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Polythiophene Derivative with Phenothiazine-Vinylene Conjugated Side Chain: Synthesis and its Application in Field-Effect Transistors

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ABSTRACT:

A new polythiophene derivative with phenothiazine-vinylene (PTZV) conjugated side chains, **PTZV-PT**, was synthesized through the Stille coupling reaction, and characterized by ^{1}H NMR, elemental analysis, GPC, TGA, DSC, UV-vis absorption spectroscopy, photoluminescence spectroscopy and cyclic voltammetry. The polymer is soluble in common organic solvents and possesses good thermal stability with 5% weight loss at the temperature of 397°C and T_g of 140°C. The weight-average molecular weight of **PTZV-PT** was 5.45×10^4 with the polydispersity index of 1.48. The absorption spectrum of **PTZV-PT** film displays a broad plateau between 300 and 600 nm. The hole mobility of **PTZV-PT** determined from space-charge-limited current model was 4.7×10^{-3} cm^2 V^{-1}s^{-1}. The field effect hole mobility of the copolymer was as high as 6.8×10^{-3} cm$^2 \cdot$V^{-1}s^{-1} with an on/off ratio of 2.5×10^4, which is among the best performance of the copolymers reported for the solution-processed organic field effect transistors (OFETs). The preliminary results indicate that **PTZV-PT** is a promising polymer material for applications in solution-processable OFETs.

Keywords: Conjugated polymers, polythiophenes, phenothiazine-vinylene side chains, hole mobility, organic field effect transistors.

1. INTRODUCTION

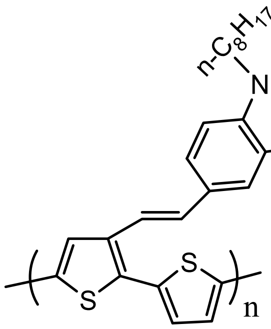
Conjugated polymers have drawn great attentions since the discovery of conducting polyacetylene in 1977. Among the conjugated polymers, polythiophene derivatives (PTs) attracted the most intensive studies for their promising applications in polymer solar cells,[1-3] light-emitting diodes,[4-6] and field-effect transistors (FETs).[7-8] In order to improve the optoelectronic properties to meet the request for different applications, chemical modifications of PTs have been well performed.

Organic field effect transistors (OFETs) attracted broad interest recently because of their promising applications in organic sensors,[9] integrated circuit, low-cost large area memories, smart cards, and driving circuits for large-area displays.[10, 11] One of the most important aspects for OFETs is that they can be fabricated by easy patterning techniques at low cost and have good compatibility with flexible plastic substrates. Thus the solution processable polymers are preferable to small molecules. Design and synthesis of new conjugated polymer semiconductors with high charge carrier mobility is highly desirable for the realization of high-performance solution processable OFETs.[12]

For the application of the conjugated polymers in polymer solar cells (PSCs) as electron donor, broad absorption in the visible region and higher hole mobility of the conjugated polymers are crucial for efficient photovoltaic materials. It is well known that the increase of effective conjugation length will broaden the absorption of π-conjugated polymers, thus, our group recently synthesized a series of polythiophene and poly(thienylene vinylene) derivatives with conjugated phenylene-vinylene,[13] thienylene-vinylene[14] or terthiophene-vinylene[15] side chains. The polymers with the conjugated side chains showed broad absorption in the visible region and higher hole mobility.[13-15]

A notable feature of conjugated polymers lies in the versatility of their molecular structure which affords wide space to construct new polymers with improved properties. Phenothiazine is a well-known heterocyclic compound with electron-rich sulfur and nitrogen heteroatoms.[16,17] Polymers and organic molecules containing phenothiazine or its derivatives possess unique optoelectronic properties for diverse applications such as OFET, [16] light emitting diodes,[18] photovoltaic devices,[19] and chemiluminescence.[20] Hwang et al[16] reported a conjugated copolymer of phenothiazine and fluorene, and the OFET based on the polymer showed a hole field effect mobility of 0.8×10^{-4} $cm^2V^{-1}s^{-1}$ and an on/off ratio of 10^3.

