

Synthesis of a Soluble Polythiophene Copolymer with Thiophene–Vinylene Conjugated Side Chain and Its Applications in Photovoltaic Devices

Bo Qu,¹ Zhongliang Jiang,² Zhijian Chen,¹ Lixin Xiao,¹ Di Tian,² Chao Gao,^{2,3} Wei Wei,^{3,4} Qihuang Gong¹

¹Department of Physics, State Key Laboratory for Artificial Microstructures and Mesoscopic Physics, Peking University, 100871, People's Republic of China

²Xi'an Modern Chemistry Research Institute, Xi'an Shaanxi, 710065, People's Republic of China

³State Key Laboratory of Transient Optics and Photonics, Xi'an Institute of Optics and precision Mechanics, Chinese Academy of Science (CAS) Xi'an Shaanxi, 710119, People's Republic of China

⁴Institute of Advanced Materials, Nanjing University of Posts and Telecommunications, Nanjing 210003, China

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ABSTRACT: A new soluble polythiophene copolymer with thiophene–vinylene conjugated side chain poly[3-(5'-octylthiénylenevinyl) thiophene]–thiophene (POTVTh–Th) was successfully synthesized and characterized using NMR, UV-visible spectroscopy, etc. To study the photovoltaic property of the copolymer, photovoltaic device of ITO/PEDOT:PSS/POTVTh–Th:[6,6]-phenyl C₆₁-butyric acid methyl ester (PC₆₁BM) (weight ratio being 1 : 1)/LiF/Al was fabricated, in which POTVTh–Th acted as the electron donor in the active

layer. Under 100 mW/cm² AM 1.5G simulated solar emission, the open-circuit voltage and the short-circuit current density of the device were 0.58 V and 2.50 mA/cm², respectively. The power conversion efficiency and the fill factor of the photovoltaic device were evaluated to be 0.42% and 0.30. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1186–1192, 2012

Key words: polythiophene; polymers; organic photovoltaic devices; solar cells; bulk-heterojunction

INTRODUCTION

Recently, organic photovoltaic cells (OPVs) have attracted much attention, because the devices based on polymers as active layer have shown the potential for cheap, large area, flexible renewable power sources.^{1–4} Nowadays, bulk heterojunction (BHJ) polymer solar cells play a leading role in realizing high power conversion efficiency (PCE). The development of novel polymer materials will further enhance the efficiency of BHJ polymer photovoltaic cells and accelerate their potential for commercial applications. Up till now, polymer photovoltaic cells based on poly(3-hexylthiophene) (P3HT) as the donor and methanofullerene (6,6)-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) as the acceptor have

exhibited high efficiency of 5%.⁵ However, the narrow absorption spectrum of P3HT hampered the further improvement of the efficiency of P3HT-based devices. To overcome this problem, some narrow band polymers as the donor have been synthesized and applied to photovoltaic devices. For example, side-chain conjugated polythiophene derivatives exhibited a broad response range to the solar irradiation spectrum in comparison with P3HT and 38% improvement of PCE was obtained.⁶

In this article, we successfully synthesized a new side-chain conjugated polythiophene copolymer, poly[3-(5'-octylthiénylenevinyl) thiophene]–thiophene (POTVTh–Th), which acted as electron donor for hybrid active layer in OPVs. The synthesis process, optical, and photovoltaic property of POTVTh–Th were investigated in detail in this work. According to the experimental results, the photovoltaic behavior of POTVTh–Th was acceptable, and POTVTh–Th is a promising donor material for OPVs.

