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Synthesis and Photovoltaic Properties of Two-Dimensional Conjugated Polythiophenes with Bi(thienylenevinylene) Side Chains

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Abstract: Three two-dimensional (2-D) conjugated polythiophenes with bi(thienylenevinylene) side chains (biTV-PTs), **P1**, **P2**, and **P3**, were designed and synthesized for application in polymer solar cells. The absorption spectral, electrochemical, and photovoltaic properties of the biTV-PTs were investigated and compared with those of poly(3-hexylthiophene) (P3HT). The biTV-PTs show a broad absorption band from 350 to 650 nm; especially, the absorption spectrum of **P3** displays a broad plateau and much stronger absorbance than that of P3HT in the wavelength range from 350 to 480 nm. Cyclic voltammograms reveal that the onset oxidation and reduction potentials of the biTV-PTs positively shifted by ca. 0.2 V in comparison with those of P3HT, indicating that the HOMO energy level of the biTV-PTs is ca. 0.2 eV lower than that of P3HT. Polymer solar cells (PSCs) were fabricated based on the blend of the polymers and 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-C-61 (PCBM) with a weight ratio of 1:1. The open circuit voltage of the PSCs based on the biTV-PTs is ca. 0.1 V higher than that of P3HT, which is benefited from the lower HOMO levels of the biTV-PTs. The maximum power conversion efficiency (PCE) of the PSCs based on **P3** reached 3.18% under AM 1.5, 100 mW/cm^2, which is 38% increased in comparison with that (2.41%) of the devices based on P3HT under the same experimental conditions. The results indicate that the 2-D conjugated biTV-PTs are promising polymer photovoltaic materials.

Introduction

Soluble polythiophene derivatives (PTs) have drawn much attention in recent years, due to their promising applications in electrochromics,[1] biosensors,[2] electrochemical supercapacitors,[3] anticorrosion,[4] polymer thin film transistors,[5] polymer light-emitting diodes (PLEDs),[6] polymer photodetectors and polymer solar cells,[7−11] etc. Among the various properties of PTs, the absorption spectrum is of crucial importance for their applications in polymer solar cells (PSCs) and electrochromics, etc. As a photoactive material in the PSCs, first of all, the conjugated polymers need effective absorption of the visible light. However, the conjugated polymers used at present, mainly poly(3-hexylthiophene) (P3HT),[10,11] only absorb a part of the visible light, which limits the utility of the sunlight. To further improve the absorption properties of the conjugated polymers, some narrower band gap polymers were synthesized and applied to the PSCs.[12] The absorption spectra of the narrow band gap polymers show absorption peaks at a longer wavelength, but

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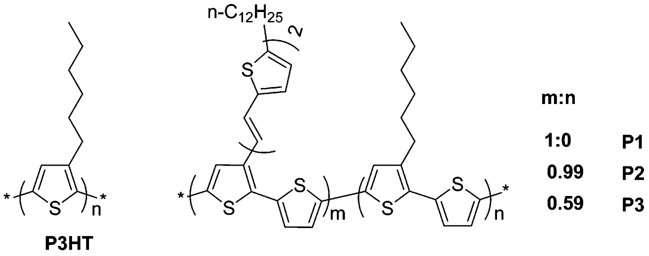
Scheme 1. Molecular Structure of P3HT and the Bi(thienylenevinylene) Substituted Polythiophenes



the shorter wavelength sunlight (such as 380−500 nm) is not absorbed if the bandwidth of their absorption is not broad enough. Obviously, the conjugated polymers with not only narrower band gaps but also broad absorption bandwidths are desirable for application in PSCs.