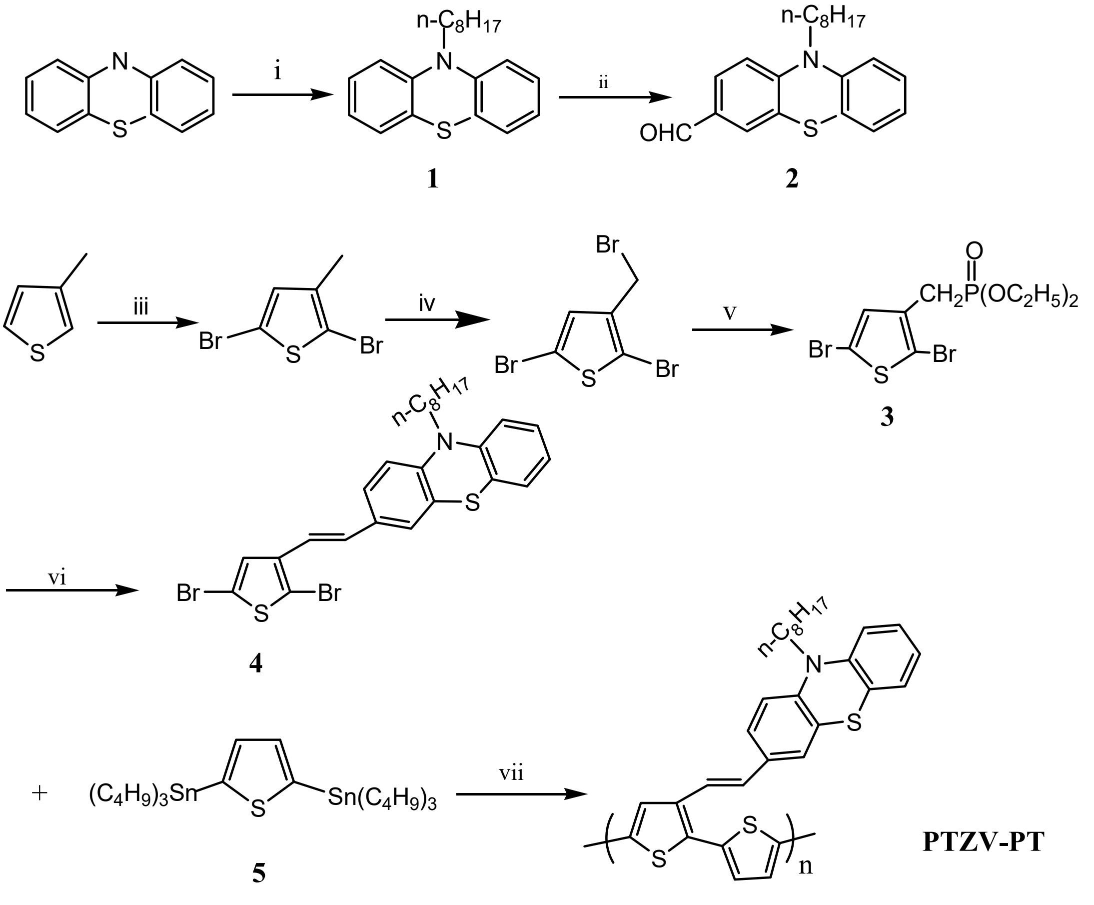
In order to investigate the effect of side-chain structure on the property of the polythiophene derivatives with conjugated side chains and to develop new conjugated polymers with high hole mobility, we synthesized a new polythiophene derivative with a hole transporting phenothiazine unit [17b] as conjugated side chains, **PTZV-PT** (see Scheme 1), via the Stille coupling reaction. The hole mobility of **PTZV-PT**, measured by the space-charge-limited current (SCLC) method, reached 4.7×10^{-3} $cm^2V^{-1}s^{-1}$ which is about three orders higher than that of the common polythiophenes (10^{-6} $cm^2V^{-1}s^{-1}$). An OFET was fabricated using **PTZV-PT** as a new p-type channel material and characterized. The hole field effect mobility of the polymer was 6.8×10^{-3} $cm^2V^{-1}s^{-1}$ with an on/off ratio of 2.5×10^4, which is among the best performance of the solution-processed OFETs. Moreover, the absorption spectrum of **PTZV-PT** film displays a broad plateau from 300 nm to 600 nm, indicating that the polymer could also be a promising photovoltaic material.



PTZV-PT

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

Scheme 2. Synthetic route of the monomers and polymer **PTZV-PT**



(i) $C_8H_{17}Br$, DMSO, NaOH, rt, 24h, 93%; (ii)$POCl_3$, DMF, 90℃,36 h, 84%;(iii) NBS, $CHCl_3$/HOAc, 2h, 85%; (iv) NBS, BPO, CCl_4, reflux, 3h, 83%; (v) $P(OC_2H_5)_3$, 160℃, 2h, 70%; (vi) 2, $NaOCH_3$, DMF, rt, 2 h, 82%; (vii) $Pd(Ph_3)_4$, toluene, reflux,12 h, 72%.

2. RESULTS AND DISCUSSION

2.1 Synthesis and Characterization of the Polymer.

The synthesis of the monomers and the corresponding polymer are outlined in Scheme 2. Phenothiazine was used as a starting material for the preparation of **1** which was in turn converted to **2** by the Vilsmeier reaction, the monomer **4** was obtained using **2** and **3** in 82% yield by the Wittig-Hornor reaction.[21]

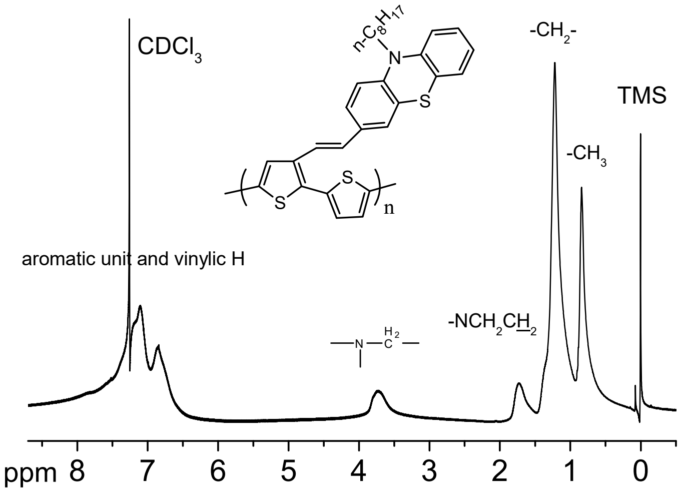


Figure 1. ^1H NMR spectra of the polymer **PTZV-PT**

The polymer **PTZV-PT** was easily prepared by the Stille coupling method[13] and identified by ^1H NMR spectroscopy （as shown in Figure 1） and elemental analysis. In Figure 1, the characteristic peaks at δ 7.36-6.93, 6.85-6.52 ppm can be assigned to the resonance of protons on phenothiazine ring, thiophene ring and vinylene group. And $–CH_2–$ linked to the nitrogen is at 3.71 ppm, the peaks at δ1.74-0.84 ppm are corresponding to the protons of the long alkyl chain. These results, combined with elemental analysis, indicate that the Stille reaction is successful and complete. The synthesized polymer **PTZV-PT** was soluble in common organic solvents, such as chloroform, toluene, and xylene at room temperature. The weight-average molecular weight (M_w) of **PTZV-PT** was 5.4×10^4 with a polydispersity index of 1.48**.**