EXPERIMENTAL

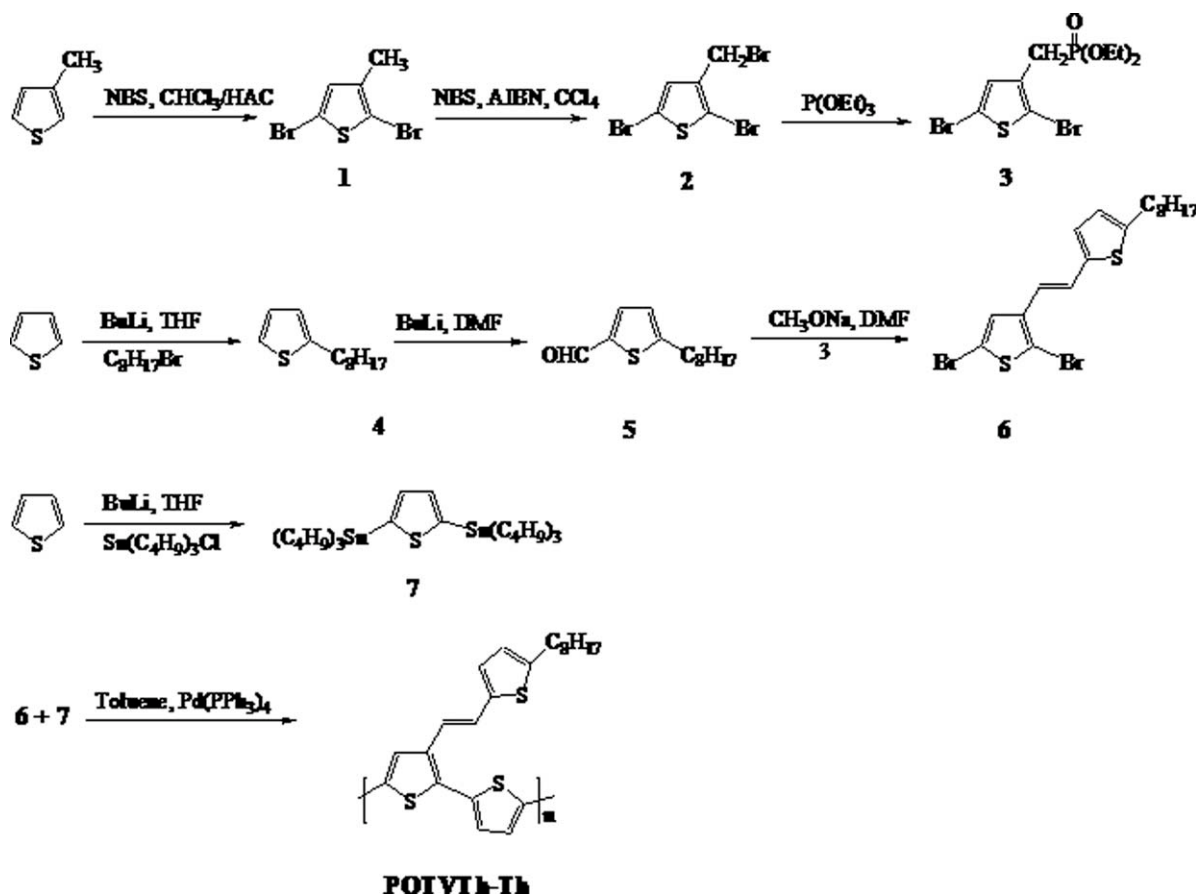
Materials and synthesis

Otherwise stated, all of the chemicals are purchased from Alfa and used as received. The copolymer was synthesized according to Scheme 1.

Correspondence to: B. Qu (bqu@pku.edu.cn), C. Gao (chaogao74@gmail.com), W. Wei (iamww@njupt.edu.cn), and Q. Gong (qhgong@pku.edu.cn).

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Scheme 1

2,5-Dibromo-3-methyl-thiophene (1)

3-methylthiophene (19.6 g, 0.2 mol) was dissolved in a mixture of chloroform (100 mL) and acetic acid (100 mL), and NBS (74.76 g, 0.42 mol) was added into the solution. The solution was heated to reflux for 2 h. Then the solution was poured into cold water, and extracted with chloroform. The combined organic layer was washed with water, and dried over anhydrous MgSO_4 . Distillation at vacuum gave compound 1 as colorless oil (45.6 g, 89% yield).

2,5-Dibromo-3-bromomethyl-thiophene (2)

Compound 1 (25.6 g, 0.1 mol) was dissolved in tetrachloridecarbon (100 mL). Then NBS (17.8 g, 0.1 mol) was added in the mixture and AIBN (0.3 g) was added as a catalyst. The solution was allowed to reflux for 3 h, cooled to room temperature, and filtered. The solution was washed with water, and dried over anhydrous MgSO_4 , filtered, and concentrated. Distillation at 112°C under 3 mmHg gave compound 2 as pale yellow oil (23.5 g, 70% yield). $^1\text{H-NMR}$ (PPM, CDCl_3): 7.00(S, 1H); 4.36(S, 2H).