To pursue the broad absorption in the visible region, the authors recently designed and synthesized a new kind of PTs with conjugated phenylenevinylene side chains (PV-PTs).[13] The PV-PTs possess two absorption peaks located in the UV and visible regions, respectively. The UV peak results from the absorption of the conjugated side chains, and the visible peak is attributed to the absorption of the $\pi-\pi^*$ transition of the conjugated main chains. By using bi(phenylenevinylene) as the side chains, the UV absorption peak is red-shifted to 370−380 nm and the polymers show a broad absorption in the visible region.[13] But in the absorption spectra of the polymers, there is a valley at around 450 nm, which needs to be further improved for application in PSCs. In this paper, we used bi(thienylenevinylene) as the conjugated side chains and made the absorption of the side chains further red-shifted to 410−440 nm. The bi(thienylenevinylene) substituted polythiophenes (biTV-PTs) of **P1**−**3** (see Scheme 1; the molecular structure of P3HT is also shown in Scheme 1 for comparison) possess a broad and strong absorption band in the region from 350 to 650 nm. Furthermore, the photovoltaic properties of the polymers were investigated by fabricating the polymer solar cells of ITO/PEDOT:PSS/polymer:PCBM(1:1, w/w)/Mg/Al. The maximum power conversion efficiency of the devices based on **P3** reached 3.18% under the illumination of AM 1.5, 100 mW/cm^2, which is 38% increased in comparison with that of the devices based on P3HT under the same experimental conditions.

Results and Discussion

Synthesis of the Polymers. The bi(thienylenevinylene) substituted polythiophenes (biTV-PTs) were synthesized by a Stille coupling route, as shown in Scheme 2. The double bonds between thiophene rings in compound **6** were formed by a Horner−Emmons reaction. The molecular structure of compound **6** was determined by a ^{1}H NMR spectrum, and there is no cis-isomer of the compound, as shown in Figure 1. The polymer **P1** is an alternate copolymer of compound **6** and 2,5-bis(tributylstannyl)thiophene, while polymers **P2** and **P3** are random copolymers of **P1** and 5,5′-poly(3-hexyl-2,2′-bithiophene), as shown in Scheme 1. The ratio of *m*:*n* was modulated by controlling the monomer ratio of compound **6** to 2,5-dibromo-3-hexylthiophene. The actual values of *m*:*n* were determined on the basis of the ^{1}H NMR spectra of the polymers (see Figure 2). In the ^{1}H NMR spectrum of **P1**, there is a peak at δ 2.60 ppm (peak 1) which is attributed to the hydrogen at position 1 on the side chain of **P1** (see the molecular structure inserted in Figure 2), while the ^{1}H NMR spectra of **P2** and **P3** display a new peak at 2.70 ppm (peak 2) which is attributed to the hydrogen at position 2 on the side chain of the segment of 3-hexyl-2,2′-bithiophene. Therefore, the ratio of *m*:*n* in **P2** and **P3** could be determined by the ratio of the integral areas of peak 1 to peak 2 in Figure 2. The values of *m*:*n* determined in this way are 0.99 for **P2** and 0.59 for **P3**, which is close to (a little higher than) that determined by the sulfur content of the elemental analysis (0.95 for **P2** and 0.53 for **P3**).

Thermal Stability. Figure 3 shows the thermogravimetric analysis (TGA) plots of the biTV-PTs. The onset decomposition temperatures of the polymers are around 300 °C in nitrogen, which indicates that the biTV-PTs are as stable as ploy(3-alkylthiophene). Obviously, the thermal stability of the biTV-PTs is adequate for their applications in PSCs and other optoelectronic devices.

Absorption Spectra. Figure 4 shows the absorption spectra of the biTV-PTs films, as well as those of monomer **6** and P3HT for comparison. Interestingly, the absorption band of the biTV-PTs covers a broad wavelength range from 350 to 650 nm, especially for **P2** and **P3**; their absorption spectra show a broad plateau in the visible region. Compared with the absorption spectra of monomer **6** and P3HT, obviously, the absorption of the biTV-PTs in the region 350−450 nm results from the conjugated bi(thienylenevinylene) side chains, and the absorption between 450 and 650 nm is attributed to the $\pi-\pi^*$ transition of the polythiophene main chains, which agrees with that observed in the PV-PTs.[13] With the decrease of the content of the conjugated side chains (the value of *m*:*n* in Scheme 1) in the biTV-PTs from **P1** to **P3**, the absorbance of 350−450 nm decreased and that of 450−650 nm increased. The absorption edge of **P2** and **P3** is at ca. 680 nm, corresponding to a band gap of 1.82 eV.

