

# A Polythiophene Derivative with Dioctyloxytriphenylamine-Vinylene Conjugated Side Chain: Synthesis, Hole Mobility, and Photovoltaic Property

Meixiu Wan,<sup>1,2</sup> Guangyi Sang,<sup>2</sup> Yingping Zou,<sup>2</sup> Songting Tan,<sup>1</sup> Yongfang Li<sup>2</sup>

<sup>1</sup>College of Chemistry and Key Laboratory of Polymeric Materials and Application Technology of Hunan Province, Xiangtan University, Xiangtan 411105, People's Republic of China

<sup>2</sup>CAS Key Laboratory of Organic Solid, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

Received 2 October 2008; accepted 11 December 2008

DOI 10.1002/app.29921

Published online 14 April 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A new polythiophene derivative with dioctyloxy triphenylamine-vinylene (DOTPAV) conjugated side-chain, DOTPAV-PT, was synthesized by the Stille coupling method and characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, elemental analysis, gel permeation chromatography, thermogravimetric analysis, UV-vis absorption spectroscopy, photoluminescence spectroscopy, and cyclic voltammetry. The polymer DOTPAV-PT is soluble in common organic solvents and possesses good thermal stability with 5% weight loss temperature of 310°C. The weight-average molecular weight of DOTPAV-PT is 8.0 K with a polydispersity index of 1.24. The hole mobility

of the polymer determined from space-charge-limited current model was  $1.25 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . The bulk heterojunction polymer solar cell with the configuration of ITO/PEDOT : PSS/polymer : PCBM (1 : 1)/Ca/Al was fabricated, and the power conversion efficiency of the device was 0.16% under the illumination of AM1.5, 100 mW cm<sup>-2</sup>. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1415–1421, 2009

**Key words:** conjugated polymers; polythiophene derivative; dioctyloxy triphenylamine-vinylene side-chain; hole mobility; polymer solar cell

## INTRODUCTION

Polythiophene (PT) and its derivatives have attracted considerable attention due to their versatile applications in the fields of conducting polymers and conjugated polymer optoelectronic devices. For the applications as the conjugated polymer optoelectronic materials, PTs are broadly used in polymer solar cells,<sup>1–4</sup> light-emitting diodes,<sup>5</sup> and field-effect transistors.<sup>6–8</sup> To improve properties and fulfill different application requirements, chemical modifications of PTs have been well performed.

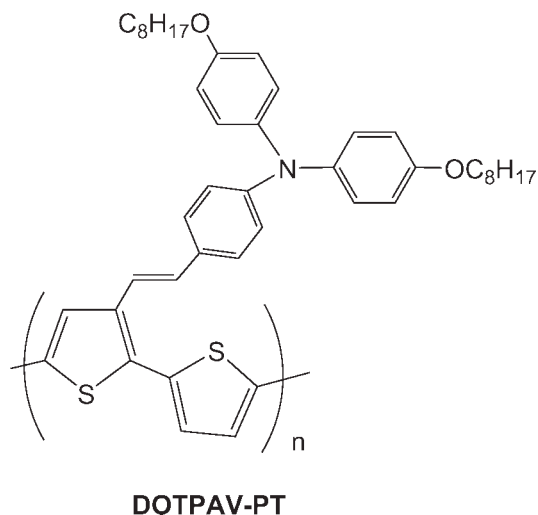
For the application of the conjugated polymers in polymer solar cells (PSCs) as the electron donor, broad absorption in the visible region and higher hole mobility of the conjugated polymers are crucial for high efficient photovoltaic materials.<sup>4</sup> At present, the main PT derivative used as the electron donor in PSCs is poly(3-hexylthiophene) (P3HT), in which the

hexyl side-chains are mainly used to improve the solubility of the polymers. As is well known, the extension of effective conjugation length will improve the properties of  $\pi$ -conjugated polymers; thus, our group recently synthesized a series of PT derivatives with the side-chains of phenylene-vinylene,<sup>9</sup> thienylene-vinylene,<sup>10</sup> terthiophene-vinylene<sup>11</sup> or phenothiazine vinylene.<sup>6</sup>

Triphenylamine is a preferred electron-donating moiety with high hole transporting and good UV-light harvesting properties,<sup>12–17</sup> and branch vinylene can broaden the absorption vision and improve mobility. Therefore further investigation of the relationship between side-chain structure and property of polymers was pursued in this work to incorporate triphenylamine vinyl into the side-chain to build a new PT derivative DOTPAV-PT (see Scheme 1). The photovoltaic properties and hole mobility of the polymer were characterized. The power conversion efficiency of the device with DOTPAV-PT as electron donor and PCBM as electron acceptor was 0.16% under the illumination of AM1.5, 100 mW cm<sup>-2</sup>. The hole mobility of DOTPAV-PT is  $1.25 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which is higher than those of common PTs ( $10^{-6}$ ), owing to the effective contribution of the triphenylamine-vinylene side-chain.

Correspondence to: S. Tan (tanst2008@163.com) or Y. Li (liyf@iccas.ac.cn).