(2,5-dibromo-thiophene-3-ylmethyl)-phosphonic acid diethyl ester (3)

Compound 2 (16.75 g, 0.05 mol) and phosphorous acid triethyl ester (8.3 g, 0.05 mol) were put into a 50-mL flask, and heated to 160°C for 3 h. The mixture was distilled at vacuum and the residue was purified by flash column chromatography eluting with petroleum ether/ ethyl acetate (1 : 1). After purification, compound 3 was recovered as pale yellow oil. $^1\text{H-NMR}$ (PPM, CDCl_3): 7.02 (s, 1H), 4.08 (m, 4H), 3.10 (d, 2H), 1.29 (t, 6H).

2-octyl-thiophene (4)

Thiophene (25.2 g, 0.3 mol) was dissolved in anhydrous tetrahydrofuran (150 mL) under the protection of nitrogen at room temperature. *N*-butyllithium (136 mL, 2.2M in hexane) was added dropwise, and the solution was stirred at room temperature for 1 h. Then 1-bromooctane (57.9 g, 0.3 mol) was added dropwise into the solution. The solution was allowed to be stirred at room temperature overnight. Cooled to room temperature and poured to cool

water. Extracted by ether and washed with brine. The organic layer was dried over anhydrous MgSO_4 , filtered, and concentrated. Distillation under 1 mmHg gave compound 4 as colorless oil (33.8 g, 57.6% yield). $^1\text{H-NMR}$ (PPM, CDCl_3): 7.11(s,1H), 6.92(s,1H), 6.79(s,1H), 2.85(t,1H), 1.88(s, 2H), 1.32(m,10H), 0.90(t,3H).

5-octylthiophene-2-carbaldehyde (5)

Compound 4 (19.6 g, 0.1 mol) was dissolved in anhydrous tetrahydrofuran (50 mL) under the protection of nitrogen at room temperature. *N*-butyllithium (50 mL, 2.2M in hexane) was added dropwise, and the solution was stirred at room temperature for 1 h. Then DMF 8.03 g was added dropwise, and the mixture was allowed to react at room temperature for 12 h before poured to cool water. Extracted by ether and washed with brine. The organic layer was dried over anhydrous MgSO_4 , filtered, and concentrated. Distillation under vacuum gave compound 5 as pale yellow oil (13.4 g, 60.9% yield). $^1\text{H-NMR}$ (PPM, CDCl_3): 9.79(s, 1H), 7.74(d, 1H), 6.88(d, 1H), 2.84(t, 2H), 1.69(m, 2H), 1.24-1.34(m, 10H), 0.86(t, 3H).

2,5-Dibromo-3-(5-octyl-thienylene-vinyl)-thiophene (6)

Compound 5 (6.7 g, 0.03 mol) was dissolved in 30 mL DMF. Under an ice-water bath, NaOCH_3 (3 g in 20 mL DMF) was added into the solution. Then compound 3 (11.8 g, 0.03 mol) was added dropwise to the solution. The reaction was remained at 0 °C for 2 h, and then the solution was poured into cold water, and extracted with ether. The organic layer was washed with water and dried over anhydrous MgSO_4 . Purification was carried out via silica gel column chromatography, using petroleum ether as the eluent. Compound 6 was obtained as pale yellow oil (7.29 g, 52.6% yield). GC-MS: $m/z = 470$. $^1\text{H-NMR}$ (PPM, CDCl_3): 7.15(s, 2H); 6.95(D,1H); 6.89(D, 1H); 6.70(s, 1H), 6.69(D,1H),6.67(D,1H), 2.80(t,2H); 1.71(m,2H); 1.29-1.4(m,8H); 0.98(t,3H).