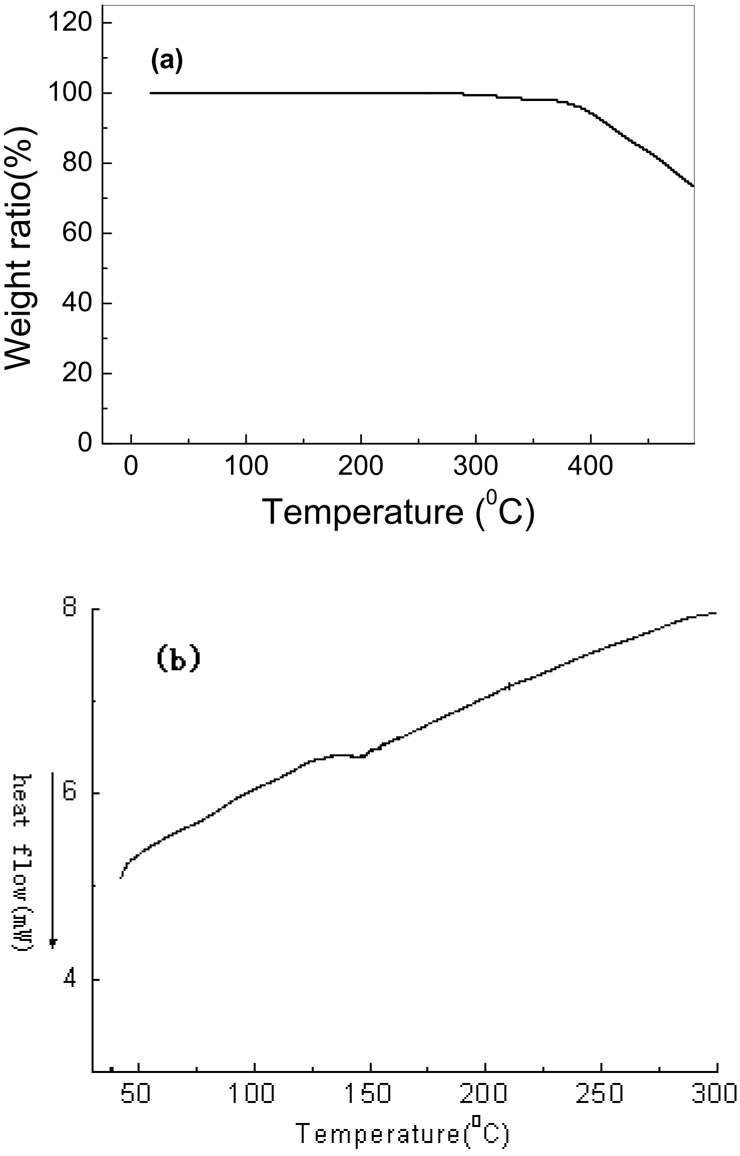


Figure 2. (a) TGA plot and (b) DSC thermogram of **PTZV-PT**

Thermal properties of **PTZV-PT** were investigated by means of DSC and thermogravimetric analysis (TGA) under nitrogen atmosphere, as shown in Figure 2. TGA plot (Figure 2a) reveals that the polymer possesses good thermal stability with the onset decomposition temperature around 300°C in nitrogen, 5% weight loss at the temperature of 397ºC. Glass transition temperature (T_g) of PTZV-PT is 140ºC, obtained from the DSC analysis (see Figure 2b). Obviously, the thermal stability of the polymer is adequate for the fabrication processes of optoelectronic devices.

2.2 UV-vis absorption and PL spectra

The UV-vis absorption spectra could provide a good deal of information on the electronic structure of the conjugated polymers. Figure 3 shows the absorption of **PTZV-PT** in dilute chloroform solution and film. There is an absorption peak located at ca. 401 nm with a shoulder peak of 529 nm. The shoulder peak of 529 nm contributed from conjugated main chains and an absorption peak at 401 nm contributed from vinyl phenothiazine moiety(the monomer 4 as model) since the model compound, monomer 4 exhibits two absorption peaks at 380 nm and 306 nm (also shown in Figure 3). The absorption peak of the short wavelength results from the conjugated side-chains. For PTZV-PT containing big side chains, probably, the steric hindrance of side chains makes the polymer main chains distorted in solution, so that the main chain absorption is weak and appears as a shoulder peak. The UV-vis absorption spectrum of **PTZV-PT** solution (see Figure 3) indicate the electron dononating substituents (phenothiazine) on the conjugated side chain have obvious influence on the short wavelength absorption of the polymer solution. The red shifts of the short wavelength absorption peak compared to poly(3-(phenylenevinyl)thiophene)s) show that the donor unit (phenothiazine) has better effective conjugation length in the side chain than that of poly(3-(phenylenevinyl)thiophene)s).[13a]

For **PTZV-PT** film absorption spectrum, the phenothiazine groups on the side chains extended the short wavelength conjugation system of the polymer compared to poly(3-(phenylenevinyl)thiophene)s),[13a] moreover, the absorption of PTZV-PT film red shifted by 70 nm in comparison with that of poly(3-arylthiophene) [22]which aryl ring was connected to the 3-position of thiophene through a saturated linkage, the results show that the phenothiazine groups on the side chains enhance the absorption window of the polymer through the linkage of the vinyl bond. In the solid film, the strong interchain interactions make the main chains extended and the conjugation degree increased which enhances the visible absorption, but because the relative big hindrance of the phenothiazine makes the absorption onset wavelength only little red-shifted compared to that of the PTZV-PT solution. **PTZV-PT** film exhibits two absorption peaks at ca. 411 and 535 nm. The results show that the vinyl linkage of phenothiazine side chain have some influence on the absorption of the PTZV-PT. The PTZV-PT film shows a very broad absorption plateau from 250 nm to 610 nm, so the full width at half-maximum (fwhm) of the absorption peak of **PTZV-PT** film is difficult to be determined. The broad absorption spectra indicate that the polymer could be a promising photovoltaic material.