Contract grant sponsor: NSFC; contract grant numbers: 50633050, 20721061.



**Scheme 1** Chemical structure of the polythiophene derivative **DOTPAV-PT**.

## MATERIALS AND METHODS

### Materials and characterization

4-Iodophenol was obtained from Acros (USA); Pd(PPh<sub>3</sub>)<sub>4</sub> and tributylstannyl chloride were purchased from Alfa Aesar (USA), and they were used as received without further purification. The other reagents were commercial grade.

<sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded by using a Bruker AM-400 spectrometer, and chemical shifts were recorded in ppm. Elemental analysis was measured on a Flash EA 1112 elemental analyzer. Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography analysis relative to polystyrene calibration [Waters 515 HPLC pump, a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT3, and HT4)] by using tetrahydrofuran as eluent at a flow rate of 1.0 mL min<sup>-1</sup> at 35°C. Thermogravimetric analysis (TGA) was conducted on a DTG-60 thermogravimetric analyzer with a heating rate of 10°C min<sup>-1</sup> under nitrogen atmosphere. The UV-vis spectra were recorded on a Hitachi U-3010 UV-vis spectrophotometer. The photoluminescence (PL) spectra were obtained with a Hitachi F-4500 fluorescence spectrophotometer.

Electrochemical cyclic voltammogram was recorded with a computer-controlled Zahner IM6e electrochemical workstation (Germany) by using polymer films on a platinum disk as the working electrode, platinum wire as the counterelectrode, and Ag/Ag<sup>+</sup> (0.1M) as the reference electrode.

The current-voltage (*I*-*V*) measurements of PSC were conducted on a computer-controlled Keithley 236 source measure unit. A Xenon lamp with AM1.5 filter was used as a white-light source, and the optical power was 100 mW cm<sup>-2</sup>. All the measurements

were automatically controlled by a computer system and performed under ambient atmosphere at room temperature.

### Synthesis of monomers

#### Octyloxyl-4-iodobenzene (1)

To a stirred mixture of 4-iodophenol (26.40 g, 0.12 mol), octylbromide (19.3 g, 0.1 mol), and dimethylformamide (100 mL) under argon was added K<sub>2</sub>CO<sub>3</sub> (27.60 g, 0.20 mol). The reaction mixture was refluxed for 15 h and cooled to room temperature. The resulting mixture was filtered and then extracted with chloroform. The organic layer was washed with a dilute solution of KOH and water and dried over anhydrous magnesium sulfate. After filtration and removal of the solvents and purification with column chromatography (silica gel, petroleum ether as eluent), 28.7 g (86%) of 1-octyloxyl-4-iodobenzene as colorless oil was obtained. Gas chromatography-mass spectrometry (GC-MS): *m/z* = 332. <sup>1</sup>H-NMR (δ/ppm, CDCl<sub>3</sub>): 0.85–0.88 (t, *J* = 5.7, 3H), 1.28–1.48 (m, 10H), 1.68–1.70 (m, 2H), 3.80–3.82 (t, *J* = 4.0, 2H), 6.67–6.68 (d, *J* = 4.0, 2H), 7.51–7.53 (d, *J* = 4.0, 2H). <sup>13</sup>C-NMR (δ/ppm, CDCl<sub>3</sub>): 137.9, 116.0, 81.9, 68.6, 31.7, 29.6, 29.0, 25.8, 22.6, 14.1.

#### Bis(4-(2'-octyloxy)phenyl)amino)benzene (2)

The mixture of **1** (10.85 g, 32 mmol), aniline (1.4 g, 15 mmol), CuCl (0.12 g, 1.2 mmol), phenanthroline (0.26 g, 1.44 mmol), KOH (14.7 g, 0.26 mol), and toluene (35 mL) was refluxed for 24 h. After cooling, the resulting mixture was poured into plenty of stirred water and extracted with chloroform. The obtained organic phase was washed several times with water, dried with magnesium sulfate, filtered, evaporated, and purified with column chromatography (silica gel, petroleum ether as eluent) to yield 6.5 g (89%) of bis(4-(2'-octyloxy)phenyl)amino)benzene as a yellowish oil. GC-MS: *m/z* = 502, <sup>1</sup>H-NMR (δ/ppm, CDCl<sub>3</sub>): 0.90–0.93 (t, *J* = 5.7, 6H), 1.30–1.51 (m, 20H), 1.74–1.84 (m, 4H), 3.87–3.89 (t, *J* = 3.8, 4H), 6.67–7.15 (m, 13H). <sup>13</sup>C-NMR (δ/ppm, CDCl<sub>3</sub>): 153.7, 145.7, 137.3, 131.8, 129.4, 126.7, 125.4, 115.0, 68.6, 31.7, 29.5, 29.2, 25.7, 22.6, 14.1. Elemental Anal. Calcd for C<sub>34</sub>H<sub>47</sub>NO<sub>2</sub>: C, 81.43; H, 9.38; N, 2.79. Found: C, 81.35; H, 9.30; N, 2.82.