Poly(3-hexylthiophene) (P3HT) is the most common conjugated polymer used in the PSCs at present.[10,11] So here we compared the absorption spectra of the three polymers with P3HT in Figure 4 and Table 1. It can be seen from Figure 4 that the absorbance of the three biTV-PTs in the range from 350 to 480 nm is much stronger than that of P3HT. As listed in Table 1, the absorbance of **P2** film is 1.30×10^{-2}/nm at 445 nm and 0.91×10^{-2}/nm at 545 nm, and that of **P3** film is 0.96×10^{-2}/nm at 452 nm and 1.06×10^{-2}/nm at 540 nm. The average absorbance of the broad visible absorption peaks of **P2** and **P3** films is quite close to that of P3HT. The full width at half-maximum (fwhm) of **P3** film is ca. 240 nm, which increased by ca. 49% in comparison with that of ca. 161 nm of P3HT film. In addition to the bandwidth of the absorption, the value of the absorbance of the conjugated polymers is more important for a good harvest of sunlight in the PSCs. In combining the bandwidth and absorbance of the absorption, the integral area of the absorbance in visible region should be a proper standard for the comparison of light harvest ability of the polymers used in PSCs. In the visible region from 380 to 780 nm, the integral area of P3HT film for 1 nm thickness is about 1.76, and that of **P3** is about 2.29, so in comparison with P3HT, the light harvest ability of **P3** increased by about 30%. Moreover, the integral areas of **P1** and **P2** films for 1 nm

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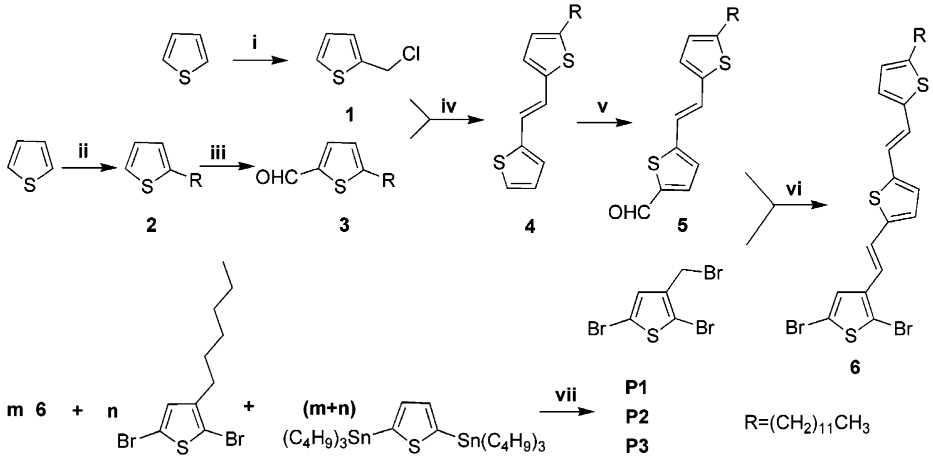
Scheme 2. Synthesis Route of the Bi(thienylenevinylene) Substituted Polythiophenes[a]



[a] (i) HCHO, HCl, 0 °C, 20 min; (ii) *n*-butyllithium, THF, ambient temperature, 1 h; then 1-bromododecane, overnight; (iii) *n*-butyllithium, THF, ambient temperature, 1 h; then *N*-carbaldehyde-piperidine, overnight; (iv) compound **1**, $P(OC_2H_5)_3$, 160 °C, 2 h; then compound **3**, DMF, CH_3ONa, 20 °C, 20 min; (v) *n*-butyllithium, THF, ambient temperature, 1 h; then *N*-carbaldehyde-piperidine, overnight; (vi) 2,5-dibromo-3-bromomethyl-thiophene, $P(OC_2H_5)_3$, 160 °C, 2 h; then compound **5**, DMF, CH_3ONa, 20 °C, 20 min; (vii) $Pd(PPh_3)_4$, toluene, reflux, argon, 12 h.