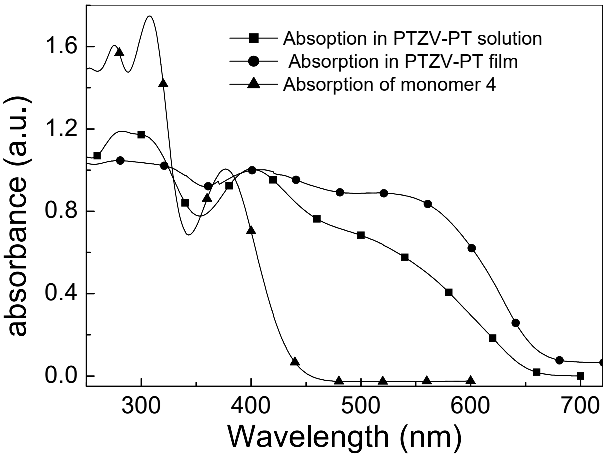


Figure 3. The absorption spectra of the polymer **PTZV-PT** and **monomer 4** in dilute $CHCl_3$ solution and **PTZV-PT** film.

Figure 4 shows PL spectra of the **PTZV-PT** solution and film. For the polymer solution, the PL peaks of **PTZV-PT** are the same at 599 nm when excited at the two wavelengths of 402 nm and 529 nm (corresponding to the absorption peak in the short wavelength and the absorption shoulder peak in the long wavelength) respectively. In comparison, monomer **4** exhibits a PL maximum at about 500 nm under the excitation of 400 nm. In the emission spectra, the emission peak at about 500 nm from PTZV(monomer 4) under the excitation wavelength of 400 nm disappeared completely, so the PL emission of PTZV-PT at 599 nm is ascribed to the emission of the polymer main chains. The above results indicate the occurrence of energy transfer from the conjugated side chains to the polymer main chains, so that the emission peak of the conjugated side chains was not observed when the conjugated side chains were excited at the wavelength of ca. 400 nm. In the film state, **PTZV-PT** exhibits a PL peak at 660 nm under the excitation of 402 nm and 535 nm, respectively, which indicates there is an intramolecular exciton energy transfer process from the conjugated side chains to the main chains when the polymer was excited at ca. 400 nm in the film state. This phenomenon was also observed for other polythiophene derivatives with conjugated side chains[13-15] and PPV derivatives with OXD side chains.[23]The exciton energy transfer ensures that all photons absorbed by the polymers are useful for the photovoltaic conversion when the polymer is used as the photovoltaic material.

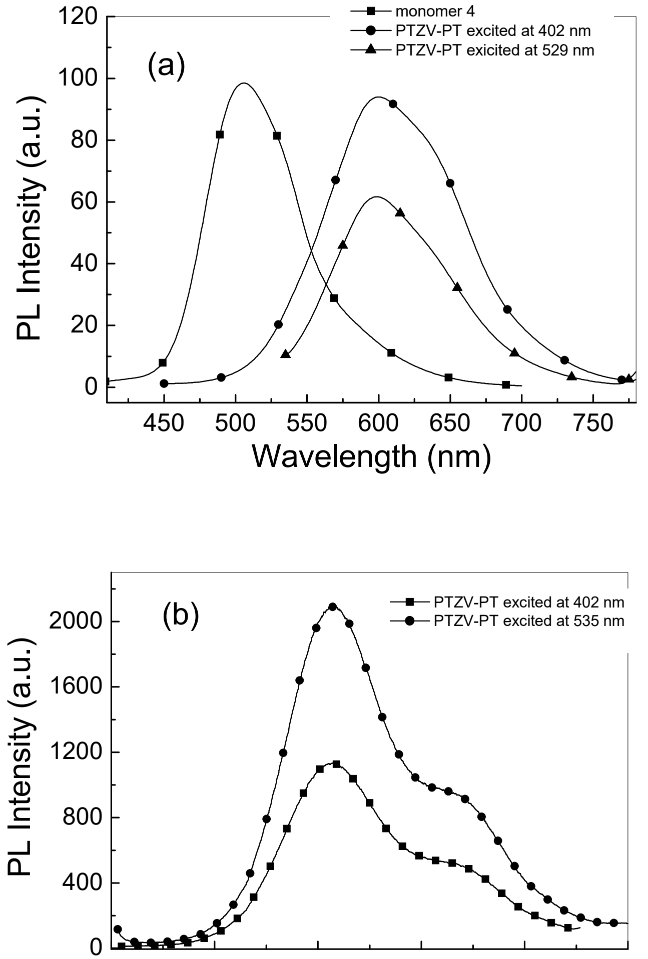


Figure 4. PL spectra of (a) **PTZV-PT** and monomer **4** in dilute $CHCl_3$ solution and (b) **PTZV-PT** film.

2.3 Electrochemical Properties.

Cyclic voltammetry was widely employed to estimate the HOMO and LUMO energy levels of the conjugated polymers, because the onset oxidation and reduction potentials obtained from the cyclic voltammograms are corresponding to the HOMO and LUMO energy levels respectively.[24] Figure 5 shows the cyclic voltammogram of the **PTZV-PT** film on Pt electrode in 0.1 mol/L Bu_4NPF_6, CH_3CN 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 **PTZV-PT**. The oxidation current for the PTZV-PT is quite high as compared to that of the reduction current, suggesting that polythiophene derivative with phenothiazine-vinylene conjugated side chain is very capable of donating electrons and, as expected, is an efficient electron-donating material due to good electron donating ability of the phenothiazine group introduced into the side chain. We can get the HOMO and LUMO levels of **PTZV-PT** from the onset oxidation potential (E_{on}^{ox}) and onset reduction potential (E_{on}^{red}) according to the following equations:[25] HOMO = $-e(E_{on}^{ox}+4.71)$ (eV); LUMO = $-e(E_{on}^{red}+4.71)$ (eV). LUMO and HOMO levels of the polymer calculated from the electrochemical measurement were −4.99 eV and −2.99 eV respectively. The energy gap of **PTZV-PT** film is 2.0 eV from the difference between the onset oxidation and reduction potentials, which is a little higher than that of the optical energy gap E_g^{opt} (1.81 eV).