#### 4-(Bis(4'-(2''-octyloxy)phenyl)amino)benzaldehyde (3)

Phosphorus oxychloride (2 mL, 21.6 mmol) was added dropwise to stirred DMF (10 mL, 130 mmol) at 0°C. The mixture was stirred for 1 h at 0°C and additionally stirred at room temperature for 1 h. After the addition of **2** (1.6 g, 3.2 mmol) in 1,2-dichloroethane (10 mL), the mixture was stirred at

90°C for 2 h. After cooling, the solution was poured into cold water. The resulting mixture was neutralized to pH 7 with 2M NaOH aqueous solution and extracted with chloroform. The extract was washed successively with plenty of water and brine. The organic extracts were dried over magnesium sulfate, evaporated, and purified with column chromatography (silica gel, ethyl acetate/petroleum ether (1/3) as eluent) to yield 1.11 g (66%) **3** as yellowish oil. GC-MS:  $m/z = 529$ .  $^1\text{H-NMR}$  ( $\delta/\text{ppm}$ ,  $\text{CDCl}_3$ ): 9.78 (s, 1H), 7.63 (d,  $J = 3.9$ , 2H), 7.15–7.09 (m, 4H), 6.95 (m, 2H), 6.86 (m, 4H), 3.89–3.86 (t,  $J = 5.7$ , 4H), 1.80 (m, 4H), 1.41–1.27 (m, 20H), 0.87–0.89 (t,  $J = 4.0$ , 6H).  $^{13}\text{C-NMR}$  ( $\delta/\text{ppm}$ ,  $\text{CDCl}_3$ ): 189.9, 153.7, 151.7, 137.5, 130.5, 131.8, 131.3, 126.7, 125.4, 115.0, 68.6, 31.7, 29.5, 29.2, 25.7, 22.6, 14.1.

(2,5-Dibromo-thiophen-3-ylmethyl)-phosphonic acid diethyl ester (**4**)

Compound **4** was synthesized as described in Ref. 9. The crude product was purified by flash column chromatography eluting with petroleum ether/ethyl acetate (1 : 1). After purification, **4** was recovered as a pale yellow oil (22 g, 70% yield). GC-MS:  $m/z = 392$ ,  $^1\text{H-NMR}$  ( $\delta/\text{ppm}$ ,  $\text{CDCl}_3$ ): 7.00 (s, 1H), 4.08 (m, 4H), 3.10 (d,  $J = 4.0$ , 2H), 1.29 (t,  $J = 5.7$ , 6H).

*N*-(4-((*E*)-2-(2,5-dibromothiophen-3-yl)vinyl)phenyl)-4-(octyloxy)-*N*-(4-(octyloxy) phenyl)benzenamine (**5**)

Under an ice-water bath, **4** (0.78 g, 2 mmol) was dissolved in 10 mL DMF, and  $\text{CH}_3\text{ONa}$  (0.162 g, 3 mmol) was added. After 10 min, **3** (1.06 g, 2 mmol) was added slowly to the solution. After 2 h, the solution was poured into methanol and filtered. The solvent was removed by the rotavapor, and the residue was purified through silica chromatography (petroleum ether/ethyl acetate (10 : 1) to obtain **5** as colorless oil (90%). GC-MS:  $m/z = 756$ .  $^1\text{H-NMR}$  ( $\delta/\text{ppm}$ ,  $\text{CDCl}_3$ ): 7.23 (m, 2H), 7.05 (s, 2H), 6.94 (s, 1H), 6.72 (m, 4H), 6.61 (m, 2H); 6.45 (m, 4H), 3.90–3.87 (t,  $J = 5.7$ , 4H), 1.79 (m, 4H), 1.39–1.27 (m, 20H), 0.92 (t,  $J = 5.7$ , 6H).  $^{13}\text{C-NMR}$  ( $\delta/\text{ppm}$ ,  $\text{CDCl}_3$ ): 153.8, 145.0, 140.0, 137.4, 133.3, 131.7, 131.2, 129.7, 127.3, 126.9, 124.9, 68.7, 31.8, 29.6, 29.2, 25.9, 22.7, 14.0.

2,5-Bis(tributylstannyl)thiophene (**6**)

This compound was synthesized by the literature procedure.<sup>9</sup> GC-MS:  $m/z = 664$ . Yield: 72%. Purity (by GC-MS)  $\geq 96\%$ .  $^1\text{H-NMR}$  ( $\delta/\text{ppm}$ ,  $\text{CDCl}_3$ ): 7.34 (s, 2H), 1.60 (m, 12H), 1.39 (m, 12H), 1.09 (m, 12H), 0.91 (t, 18H). Elemental Anal. Calcd. for  $\text{C}_{28}\text{H}_{56}\text{SSn}_2$ : C, 50.80; H, 8.47; found: C, 50.68; H, 8.40.