2,5-Bis(tributylstannyl)thiophene (7)

Thiophene (8.4 g, 0.10 mol) was dissolved in 60 mL THF under the protection of nitrogen. *N*-butyllithium (100 mL, 0.22 mol, 2.2M in hexane) was added dropwise, and the solution was stirred at reflux for 1 h. Tributylchlorostannane (73 g, 0.22 mol) was added in one portion at room temperature and the solution was stirred at room temperature overnight. Then the solution was poured 200 mL into cool water, and extracted with CHCl_2 . The organic layer was washed with water and dried over anhydrous MgSO_4 . The removal of solvent gave a

crude product. Distillation under vacuum (0.1 mmHg/230 °C), compound 7 was obtained as a pale yellow oil (33.7 g, 51% yield). GC-MS: $m/z = 664$. $^1\text{H-NMR}$ (PPM, CDCl_3) 7.34(s, 2H); 1.60(m, 12H); 1.39(m, 12H); 1.09(m,12H); 0.91(t, 18H).

Synthesis of polymer poly[3-(5'-octylthienylenevinyl)thiophene]-thiophene

Totally, 0.46 g (1 mmol) 2,5-Dibromo-3-(5-octyl-thienylene-vinyl)-thiophene was put into a three-neck flask, and 20 mL degassed toluene was added under the protection of argon. The solution was flushed with argon for 30 min, and then 11 mg $\text{Pd}(\text{PPh}_3)_4$ and 0.66 g (1 mmol) 2,5-Bis(tributylstannyl)thiophene were added. After another being flushed with argon for 30 min, the reactant was heated to reflux for 12 h. Then the reactant was cooled to room temperature, poured into stirred methanol, and filtered. The resulted crude product was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. Reprecipitated from methanol to give the copolymer POTVTh-Th 0.32 g, yield 84%. The molecular weight was decided by GPC as: $M_w = 12475$, PDI = 1.34.

Characterization

$^1\text{H-NMR}$ spectra were recorded at 500 MHz on a Bruker DRX-500 spectrometer. Molecular weights and distributions of the copolymer were determined by using GPC, THF as eluent, and polystyrene as the standard. The optical absorption spectra were taken by a Unico UV-2102 scanning spectrophotometer. Thermogravimetric analyses (TGA) of the polymers were recorded on a Universal V2.4F TA instrument. Differential scanning calorimetry (DSC) of the polymer was performed under nitrogen at a heating rate of 20 °C/min with a TA DSC-2910 instrument. The electrochemical cyclic voltammetry was conducted on a CHI 660D Electrochemical Workstation with Pt disk, Pt plate, and Ag/Ag^+ electrode as working electrode, counter electrode, and reference electrode respectively in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. Polymer thin films were formed by drop-casting 1.0 μL of polymer solutions in THF (analytical reagent, 1 mg/mL) onto the working electrode, and then dried in the air.

OPVs fabrication and characterization

To study the photovoltaic property of POTVTh-Th, OPV device with the structure of ITO/Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS)/POTVTh-Th:PC₆₁BM (weight ratio being 1 : 1)/LiF/Al, was successfully fabricated.

ITO-coated glass with sheet resistance of 20Ω per square acted as the anode, and it was cleaned thoroughly in deionized water, acetone, and anhydrous ethanol in sequence using an ultrasonic cleaner, and then ITO substrates were treated with oxygen plasma and UV irradiation for 60 seconds. Diluted PEDOT:PSS solution was filtered through $0.45 \mu\text{m}$ filters, and spin-coated onto ITO substrates. Then substrates were annealed at 200°C under vacuum condition. POTVTh-Th:PCBM was dissolved in ortho-dichlorobenzene and the concentration was 30 mg/mL . Solution was filtered through $0.22\text{-}\mu\text{m}$ filters, and dropped onto PEDOT:PSS layer at 800 rpm. Then, the organic active layer was baked at 150°C in vacuum. The thickness of the layers were measured by AFM (Agilent Technologies 5500), and the thickness of PEDOT:PSS and POTVTh-Th:PCBM layers was 26 and 105 nm, respectively. The buffer layer (LiF) and cathode (Al) were thermally evaporated in sequence onto the active layer at the vacuum pressure of 3.6×10^{-6} Torr, and the evaporation rates of LiF and Al were 0.1 \AA/s and 2.5 \AA/s , respectively. The thickness of LiF and Al layers was 0.5 and 150 nm, monitored by a quartz crystal microbalance. The effective area of the device was measured to be 0.1 cm^2 .

The current density-voltage (I - V) curves were recorded with Keithley 2611 source meter under dark and illumination conditions. The average power of a solar simulator (Newport Thermal Oriel 69911 300W) with AM 1.5G filter was 100 mW/cm^2 . A calibrated mono silicon diode is used as a reference and all measurements were carried out at room temperature.