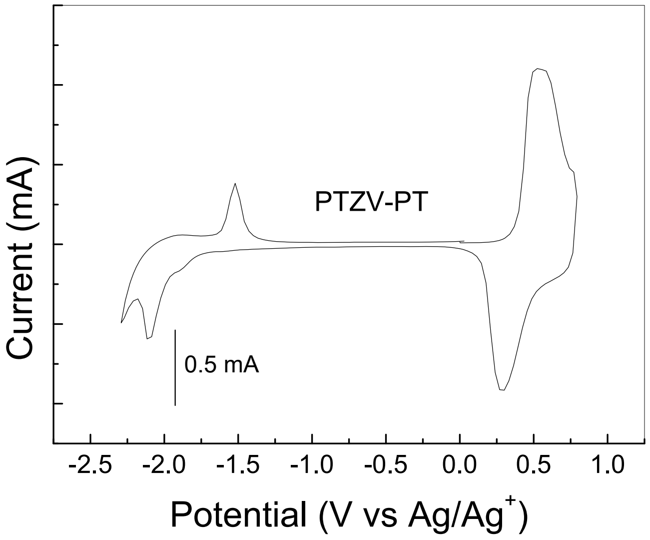


Figure 5. Cyclic voltammogram of **PTZV-PT** film on platinum electrode in 0.1 mol/L Bu_4NPF_6, CH_3CN solution.

2.4 Hole mobility

Hole mobility of PTZV-PT was measured by the space-charge-limited current (SCLC) method[26] with a device structure of ITO/PEDOT:PSS/polymer/Au. The results were plotted as $\ln(JL^3/V^2)$ vs. $(V/L)^{0.5}$ and shown in Figure 6. The hole mobility of **PTZV-PT** calculated from the data in Figure 6 was 4.7×10^{-3} $cm^2V^{-1}s^{-1}$, which is much higher than that of PPVs (10^{-7} $cm^2V^{-1}s^{-1}$)[26a] and PTs(10^{-6} $cm^2V^{-1}s^{-1}$).[26d] This result indicates that the hole transporting phenothiazine unit strongly enhanced the hole mobility of the polymers.

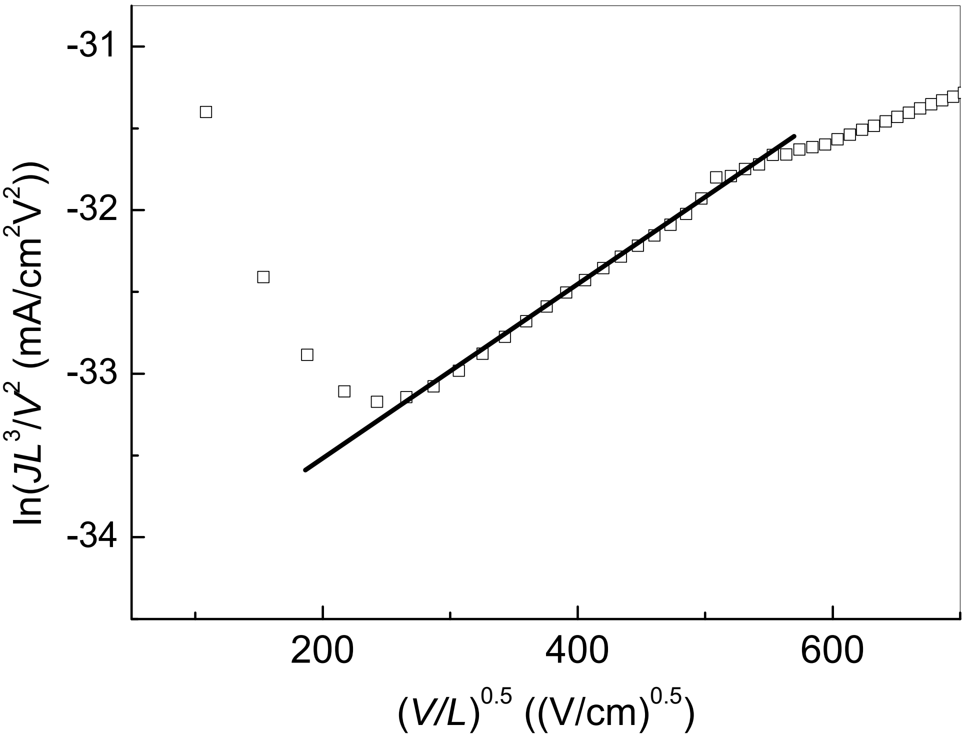


Figure 6. Current-voltage data from the device ITO/PEDOT: PSS/**PTZV-PT**/Au, plotted in the format ln(JL^3/V^2) vs. $(V/L)^{0.5}$, where J is the current density, L is the thickness of the polymer layer. The lines are the fit to the respective experimental points.

2.5 Organic Field Effect Transistors

The structure order and crystallization of PTZV-PT were investigated by atomic force microscopy (AFM) and film X-ray diffraction (XRD). Figure 7a and 7b show the AFM photographs of **PTZV-PT** films on SiO_2 substrate without and with octadecyltrichlorosilane(OTS) treatment, respectively. Pin holes are commonly observed in Figure 7a, which may attribute to the sudden evaporation of solvents through a thick polymer layer. PTZV-PT film on OTS-modified SiO2/Si substrates exhibited smoother and more homogenous morphology.