### Synthesis of polymer DOTPAV-PT

$\text{Pd}(\text{PPh}_3)_4$  (15 mg, 0.013 mmol), monomer **5** (0.3 g, 0.39 mmol), and monomer **6** (0.26 g, 0.39 mmol)

were put into a three-necked flask. The mixture was flushed with argon for 10 min, and then 10 mL toluene was added. For the protection of argon, the reactant was heated to reflux for 12 h. The mixture was cooled to room temperature and poured into 30 mL methanol and then filtered into a Soxhlet thimble. Soxhlet extractions were performed with methanol, hexane, and  $\text{CHCl}_3$ . The polymer was recovered from the  $\text{CHCl}_3$  fraction by rotary evaporation. The solid was dried under vacuum overnight, with a yield of 80%.  $^1\text{H-NMR}$  ( $\delta/\text{ppm}$ ,  $\text{CDCl}_3$ ): 8.04–6.68 (m, 17H), 3.76 (br, 4H), 2.02 (br, 4H), 1.61–1.00 (br, 20H), 0.89–0.82 (br, 6H). Elemental Anal. Calcd. for  $(\text{C}_{44}\text{H}_{51}\text{S}_2\text{N})_n$ : C, 80.37; H, 7.76; N, 2.13, found: C, 80.30; H, 7.68; N, 2.15.

## RESULTS AND DISCUSSION

### Synthesis and characterization

The synthesis of the monomers and the corresponding polymer is outlined in Scheme 2. The monomer was synthesized by Wittig–Hornor reaction between (2,5-dibromo-thiophen-3-ylmethyl)-phosphonic acid diethyl ester and a corresponding substituted monoaldehyde. The alkylation of 4-iodophenol with octylbromide in the presence of  $\text{K}_2\text{CO}_3$  gave **1**, and subsequently converted to **2**, according to the modified Ullmann condensation reaction,<sup>18</sup> which was in turn converted to **3** by the Vielsmier reaction.<sup>19</sup> Monomer **5** was obtained from **3** and (2,5-dibromothiophen-3-ylmethyl)-phosphonic acid diethyl ester in 90% yield by the Wittig–Hornor reaction.<sup>20</sup>

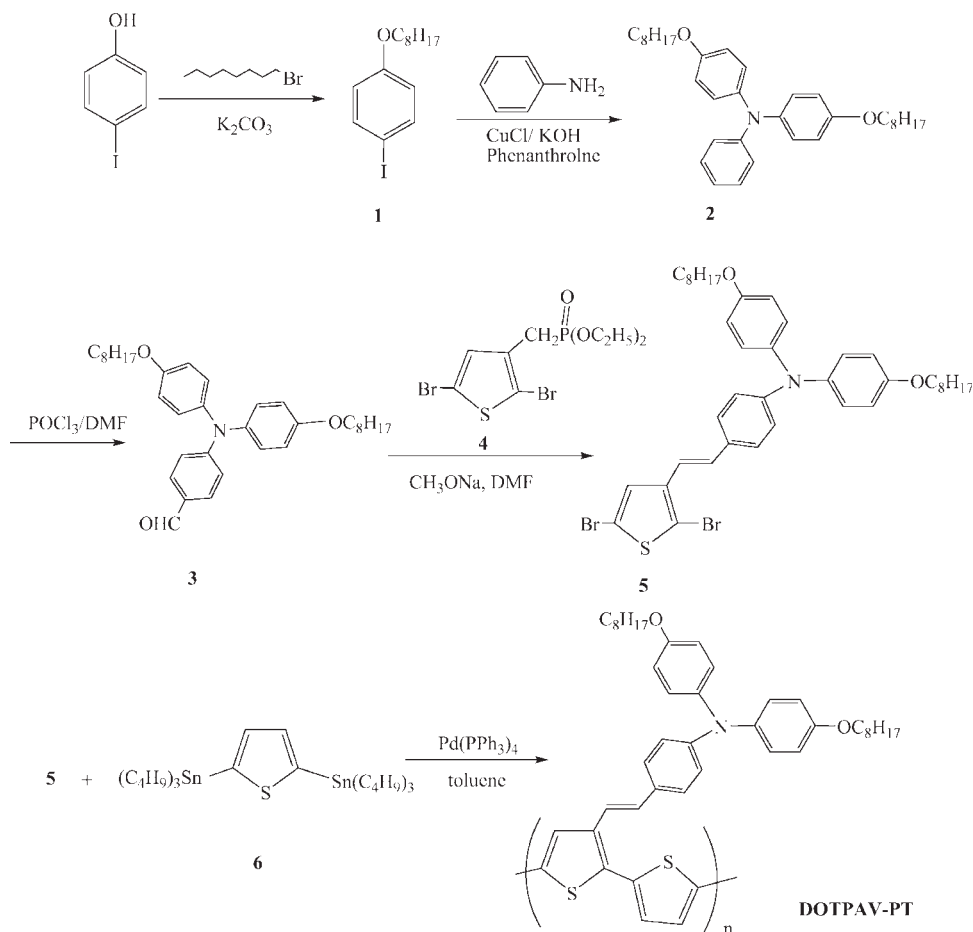
The polymer DOTPAV-PT was easily prepared by the Stille coupling method<sup>9</sup> and identified by  $^1\text{H-NMR}$  spectroscopy and elemental analysis. The synthesized polymer was soluble in common organic solvents, such as chloroform, toluene, and xylene, at room temperature. The weight-average molecular weight ( $M_w$ ) of DOTPAV-PT was 8000 with a polydispersity of 1.24.