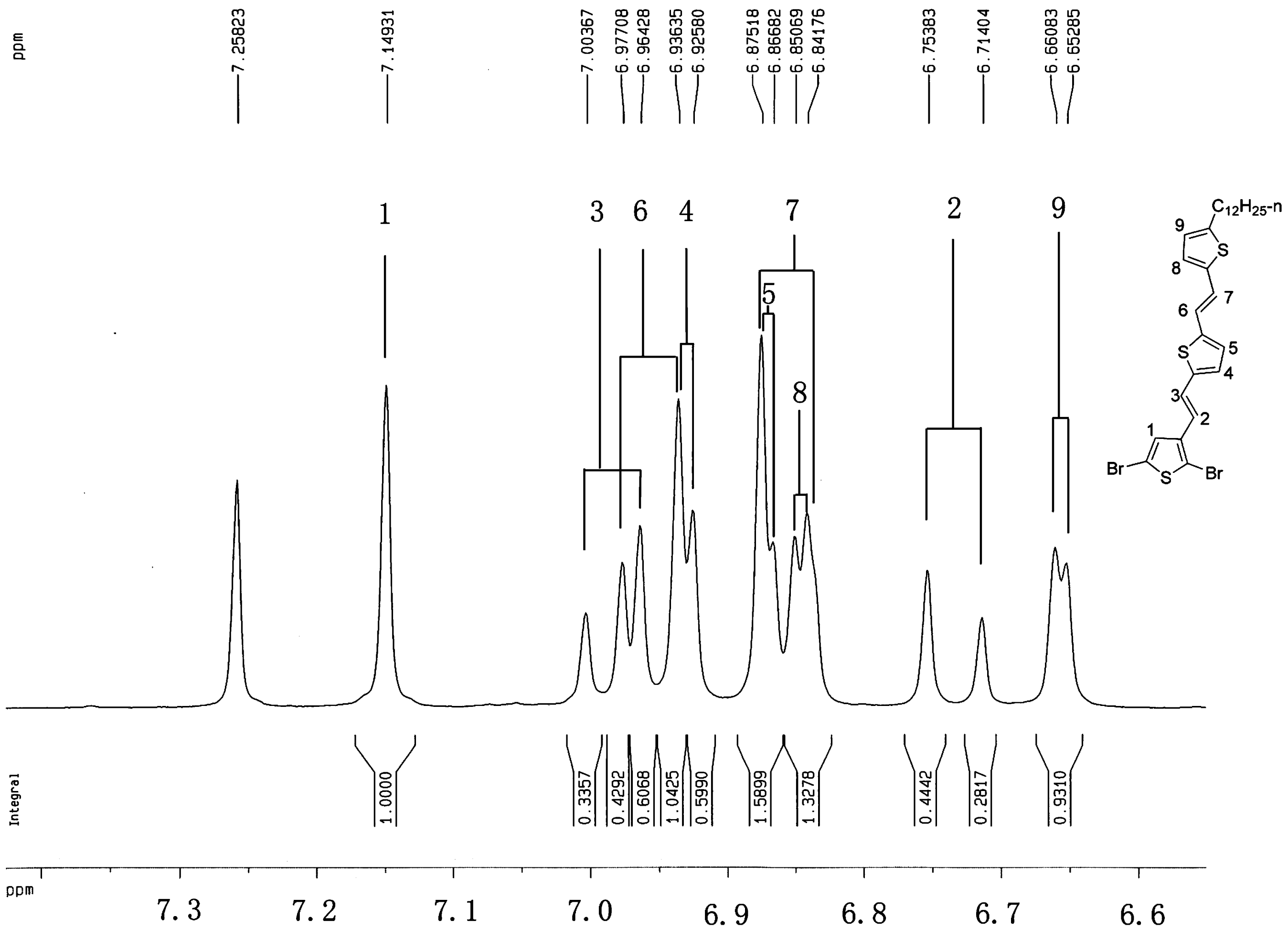


Figure 1. ^1H NMR spectrum of compound **6**.

thickness are both about 2.60, which are 50% more than that for P3HT, so, from this point of view, these two polymers also have a much higher light harvest ability than P3HT.