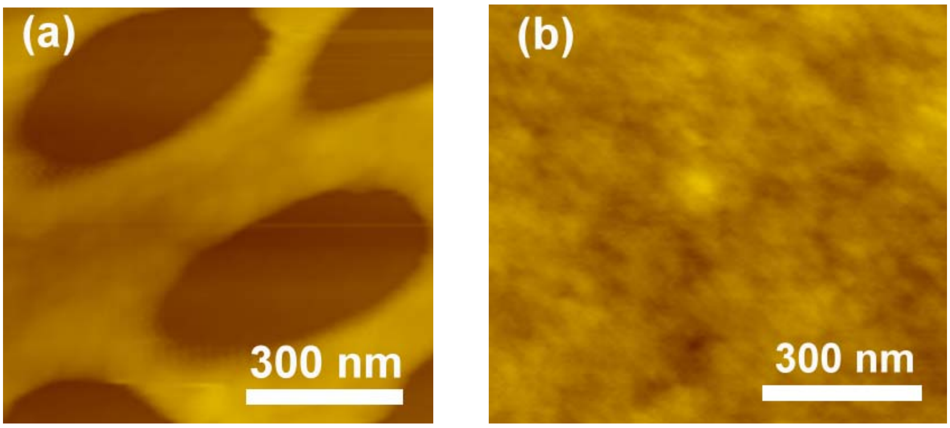


Figure 7. AFM tapping mode topographical images of **PTZV-PT** films on (a) SiO_2 surface and (b) OTS-modified SiO2/Si substrates.

To evaluate the crystallinity of polymer, XRD measurements were taken of thick spin coated films on SiO_2 substrate without and with OTS modifications. As shown in Figure 8a and 8b, both of the two films showed broad and weak diffraction peaks, revealing its poor crystallinity.

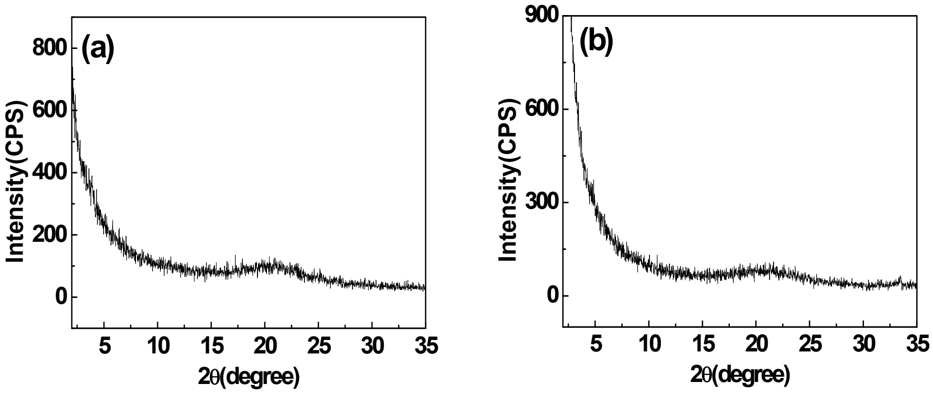


Figure 8. XRD patterns of spin-coated PTZV-PT thin films (50 nm thickness) on (a) SiO_2 surface and (b) OTS-modified SiO2/Si substrates.

The OFETs based on **PTZV-PT** were found to exhibit typical p-type FET characteristics. When bare SiO_2 was used as substrate the field mobility was very low (around 4× 10^{-4} $cm^2V^{-1}s^{-1}$) due to the poor film morphology (Figure 7a). OTS modified substrate produced much better morphology (Figure 7b) as well as improved device performances. The typical current-voltage characteristics of OFETs on OTS modified SiO_2 substrates are shown in Figure 9. The devices showed ideal transistor performance with apparent saturation behavior, as shown in Figure 9a and 9b. I_{DS} can be described using

$$I_{DS} = \mu(W/2L)C_i(V_G - V_T)^2$$

where I_{DS} is the drain current, C_i is the capacitance per unit area of the gate dielectric layer, V_{DS} is the drain voltage, V_G is the gate voltage, V_T is the threshold voltage, μ is the field-effect mobility, and W and L are the channel width and length dimensions, respectively. The mobility was calculated by plotting $I_{DS}^{1/2}$ versus V_G (see Figure 7b) and equating the slope of this plot to $\mu(W/2L)$ C_i. The threshold of the device was determined from the relationship between the square root of I_D at the saturated regime, and V_G was determined by extrapolating the measured data to $I_{DS} = 0$. The film on OTS-modified SiO_2/Si substrates was much better with visible small domains compared to that of the film onto SiO_2/Si substrates. These small domains might have positive effect on the charge transportations as has been observed in other polymers with high mobility. OFETs based on **PTZV-PT** afforded very high hole mobility up to 6.8 × 10^{-3} $cm^2V^{-1}s^{-1}$ with an on/off ratio of 2.5 × 10^4 and threshold voltage of -1V. About 20 OFET devices were fabricated, the mobility was around 4.6 × 10^{-3} $cm^2V^{-1}s^{-1}$ to 7.3× 10^{-3} $cm^2V^{-1}s^{-1}$ with good reproducibility. Though the carrier mobility of

PTZV-PT is not as good as those of the best devices previously reported[27]such as regioregular poly(3-hexylthiophene) (0.01-0.1 cm^{2}Vs)) [7a] or some polymers with fused rings,[7c, 27] they are among the best performance of the regiorandom alternating copolymers for OFETs reported. Further improvement of mobility can be achieved by using more favorable device fabrication conditions (e.g. different solvents, surface treatment, thermal treatment under other conditions, etc). It has been reported that phenothiazine has electron-rich sulfur and nitrogen heteroatoms and highly nonplanar structure for p-stacking aggregation and intermolecular excimer formation of low-ionizationpotential conjugated polymer semiconductors[16, 28]. This is why superior hole mobility has been achieved even though the films of **PTZV-PT** were in amorphous form. These results demonstrate that the conjugated polymers with phenothiazine-vinylene conjugated side chains are promising materials for high performance solution processable OFETs.