### Thermal analysis

Thermal stability of the DOTPAV-PT was investigated with TGA under nitrogen atmosphere as shown in Figure 1. The figure shows that the polymer has good thermal stability with the onset decomposition temperature around 298°C in nitrogen, and 5% weight loss temperature of DOTPAV-PT was found to be 310°C. Obviously, the thermal stability of the polymer is adequate for the fabrication processes of PSCs and other optoelectronic devices.

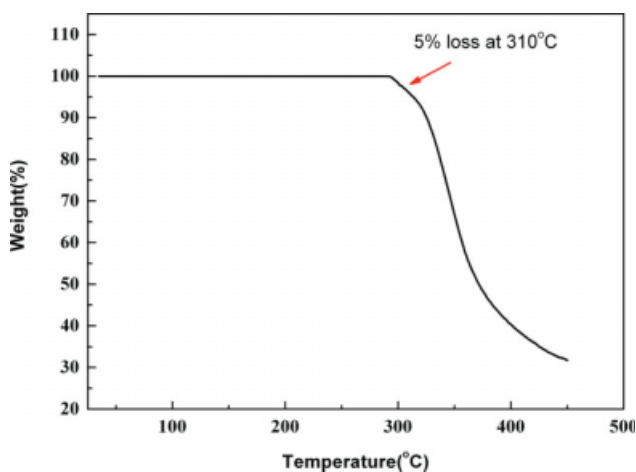
### UV-vis absorption and PL spectra of the polymer

The UV-vis absorption spectra could provide a great deal of information on the electronic structures of



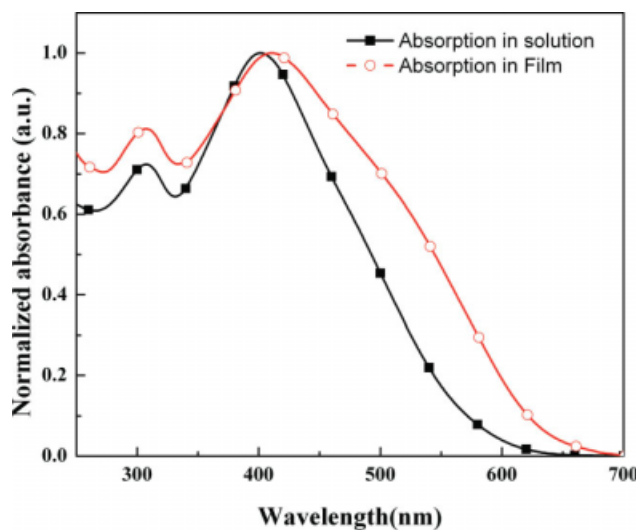
**Scheme 2** Synthetic routes of the monomers and polymer DOTPAV-PT.

the conjugated polymers. Figure 2 shows the UV-vis absorption spectra of the polymer solution and film. DOTPAV-PT solution shows a maximum absorption peak at ca. 400 nm that belongs to the absorption of the conjugated side-chains. The absorption peak of