Photoluminescence Spectra. Photoluminescence (PL) spectra could provide a good deal of information on the electronic structures of the conjugated polymers. Figure 5 shows the PL spectra of the biTV-PTs and monomer **6** solutions in dichloromethane, excited at 410 nm. The monomer exhibits a PL maximum at about 480 nm, while the three biTV-PTs show a PL peak at ca. 580 nm and there is not any PL emission at the wavelengths corresponding to the monomer PL emission. Obviously, the PL peak of the biTV-PTs is entirely attributed

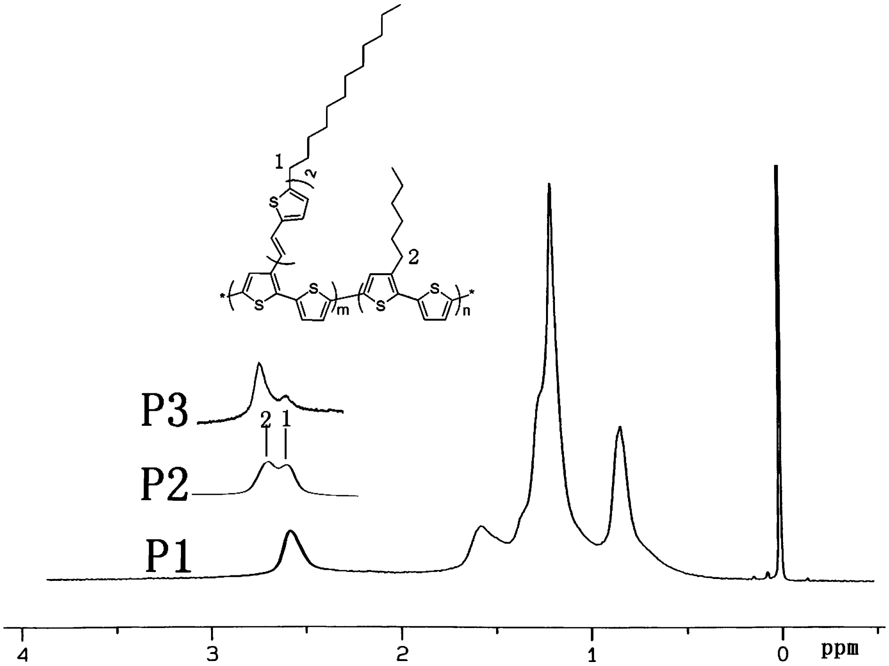


Figure 2. ^{1}H NMR spectra of **P1**, **P2**, and **P3** for the determination of composition.

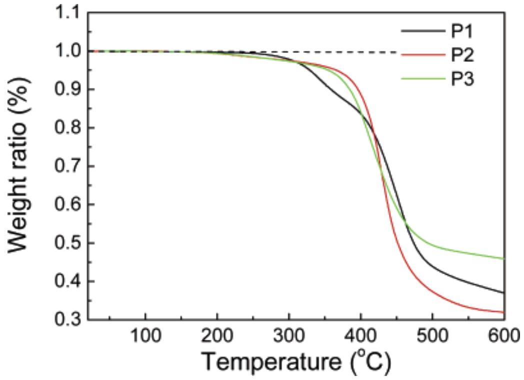


Figure 3. TGA plots of the biTV-PTs with a heating rate of 10 °C/min under inert atmosphere.

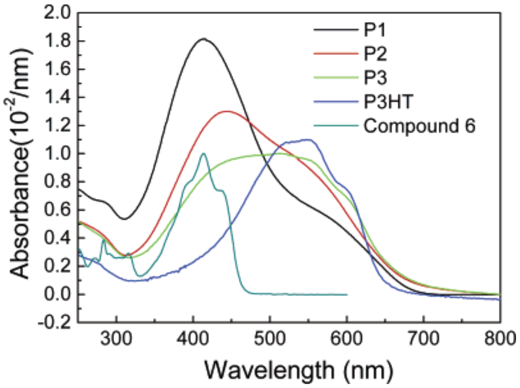


Figure 4. Absorption spectra of the polymer films of biTV-PTs and P3HT and compound **6** solution in dichloromethane.

Table 1. Absorption Spectral Properties of the biTV-PTs and P3HT

polymers	λ_{max}(nm)/Absorbance[a] (10^{-2}/nm) short wavelength absorption	long wavelength absorption	full width at half maximum[b] (nm)	integral area[c] for 1 nm thickness
P3HT		552/1.10	161	1.76
P1	413/1.82	566/0.58	115	2.60
P2	445/1.30	545/0.91	210	2.60
P3	452/0.96	540/1.06	240	2.29

[a] The absorbance values were obtained by dividing the maximum absorbance by the thickness of the films. [b] The absorption in the UV region is not included. [c] Integration was taken in the whole visible range from 380 to 780 nm.