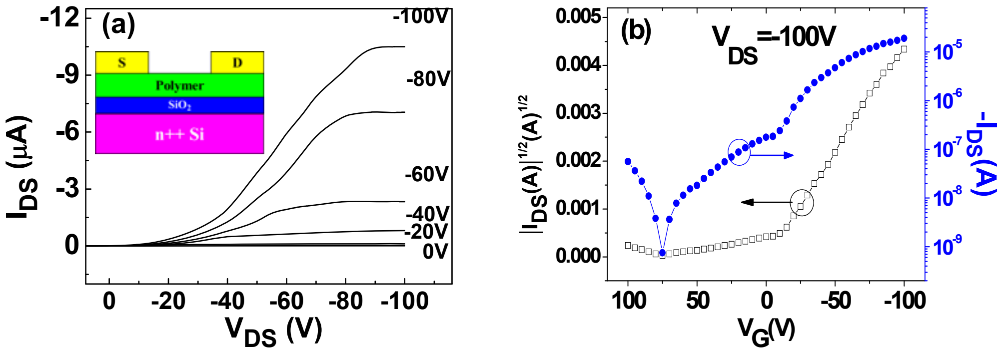


Figure 9. (a) Output and (b) transfer characteristics of PTZV-PT OFETs on OTS modified SiO_2. I_{DS} was obtained at V_{DS} = –100 V for transfer characteristics. The drain-source channel length (L) and width (W) are 50 μm and 3000 μm respectively.

3. Conclusions

In summary, we have synthesized a new polythiophene derivative with conjugated phenothiazine-vinylene side chains, **PTZV-PT**, by the Stille coupling method. The polymer possesses good solubility in common organic solvents and high thermal stability. The absorption spectra of the **PTZV-PT** film show a broad absorption band covering the wavelength range from 250 to 650 nm, which is composed of the absorption of the conjugated side chains peaked at ca. 411 nm and that of the conjugated main chains peaked at ca. 535 nm. The PL spectra of **PTZV-PT** revealed that exciton energy transfer occurred from the conjugated side chains to the main chains of the polymer. The hole mobility of the polymer measured by SCLC method reached 4.7×10^{-3} $cm^2V^{-1}s^{-1}$, which is a relatively higher value for conjugated polymers, indicating that the conjugated phenothiazine-vinylene side chains may promote the hole transportation of the polymer. OFETs based on **PTZV-PT** provide superior FET performance, affording a hole mobility of 6.8×10^{-3} $cm^2V^{-1}s^{-1}$ with an on/off ratio of 2.5×10^4. These results suggest that the copolymers with phenothiazine-vinylene conjugated side chain represent a useful class of solution processable semiconductors for fabrication of OFET circuits for printed electronics. The broad absorption and higher hole mobility indicate **PTZV-PT** could also be a promising polymer photovoltaic material.

4. EXPERIMENTAL SECTION

Materials

3-Methyl thiophene was purchased from Aldrich Chemical Co, $Pd(Ph_3)_4$, $(C_4H_9)_3SnCl$, BuLi were obtained from Alfa Asia Chemical Co, and they were used as received. Tetrahydrofuran (THF) was dried over Na/benzophenone ketyl and freshly distilled prior to use. Toluene was dried over molecular sieves and freshly distilled prior to use. The other chemical reagents were common commercial level and used as received without further purification.

Synthesis of monomers and polymer

The synthetic routes of the monomers and polymer are shown in Scheme 2. The detailed synthetic procedures are as follows:

10-n-Octylphenothiazine (1) Phenothiazine (10 g, 50 mmol), sodium hydroxide (20.0 g, 500 mmol), and dimethyl sulfoxide (DMSO) (100 mL) were placed in a 250 mL two-necked flask, the mixture was stirred for half an hour, octyl bromide (7.7 mL, 55 mmol) was added dropwisely to the reaction mixture in twenty minutes, and then this mixture was stirred for 24 h at room temperature. The reaction mixture was poured into water, extracted with methylene chloride and then dried with $MgSO_4$. The resulting liquid was purified by column chromatography using petroleum ether as eluent. The product yield was 93% (13.2 g) as colorless liquid. MS: m/z= 311(M^+). ^1H NMR (*δ/ppm*, $CDCl_3$): 7.11-7.09 (m, 4H), 6.89-6.80 (dd, 4H), 3.80-3.77(t, 2H), 1.77 (d, 2H), 1.37-1.24 (m, 10H), 0.87(t, 3H).

10-*n*-Octylphenothiazine-3-carbaldehyde (2) A 100 mL three-necked flask containing 10 mL (220 mmol) of anhydrous DMF was cooled in an ice bath. To this solution, 3 mL (32 mmol) of phosphorus oxychloride was added dropwisely for 30 min. Compound 1 (5.486 g, 17.64 mmol) in 30 mL of 1, 2-dichloroethane was added to the above solution and heated to ca. 90°C for 36 h. This solution was cooled to room temperature, poured into ice water, and neutralized to pH 6-7 by dropwise addition of saturated aqueous sodium hydroxide solution. The mixture was extracted with chloroform. The organic layer was dried with anhydrous $MgSO_4$ and then concentrated under reduced pressure. The crude product was purified by column chromatography. The product was obtained (5 g, 84%) using petroleum ether and ethyl acetate (10:1) as the eluent by column chromatography under reduced pressure. FTIR (KBr, cm^{-1}): 2730 (s,-CHO). MS: m/z= 339(M^+). ^1H NMR (*δ/ppm*, $CDCl_3$): 9.71 (s, 1H), 7.56 (d, 1H), 7.50 (s, 1H), 7.10-7.02(m, 2H), 6.88(t, 1H), 6.81 (t, 2H), 3.82 (t, 2H), 1.77(q, 2H), 1.28 (m, 10H), 0.85(m, 3H). Calculated for $C_{21}H_{25}NSO$: C, 74.33; H, 7.37; N, 4.13; found: C, 74.21; H, 7.28; N, 4.11.