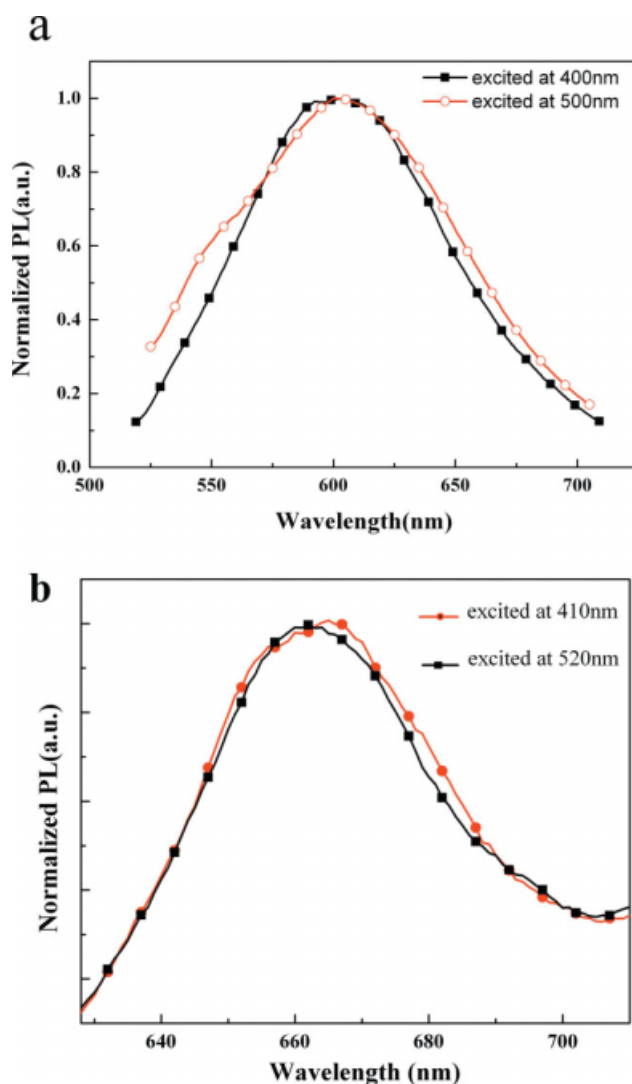


**Figure 1** TGA plot of DOTPAV-PT with a heating rate of  $10^\circ\text{C min}^{-1}$  under inert atmosphere. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

the polymer film is red-shifted to ca. 410 nm in comparison with that of the solution, and the polymer film shows a shoulder absorption peak at 520 nm



**Figure 2** The absorption spectra of DOTPAV-PT in chloroform solution and solid film. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 3** Photoluminescent spectra of DOTPAV-PT (a) solution in  $\text{CHCl}_3$  and (b) film. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

that corresponds to the  $\pi$ - $\pi^*$  transition of the conjugated main-chains of the polymer. The weakened absorption in the visible region indicates that the triphenylamine twisted the main chain, and the effective conjugated length in the main chain in DOTPAV-PT decreased. The absorption band edge of DOTPAV-PT film is 655 nm, indicating an optical band gap of 1.89 eV.

Figure 3 shows the PL spectra of the polymer solution and film excited at different wavelengths. Figure 3(a) corresponds to the PL spectrum of the solution of DOTPAV-PT in chloroform solution with the peak at 613 nm after the excitation of both 400 and 500 nm. As shown in Figure 3(b), the DOTPAV-PT film exhibits the PL peak at 660 nm under the excitation both at 410 nm (excited at conjugated side-chains) and at 520 nm (excited at conjugated

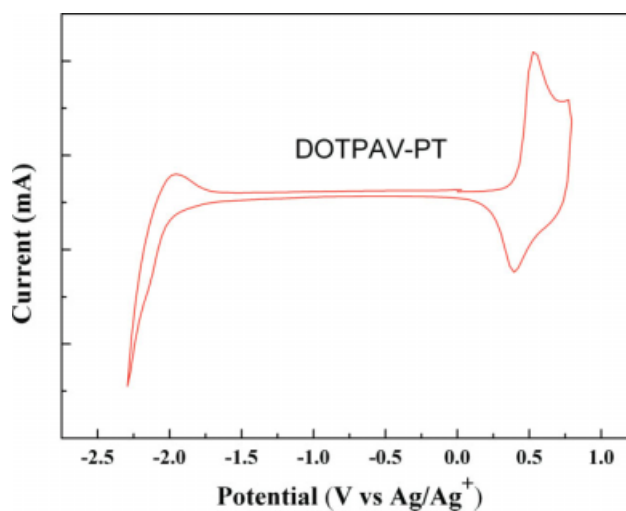
main chains), which indicates that there is a thorough internal exciton energy transfer process from the conjugated side-chains to the main-chains when the polymer was excited at the conjugated side-chains. The phenomenon ensures that all photons absorbed by the polymers are useful for the photo-voltaic conversion.

### Electrochemical properties

Cyclic voltammogram (CV) was employed to estimate the HOMO and LUMO energy levels of the polymers.<sup>21,22</sup> Figure 4 shows the cyclic voltammogram of the DOTPAV-PT film on PT electrode in  $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NPF}_6$ ,  $\text{CH}_3\text{CN}$  solution. It can be seen that there are reversible *p*-doping/dedoping (oxidation/re-reduction) processes at positive potential range and *n*-doping/dedoping (reduction/re-oxidation) processes at negative potential range for DOTPAV-PT. It is well known that the onset potentials of the *p*- and *n*-doping correspond to the HOMO and LUMO energy levels of the conjugated polymers. Therefore, we can get the HOMO and LUMO energy level of DOTPAV-PT according to the equations<sup>23</sup>:  $\text{HOMO} = -e(E_{\text{on}}^{\text{ox}} + 4.71)$  (eV);  $\text{LUMO} = -e(E_{\text{on}}^{\text{red}} + 4.71)$  (eV). LUMO and HOMO levels of DOTPAV-PT were calculated to be  $-2.96$  and  $-5.07$  eV. The band gap calculated from the electrochemical measurement is 2.11 eV. The electrochemical band gap is a little larger than that of the optical band gap, which is a common phenomenon for the conjugated polymers.

### Hole mobility

The hole mobility is an important parameter to investigate the charge transport of the polymers.