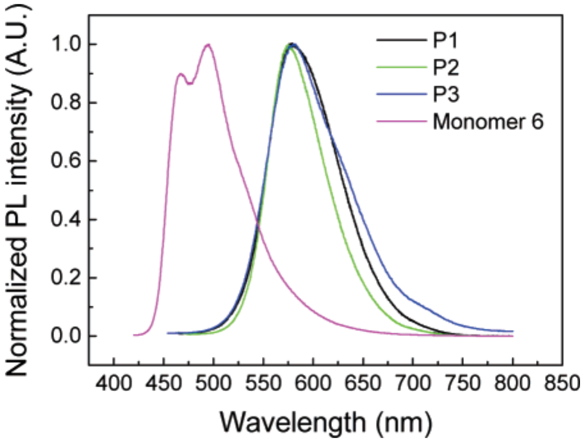


Figure 5. Photoluminescence spectra of the solutions of the biTV-PTs and the monomer **6** in dichloromethane, excited at 410 nm.

to the recombination of the excitons in the main chains, although the polymers were excited at the wavelength (410 nm) corresponding to the absorption of the conjugated side chains in the PL measurement. The results indicate that quick and complete energy transfer occurs from the conjugated side chains to the polymer main chains after the conjugated side chains absorb the photons in the wavelength range 350−450 nm. This phenomenon ensures that all photons absorbed by the polymers are useful for the photovoltaic conversion.

Electrochemical Properties. The electrochemical cyclic voltammetry was performed for determining the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the conjugated

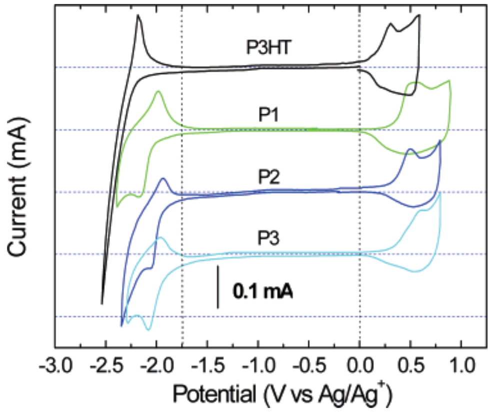


Figure 6. Cyclic voltammograms of the three biTV-PTs and P3HT films on a platinum electrode in 0.1 mol/L Bu_4NPF_6, acetonitrile solution.

Table 2. Electrochemical Onset Potentials and Electronic Energy Levels of the Polymer Films

polymers	φ_{ox} (V *vs* Ag/Ag$^+$)/ E_{HOMO} (eV)	φ_{red} (V *vs* Ag/Ag$^+$)/ E_{LUMO} (eV)	E_g^{ec} (eV)	$E_g^{opt\ a}$ (eV)
P3HT	0.05/−4.76	−1.97/−2.74	2.02	1.80
P1	0.25/−4.96	−1.74/−2.97	1.99	1.81
P2	0.23/−4.94	−1.76/−2.95	1.99	1.82
P3	0.22/−4.93	−1.75/−2.96	1.97	1.82

[a] The optical band gap was obtained from the equation $E_g^{opt} = 1240/\lambda_{edge}$, where λ_{edge} is the onset value of absorption spectrum in long wavelength direction.

polymers.[14] Figure 6 shows the cyclic voltammograms of the biTV-PTs films on a Pt electrode in 0.1 mol/L Bu_4NPF_6, acetonitrile solution. The three biTV-PTs have similar onset oxidation potentials (φ_{ox}) and onset reduction potentials (φ_{red}). The cyclic voltammogram of P3HT was also measured and put in Figure 6 for comparison. It can be seen that the onset oxidation and reduction potentials of the biTV-PTs positively shifted by ca. 0.2 V in comparison with those of P3HT. From the values of φ_{ox} and φ_{red}, the HOMO and the LUMO as well as the band gaps (E_g^{ec}) of the polymers were calculated according to the following equations.[14b]

$$\mathrm{HOMO} = -e(\varphi_{ox} + 4.71)\ (\mathrm{eV})$$

$$\mathrm{LUMO} = -e(\varphi_{red} + 4.71)\ (\mathrm{eV})$$

$$E_g^{ec} = e(\varphi_{ox} - \varphi_{red})\ (\mathrm{eV})$$

where the unit of potential is V vs Ag/Ag$^+$.