RESULTS AND DISCUSSION

Thermal properties

The DSC thermogram was obtained from the second heating of the polymer. As shown in Figure 1, unlike

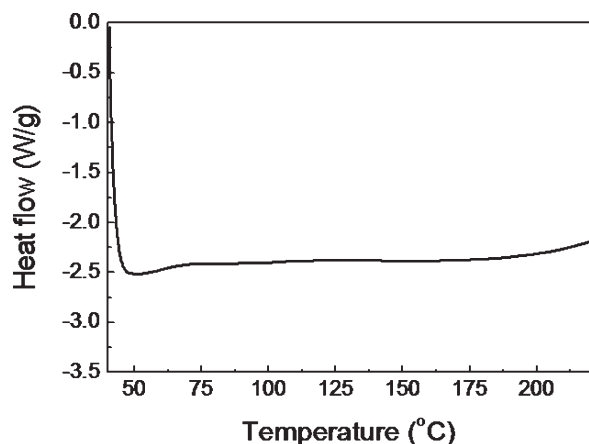


Figure 1 The DSC plot of POTVTh-Th.

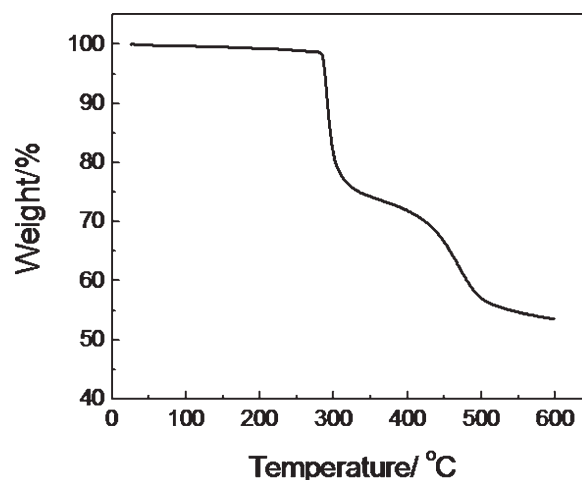


Figure 2 The TGA plot of POTVTh-Th.

P3HT (with a melting point of 123°C), no additional melting transition and glass transition temperature were observed for the polymer, indicating that POTVTh-Th is amorphous.

Figure 2 shows the thermogravimetric analysis (TGA) plots of the POTVTh-Th. The onset decomposition temperature of the polymers is around 280°C in nitrogen, which indicates that the thermal property of POTVTh-Th is adequate for further application in photovoltaic solar cells and other optoelectronic devices.

Spectra properties of POTVTh-Th

The homopolymer POTVTh of 2,5-Dibromo-3-(5-octyl-thienylene-vinyl)-thiophene (compound 6) synthesized by GRIM method has been used as donor in photovoltaic solar cells.⁷ So here we compared the absorption spectra of POTVTh-Th with those of POTVTh in Figure 3. There are two main absorption

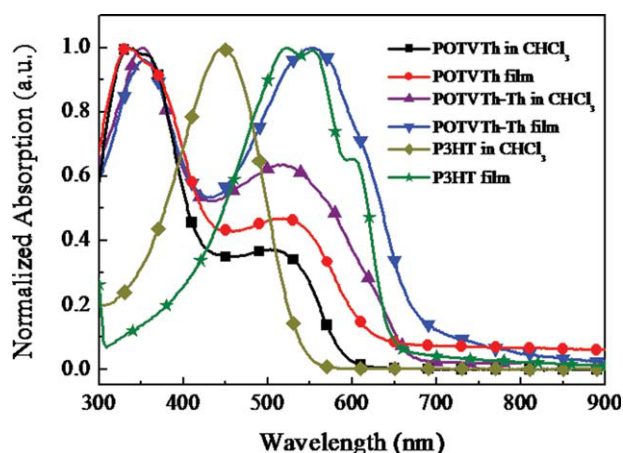


Figure 3 Absorption spectra of POTVTh, POTVTh-Th, and P3HT. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

peaks in Figure 3 for POTVTh and POTVTh-Th, the absorption peaks in visible range came from the π - π^* transition of the conjugated main chains, and those in UV range originated from the conjugated side-chains.⁷ Furthermore, for films, the absorption band edge of POTVTh-Th red-shifted by ca. 56 and 33 nm in comparison with that of POTVTh and P3HT respectively, this indicated that the band gap of POTVTh-Th was reduced for some extent.