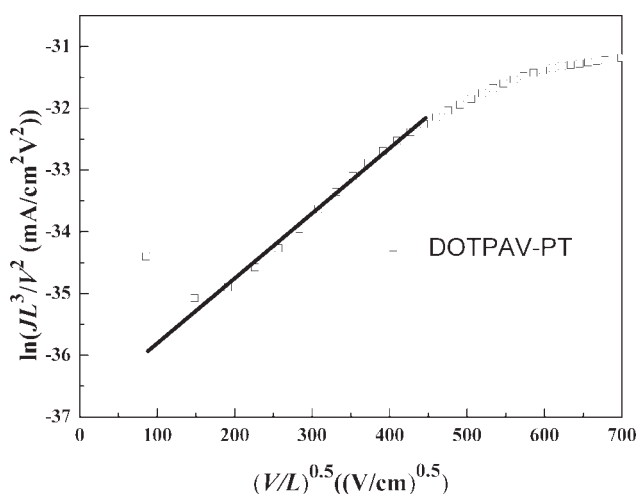


**Figure 4** Cyclic voltammogram of DOTPAV-PT film on platinum electrode in  $0.1 \text{ mol L}^{-1} \text{ Bu}_4\text{NPF}_6$ ,  $\text{CH}_3\text{CN}$  solution. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

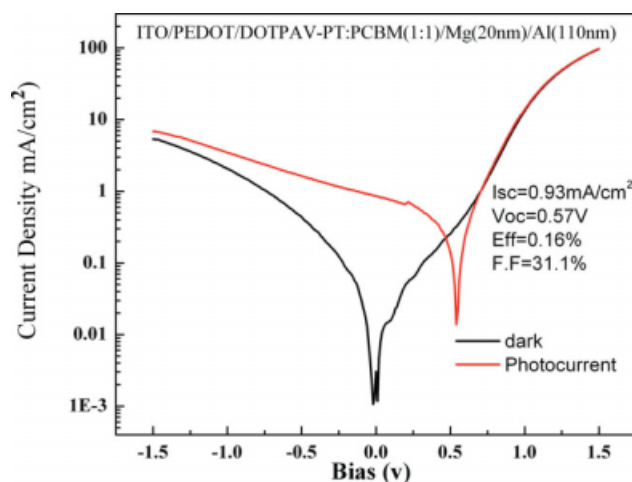
Here we used a device structure of ITO/PEDOT: PSS/polymer/Au for the hole mobility measurement based on the space-charge-limited current (SCLC) model.<sup>24–27</sup> The results are plotted as  $\ln(JL^3/V^2)$  vs.  $(V/L)^{0.5}$  and are shown in Figure 5. The hole mobility of **DOTPAV-PT**, which can be calculated from the intercept of the corresponding line, is  $1.25 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , higher than those of common PTs ( $10^{-6}$ ).<sup>28</sup> The remarkable increase in hole mobility of the polymer roots in the presence of the excellent hole transporting unit triphenylamine in the side-chains, which further identify the superiority of triphenylamine, contained **DOTPAV-PT** on hole mobility.

### Photovoltaic property

We fabricated the PSCs with a structure of ITO/PEDOT : PSS (30 nm)/**DOTPAV-PT**: PCBM (1 : 1 wt %)/Ca(20 nm)/Al(110 nm) to check the photovoltaic property of the polymer. The photosensitive layer was prepared by spin-coating a blend solution of the polymer and PCBM in *o*-dichlorobenzene on the ITO/PEDOT : PSS electrode. In this bulk heterojunction-typed PSC, the polymer is used as electron donor and PCBM is used as electron acceptor. Figure 6 shows the  $I$ - $V$  curve of the PSC based on **DOTPAV-PT**/PCBM. The open circuit voltage ( $V_{oc}$ ), short circuit current density ( $I_{sc}$ ), and fill factor of the device are 0.57 V, 0.93  $\text{mA cm}^{-2}$ , and 31.1%, respectively. The power conversion efficiency (PCE) of the device is 0.16% under the illumination of AM1.5; 100  $\text{mW cm}^{-2}$ .



**Figure 5** Current-voltage plot from the device ITO/PEDOT : PSS/**DOTPAV-PT**/Au, plotted in the format  $\ln(JL^3/V^2)$  vs.  $(V/L)^{0.5}$ , where  $J$  is the current density, and  $L$  is the thickness of the polymer layer. The line is the fit to the respective experimental points.



**Figure 6**  $I$ - $V$  curves of the polymer solar cell based on the blend of **DOTPAV-PT**/PCBM (1 : 4 w/w) at dark and under the illumination of AM 1.5, 100  $\text{mW cm}^{-2}$ . [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

### CONCLUSIONS

**DOTPAV-PT** bearing the side-chain with dioctyltolyl triphenylamine moiety through a vinylene bridge was synthesized by the Stille coupling method. Photovoltaic property of the polymer was investigated with the polymer solar cells based on the blend of the polymer as donor and PCBM as acceptor (1 : 1, w/w) under AM 1.5, 100  $\text{mW cm}^{-2}$ . The PCE of the PSC based on **DOTPAV-PT** was 0.16%. The hole mobility of the polymer reached  $1.25 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  by SCLC method, which is higher than those of common PTs, owing to the existence of triphenylamine in the side-chain. The results presented here could provide guidelines for further molecular design and structural modifications of polythiophenes for solar cells.