The results of the electrochemical measurements are listed in Table 2. Band gaps of the three 2-D conjugated biTV-PTs are similar to that of P3HT, but their HOMO and LUMO dropped by ca. 0.2 eV in comparison with those of P3HT. The electrochemical band gaps (E_g^{ec}) are larger than those of the optical band gaps (E_g^{opt}) for all four polymers, which agrees with that observed for other PT derivatives.[15] Since open circuit voltage (V_{oc}) of polymer solar cells is related to the difference of the LUMO of the electron acceptor and the HOMO of the electron donor,[16] the lower HOMO of the biTV-PTs could be beneficial to a higher V_{oc} of the PSCs with the polymers as donor materials.

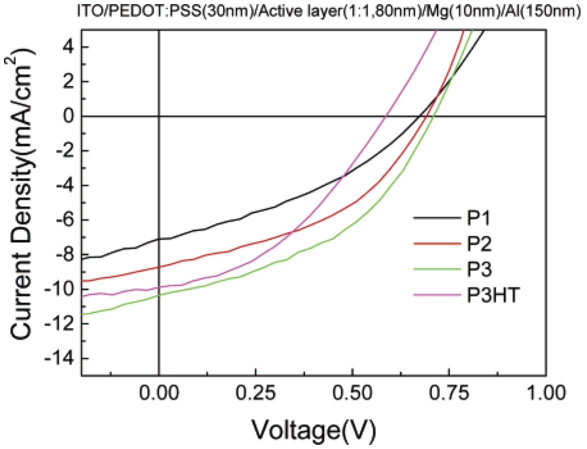


Figure 7. $I-V$ curves of the polymer solar cells based on **P1**, **P2**, **P3**, and P3HT under the illumination of AM 1.5, 100 mW/cm^2.

Table 3. Photovoltaic Properties of the Polymer Solar Cells

polymers	V_{oc} (V)	I_{sc} (mA/cm^2)	FF (%)	PCE (%)
P1	0.66	7.11	36	1.71
P2	0.69	8.74	43	2.57
P3	0.72	10.3	43	3.18
P3HT	0.60	9.9	41	2.41

Photovoltaic Properties. The motivation of the design and synthesis of the 2-D conjugated PTs is to look for new conjugated polymers for the application in polymer solar cells (PSCs). To check the photovoltaic properties of the biTV-PTs, we fabricated the PSCs with the structure of ITO/PEDOT-PSS/polymer:PCBM(1:1, w/w)/Mg/Al where the polymer (**P1**, **P2**, **P3**, or P3HT) was used as the electron donor and PCBM (1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-C-61) was used as the electron acceptor. The device based on P3HT is for comparison because P3HT is the most efficient PT derivative used in the PSCs at present[10,11]

Figure 7 shows the $I-V$ curves of the PSCs under the illumination of AM 1.5, 100 mW/cm^2, and Table 3 lists the photovoltaic properties obtained from the $I-V$ curves for the best devices. In comparison with the device based on P3HT, the open circuit voltage (V_{oc}) of the devices based on the biTV-PTs increased by ca. 0.1 V. The higher V_{oc} is expected from the lower HOMO energy levels of the biTV-PTs (see Table 2), as mentioned above. For the best devices, the power conversion efficiency (PCE) of the PSC based on **P3** reached 3.18%, increased by 38% in comparison with the PCE 2.41% of the device based on P3HT under the same experimental conditions. We fabricated five devices for every polymer sample in the investigation of the photovoltaic properties. Under the illumination of AM 1.5, 100 mW/cm^2, the PCE values of the five PSCs based on P3 were 2.90%, 3.05%, 3.13%, 3.08%, and 3.18%, respectively, with the average PCE of 3.07%, while those of the five PSCs based on P3HT were 2.38%, 2.35%, 2.41%, 2.39%, and 2.37%, respectively, with an average PCE of 2.38%.