The band gaps of conjugated polymers are mainly depended on the conjugating length. For P3HT, the absorption edge of the film is limited to 650nm, so the band gap of P3HT is 1.90eV. In the conjugated main chain of POTVTh-Th, the thiophene unit with big conjugated side chain was neighbored with an unsubstituted thiophene ring, thus the steric hindrance of the copolymer will be decreased. As a result of that, two-dimension conjugated structure⁴ could more readily form in POTVTh-Th than that of POTVTh and P3HT. Therefore, the conjugation of the polymer chain could be extended, and the band gap of POTVTh-Th is reduced, as revealed in the red-shifting absorption band edge of POTVTh-Th (Fig. 3). The E_g value of POTVTh-Th film was evaluated to be 1.85eV from UV/Vis absorption spectrum.⁸⁻¹¹ POTVTh-Th had low energy band gap, which facilitated high absorption in green-red region of solar spectrum.

Furthermore, in comparing with POTVTh, POTVTh-Th not only has 56 nm red-shifts in its absorption spectrum, but also higher absorption peak intensity as shown in Figure 3. The enhanced absorption peak intensity was mainly attributed to the decreased steric hindrance of the conjugated the polymer as described above.

Electrochemical properties

The electrochemical property is one of the most important properties of the conjugated polymers, and many applications of the conjugated polymers depend on the electrochemical properties. We studied the redox potentials of the polymers by cyclic voltammetry (CV).

Figure 4 shows the cyclic voltammogram of POTVTh-Th and P3HT films on Pt electrode. It can be seen that there are p-doping/dedoping (oxidation/rereduction) processes at positive potential range and n-doping/dedoping (reduction/oxidation) processes at negative potential range. The HOMO and LUMO energy levels of the polymer were calculated from the onset oxidation potentials (φ_{ox}) and the onset reduction potentials (φ_{red}) and by assuming the energy level of ferrocene/ferrocenium (Fc/Fc⁺) to be -4.7eV below the vacuum level.¹² The former potential of Fc/Fc⁺ was measured as 0.09 eV against Ag/Ag⁺. The energy gap (E_g^{ec}) of the poly-

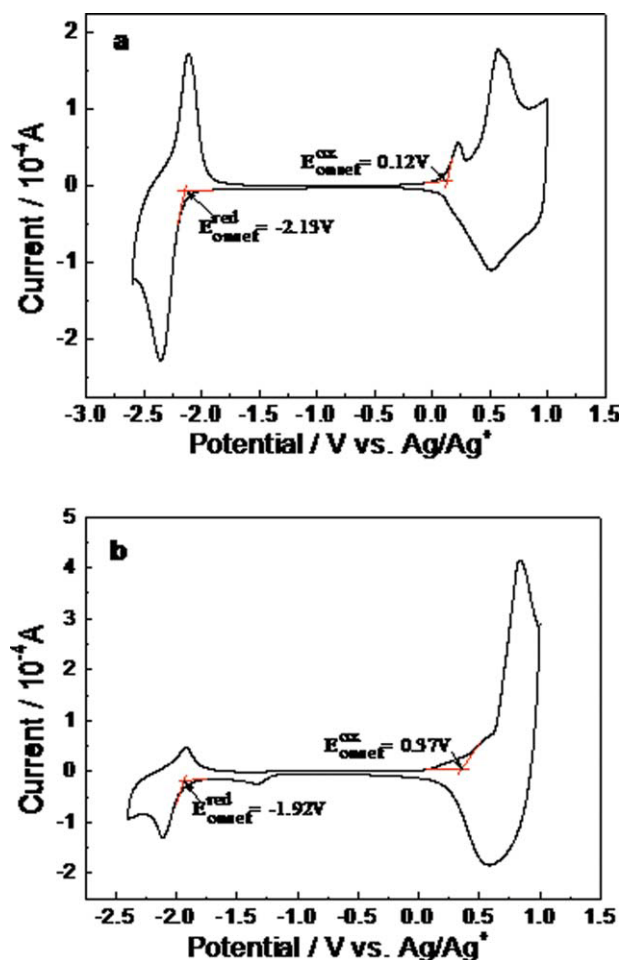


Figure 4 Cyclic voltammogram of P3HT (a) and POTVTh-Th (b) films on Pt electrode 0.1 mol/L Bu₄NPF₆, CH₃CN solution with a scan rate of 100 mV/s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mer was calculated from the HOMO and LUMO energy levels. The calculating equations are as follows¹³:

