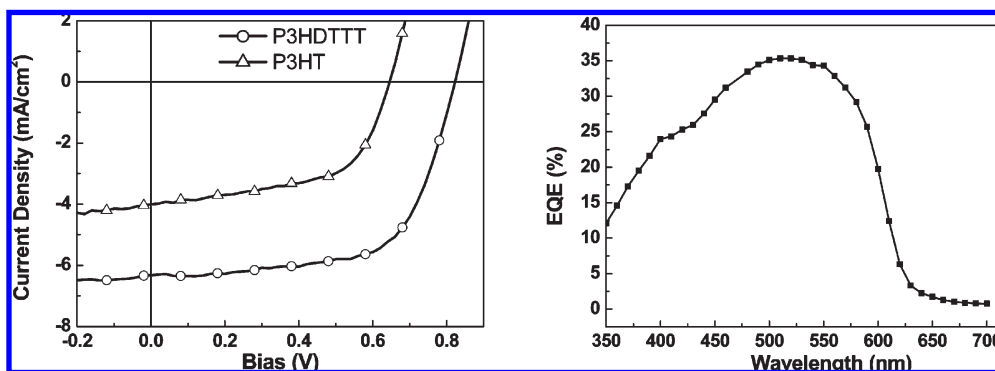


Figure 2. (a) *I*–*V* curves of P3HDTTT/PCBM- and P3HT/PCBM-based solar cell devices under illumination of AM 1.5G, 100 mW/cm². (b) IPCE curve of the P3HDTTT/PCBM-based device.

Table 1. Photovoltaic Properties of P3HDTT- and P3HT-Based Polymer Solar Cells

	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
P3HDTT:PCBM	0.82	6.33	0.66	3.40
P3HT:PCBM ^a	0.64	4.00	0.58	1.49
P3HT:PCBM ^b	0.61	10.6	0.67	4.37

^aThe device was fabricated by the same condition as used in the P3HDTT/PCBM-based device. ^bThese data were collected from our previous work, ref 7.

In conclusion, a new P3AT derivative, P3HDTT, was designed and prepared. By reducing the number of electron donating groups, the alkyl side chains, the HOMO level of P3ATs were successfully reduced from -4.9 eV as for P3HT to -5.3 eV as for P3HDTT, without changing their optical band gap. Photovoltaic properties of P3HDTT were initially investigated and compared with that of P3HT. A PCE of 3.4% was observed with a V_{oc} of 0.82 V under illumination AM 1.5G, 100 mW/cm². These photovoltaic results as well as the simple synthesis process of P3HDTT make this polymer being a potential photovoltaic material. Additionally, if J_{sc} of the P3HDTT/PCBM photovoltaic system can be improved to 10 mA/cm², over 5% efficiency would be realized, and then this material will become a very potential material for organic tandem solar cells to replace P3HT as absorber for the sunlight in short wavelength region.¹⁹

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