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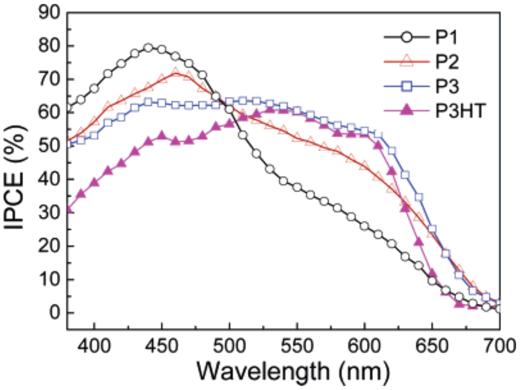

Figure 8. IPCE curves of the PSCs based on **P1**, **P2**, **P3**, and P3HT.

In comparison with the average PCE values, the photovoltaic efficiency of **P3** increased by 29% vs that of P3HT.

Figure 8 shows the input photon to converted current efficiency (IPCE) of the PSCs for the best devices. The shape of the IPCE curves of the devices based on the biTV-PTs is very similar to their absorption spectra, indicating that all the absorption of the polymers contributed to the photovoltaic conversion. As mentioned above, the integral area of the absorbance of **P1** and **P2** in the visible region is higher than that of **P3**, but the PCE of the devices based on **P1** and **P2** is lower than that of **P3**, probably due to the weaker absorbance of **P1** and **P2** in the longer wavelength range from 550 to 650 nm. Obviously, the strong and uniform absorbance of the conjugated polymers in the whole visible region should be very important for a high efficiency polymer photovoltaic material. Comparing the IPCE curves of P3 and P3HT, it can be seen that the IPCE values of the two polymers in the wavelength range from 530 to 610 nm are similar, while the values of **P3** in the wavelength ranges of 380−530 nm and 610−680 nm are higher than those of P3HT, so that the PCE of the device based on **P3** is higher than that of P3HT. The results indicate that the 2-D conjugated biTV-PTs are promising materials for the application in polymeric solar cells.

Conclusion

In this paper, three bi(thienylenevinylene) substituted polythiophenes (biTV-PTs), **P1**−**3** (see Scheme 1 in the text), were synthesized for obtaining the conjugated polymers with broad and strong visible absorption for the application in polymer solar cells (PSCs). The biTV-PTs were characterized by TGA, absorption and photoluminescence spectroscopy, cyclic voltammetry, and photovoltaic measurements. The absorption spectra of the biTV-PTs films show a broad absorption band covering the wavelength range from 350 to 650 nm, which is composed of the absorption of the conjugated side chains peaked at ca. 410 nm and that of the conjugated main chains peaked at ca. 550 nm. Especially, the absorption spectrum of **P3** shows a high and broad plateau, and its absorbance is stronger than that of poly(3-hexylthiophene) (P3HT) in the range 350−480 nm. The PL spectra of the biTV-PTs reveal that complete exciton energy transfer occurs from the conjugated side chains to the main chains of the biTV-PTs. The electrochemical measurements indicate that the HOMO energy level of the biTV-PTs is ca. 0.2 eV lower that that of P3HT. Photovoltaic properties of the biTV-PTs were investigated with the polymer solar cells (PSCs) based on the blend of the polymers and PCBM (1:1, w/w) under AM 1.5, 100 mW/cm^2. The open circuit voltage of the PSCs based on the biTV-PTs is ca. 0.7 V, ca. 0.1 V higher than that of P3HT, which is benefited from the lower HOMO levels of the biTV-PTs. The maximum power conversion efficiency (PCE) of the PSCs based on **P3** reached 3.18%, increased by 38% in comparison with that of the devices based on P3HT under the same experimental conditions. The average PCE value of five PSCs based on **P3** was 3.07%, increased by 29% vs that of P3HT. The results indicate that the 2-D conjugated biTV-PTs are promising polymer materials for application in polymer solar cells.

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Supporting Information Available: Experimental details of the synthesis of the polymers, the fabrication and characterization of the polymer solar cells, measurements, and instruments. This information is available free of charge via the Internet at http://pubs.acs.org.

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