$$E_{\text{HOMO}} = -e(\varphi_{\text{ox}} + 4.72)(\text{eV});$$

$$E_{\text{LUMO}} = -e(\varphi_{\text{red}} + 4.72)(\text{eV});$$

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

Where the units of φ_{ox} and φ_{red} are V vs. Ag/Ag⁺. The electrochemical potentials and energy levels of P3HT, POTVTh-Th, and POTVTh are shown in Table I. The φ_{ox} and φ_{red} of POTVTh-Th are 0.37 V and -1.92 V, respectively. The HOMO and LUMO energy levels of POTVTh-Th are -5.09 and -2.80 eV, respectively. The electrochemical energy bandgap of POTVTh-Th is 2.29 eV, seems somewhat larger than the optical band gap estimated from Uv-vis spectra (1.85eV), but still within the range of error (0.2-0.5 eV). According to Figure 4 and Table I, the HOMO energy level of POTVTh-Th (-5.09eV)

TABLE I
Electrochemical Potentials and Energy Levels of P3HT, POTVTh-Th, and POTVTh

	$E_{\text{onset}}^{\text{ox}}$ (V)	$E_{\text{onset}}^{\text{re}}$ (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{g}^{ec} (eV)	$E_{\text{g}}^{\text{opt}}$ (eV) ^a
P3HT	0.12	-2.13	-4.83	-2.59	2.24	1.91
POTVTh-Th	0.37	-1.92	-5.09	-2.80	2.29	1.85
POTVTh	0.06	-1.72	-4.76	-2.98	1.78	1.77 [7]

^a Optical band gaps determined from the onset of electronic absorption of the polymer films [$E_{\text{g}}^{\text{opt}}=1240/\lambda(\text{nm})$].

was found to be lower than that of P3HT (-4.83eV). It should be noted that the HOMO/LUMO values of POTVTh were -4.76 eV and -2.98 eV,⁷ which mainly because of the different Electrochemical Workstation and electrode systems.

Photovoltaic properties

To investigate the photovoltaic performance of the POTVTh-Th, the bulk heterojunction-typed polymer solar cell was fabricated with the structure of ITO/PEDOT:PSS/POTVTh-Th:PC₆₁BM/LiF/Al. The schematic diagram of energy levels of P3HT, POTVTh-Th, and PC₆₁BM is depicted in Figure 5.¹⁴ As shown in Figure 5, the LUMO level of PC₆₁BM is ca. 1.1 eV lower than that of POTVTh-Th, so electron transfer from the exciton of POTVTh-Th to the LUMO of PC₆₁BM will occur automatically at the interface of the donor/acceptor interface.

OPV devices were fabricated and the device structure as well as experimental process was elucidated above. The annealed POTVTh-Th:PC₆₁BM film was transparent which implied its acceptable morphology. The current density versus voltage (J-V) curves of the photovoltaic device under dark and 100 mW/cm² AM 1.5G simulated solar irradiation conditions are shown in Figure 6. According to the experimental results, V_{oc} and J_{sc} of the device under irradiation were 0.58 V and 2.50 mA/cm², respectively. The PCE and FF values were calculated to be 0.42% and

0.30. Moreover, we also fabricated OPV devices based on POTVTh-Th:PC₆₁BM with different blend ratio (2 : 1 and 1 : 2), but the J_{sc} value of those devices was too weak to be detected. The heavy doping component in these two OPV devices (2 : 1 and 1 : 2) tended to crystallization in the active layer, which might deteriorate the film morphology and device performance. Therefore, J_{sc} value became too poor to be measured in this work. Despite the higher V_{oc} value, the J_{sc} and PCE were still lower than that of the homopolymer POTVTh device (6.07 mA/cm² and 1.30%)⁷ as described in Table II. In addition, it is found that the V_{oc} of POTVTh-Th-based PSCs is 0.58 V, which is lower than expected (even lower than that of P3HT with a higher HOMO), indicated bad charge transport properties, as revealed also in the low FF.¹⁵