### References

- Liu, J. S.; Kadnikova, E. N.; Liu, Y. X.; McGehee, M. D.; Frechet, J. M. J. *J Am Chem Soc* 2004, 126, 9486.
- Svensson, M.; Zhang, F.; Veenstra, S. C.; Verhees, W. J. H.; Hummelen, J. C.; Kroon, J. M.; Inganaes, O.; Andersson, M. R. *Adv Mater* 2003, 15, 988.
- Hou, J. H.; Tan, Z. A.; Yan, Y.; He, Y. J.; Yang, C. H.; Li, Y. F. *J Am Chem Soc* 2006, 128, 4911.
- Li, Y. F.; Zou, Y. P. *Adv Mater* 2008, 20, 2952.
- Yang, R.; Tian, R.; Yang, Y.; Hou, Q.; Cao, Y. *Macromolecules* 2003, 36, 7453.
- Zou, Y. P.; Wu, W. P.; Sang, G. Y.; Yang, Y.; Liu, Y. Q.; Li, Y. F. *Macromolecules* 2007, 40, 7231.
- Bao, Z. *Adv Mater* 2000, 12, 227.
- Ong, B. S.; Wu, Y. L.; Liu, P.; Gardner, S. *J Am Chem Soc* 2004, 126, 3378.
- Hou, J. H.; Huo, L. J.; He, C.; Yang, C. H.; Li, Y. F. *Macromolecules* 2006, 39, 594.

10. Hou, J. H.; Tan, Z. A.; He, Y. J.; Yang, C. H.; Li, Y. F. *Macromolecules* 2006, 39, 4657.
11. Zhou, E. J.; Tan, Z. A.; Huo, L. J.; He, Y. J.; Yang, C. H.; Li, Y. F. *J Phys Chem B* 2006, 110, 26062.
12. Zou, Y. P.; Sang, G. Y.; Wan, M. X.; Tan, S. T.; Li, Y. F. *Macromol Chem Phys* 2008, 209, 1454.
13. Yang, W. J.; Kim, D. Y.; Kim, C. H.; Jeong, M.-Y.; Lee, S. K.; Jeon, S.-J.; Cho, B. R. *Org Lett* 2004, 6, 1389.
14. Porres, L.; Mongin, O.; Katan, C.; Charlot, M.; Pons, T.; Mertz, J.; Blanchard-Desce, M. *Org Lett* 2004, 6, 47.
15. Pu, Y. J.; Soma, M.; Kido, J.; Nishide, H. *Chem Mater* 2001, 13, 3817.
16. Lee, H. J.; Sohn, J.; Hwang, J.; Park, S. Y.; Choi, H.; Cha, M. *Chem Mater* 2004, 16, 456.
17. Roquet, S.; Cravino, A.; Leriche, P.; Aleveque, O.; Frere, P.; Roncali, J. *J Am Chem Soc* 2006, 128, 3459.
18. Semmelhack, M. F.; Helquist, P.; Jones, L. D.; Keller, L.; Mendelson, L.; Ryono, L. S.; Smith, J. G.; Stauffer, R. D. *J Am Chem Soc* 1981, 103, 6460.
19. Li, H. C.; Geng, Y. H.; Tong, S. W.; Tong, H.; Hua, R.; Su, G. P.; Wang, L. X.; Jing, X. B.; Wang, F. S. *J Polym Sci Part A: Polym Chem* 2001, 39, 3278.
20. Wadsworth, W. S.; Emmons, W. D. *J Am Chem Soc* 1961, 83, 1733.
21. Li, Y. F.; Cao, Y.; Gao, J.; Wang, D. L.; Yu, G.; Heeger, A. J. *Synth Met* 1999, 99, 243.
22. Sun, Q. J.; Wang, H. Q.; Yang, C. H.; Li, Y. F. *Mater Chem* 2003, 13, 800.
23. Yamamoto, T.; Komarudin, D.; Arai, M.; Lee, B.-L.; Suganuma, H.; Asakawa, N.; Inoue, Y.; Kubota, K.; Sasaki, S.; Fukuda, T.; Matsuda, H. *J Am Chem Soc* 1998, 120, 2047.
24. Malliaras, G. G.; Salem, J. R.; Brock, P. J.; Scott, C. *Phys Rev B* 1998, 58, 13411.
25. Martens, H. C. F.; Brom, H. B.; Blom, P. W. M. *Phys Rev B* 1999, 60, 8489.
26. Yang, C. H.; Hou, J. H.; Zhang, B.; Zhang, S. Q.; He, C.; Fang, H.; Ding, Y. Q.; Ye, J. P.; Li, Y. F. *Macromol Chem Phys* 2005, 206, 1311.
27. Hou, J. H.; Yang, C. H.; He, C.; Li, Y. F. *Chem Commun* 2006, 871.
28. Roman, L. S.; Inganas, O. *Synth Met* 2002, 125, 419.