On the basis of the above experimental results, it is revealed that the new side-chain conjugated polythiophene copolymer POTVTh-Th showed promising as organic photovoltaic materials according to the enhanced absorption property and open-circle voltage in comparing with that of its homopolymer POTVTh. However, more work is needed to do, such as preparing high quality polymer, optimizing the solar cell structure (for example, film thickness, or electrode materials, other high LUMO electron-

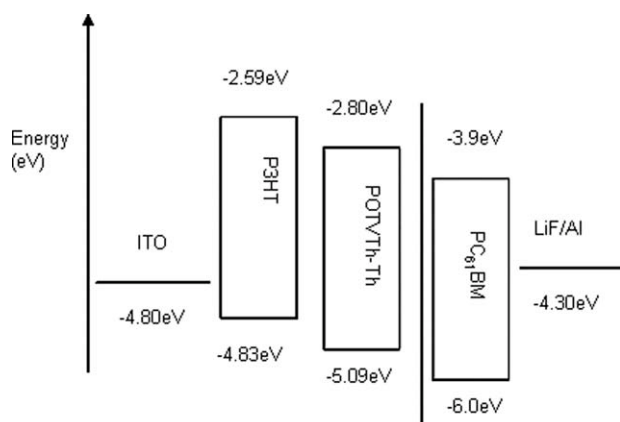


Figure 5 Schematic illustration of relative position of HOMO/LUMO energy levels of P3HT, POTVTh, and PC₆₁BM.

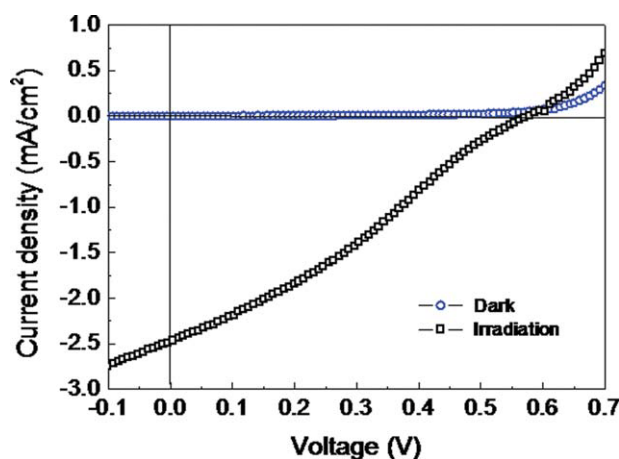


Figure 6 Current density vs. voltage characteristics of the photovoltaic device in the dark and under AM 1.5 G irradiation of 100 mW/cm². [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE II
Characteristic Properties of Polymer Solar Cells Based on POTVTh, POTVTh-Th and P3HT

Polymer	Donor/Acceptor	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE(%)	Reference
POTVTh	POTVTh/PC ₆₁ BM = 1 : 1	0.50	6.07	0.36	1.30	7
POTVTh-Th	POTVTh-Th/PC ₆₁ BM = 1 : 1	0.58	2.50	0.30	0.42	This work
P3HT	P3HT/ PC ₆₁ BM = 1 : 0.8	0.63	9.5	0.68	5	5

acceptors) or processing conditions (for example, thermal or solvent annealing) so as to substantially improve the solar cell performance.^{15–19}

CONCLUSION

A new side chain conjugated polythiophene copolymer POTVTh-Th was synthesized and characterized. Absorption spectrum of the copolymer is obviously red-shifted in visible range in comparison with its homopolymer POTVTh. The polymer photovoltaic cells based on POTVTh-Th and PC₆₁BM were fabricated and characterized. The PCE of the photovoltaic cells with the weight ratio of POTVTh:PC₆₁BM = 1 : 1 is 0.42%. More work is needed to do such as improve the molecular weight of the polymer, optimize the solar cell structure and processing conditions so as to enhance the photovoltaic performance of the side-chain conjugated polythiophene copolymer.

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