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

Compound **3** was synthesized with the route reported in Ref[29], the crude product was purified by flash column chromatography eluting with petroleum ether/ethyl acetate (1:1). After purification, compound **3** was recovered as a pale yellow oil (22 g, 70% yield). MS: m/z= 390(M^+). ^1H NMR (*δ/ppm*, $CDCl_3$): 7.00 (s, 1H), 4.08 (m, 4H), 3.10 (d, 2H), 1.29 (t, 6H).

2, 5-dibromo-3-(10-n-octyl- phenothiazine-vinylene) thiophene Monomer (4)

Under an ice–water bath, compound **3** (2.1 g, 5.3 mmol) was dissolved in 10 mL DMF and CH_3ONa (0.4 g, 7.3 mmol) was added. After 5 min, compound **2** (1.77 g, 5.24 mmol) was added dropwisely to the solution. After 2 h, the solution was poured into methanol, filtered, and the orange-brown liquid of **4** was obtained (2.48 g, 82%) using petroleum ether as eluent. FTIR (KBr, cm^{-1}): 965(s, trans CH=CH). MS-TOF: m/z= 577(M^{+}). ^{1}H NMR (*δ/ppm*, $CDCl_3$): 7.24-7.18(d, 2H), 7.13-7.09(d, 3H), 6.89-6.68(m, 5H), 3.80(s, 2H), 1.77(t, 2H), 1.42-1.41(s, 2H), 1.25(s, 8H), 0.86(s, 3H). Calculated for $C_{26}H_{27}NS_2Br_2$: C, 54.07; H, 4.68; N, 2.43; found: C, 53.92; H, 4.65; N, 2.45.

2, 5-bis(tributylstannyl)thiophene (**5**). This compound was synthesized by the literature procedure.[13a] GC-Ms: m/z = 664. Yield: 72%. Purity (by GC-Ms) ≥96%. ^{1}H NMR (*δ/ppm,* $CDCl_3$): 7.34 (s, 2H), 1.60 (m, 12H), 1.39 (m, 12H), 1.09 (m, 12H), 0.91 (t, 18H). Calculated for $C_{28}H_{56}SSn_2$: C , 50.78; H , 8.52; found: C , 50.12; H , 8.75.

Synthesis of polymer PTZV-PT

$Pd(PPh_3)_4$ (50 mg， 0.043 mmol)，monomer **4** (0.594, 1.03 mmol)， monomer **5** (0.69 g， 1.03 mmol) were put into a three-necked flask. The mixture was flushed with argon for 10 min, and then 18 mL toluene was added. At 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 of methanol and then filtered into a Soxhlet thimble. Soxhlet extractions were performed with methanol, hexane, and $CHCl_3$. The polymer was recovered from the $CHCl_3$ fraction by rotary evaporation. The solid was dried under vacuum overnight. The dark-purple polymer of **PTZV-PT** was obtained for 350 mg (yield: 68%). ^{1}H NMR (*δ/ppm*, $CDCl_3$): 7.36-7.08 (br, 7H), 6.82-6.52 (br, 5H), 3.74-3.71 (br, 2H), 1.74-1.72 (br, 2H), 1.22 (br, 10H), 0.97-0.82 (br, 3H). ^{13}C NMR (*δ/ppm*, $CDCl_3$): 144.7, 131.6, 127.3, 124, 122.3, 115.2, 114.9, 47.5, 31.9, 29.6, 26.7, 22.9, 14.1. Elemental Anal. Calcd. For $(C_{30}H_{29}S_3N)_n$: C, 72.14; H, 5.81; N , 2.81. Found: C, 72.04; H, 5.74; N, 2.76. M_w: 5.4 × 10^4 ; PDI:1.48.

Instruments and Measurements

^{1}H NMR spectra were recorded using a Bruker AM-400 spectrometer, with tetramethylsilane (TMS) as the internal reference, chemical shifts were recorded in ppm. Elemental analysis was measured on a Flash EA 1112 elemental analyzer. Fourier transforms infrared (FT-IR) spectra were recorded on a BIO FTS-135 spectrometer by dispersing samples in KBr disks. Molecular weight and polydispersity of polymers were determined by gel permeation chromatography (GPC) analysis with polystyrene as standard (Waters 515 HPLC pump, a Waters 2414 differential refractometer, and three Waters Styragel columns (HT2, HT3, and HT4)) using THF as eluent at a flow rate of 1.0 mL/min at 35°C. Thermogravimetric analysis (TGA) was conducted on a Shimadzu DTG-60 thermogravimetric analyzer with a heating rate of 10 K/min under a nitrogen atmosphere. Differential scanning calorimetric measurements (DSC) of the polymer was performed under nitrogen at a heating rate of 20 K/min with a Perkin Elmer DSC-7 instrument. The UV–vis absorption spectra were recorded on a JASCO V-570 spectrophotometer. The photoluminescence (PL) spectra were obtained with a JASCO FP-6600 Fluorescence spectrophotometer.

The cyclic voltammogram was recorded with a Zahner IM6e electrochemical workstation (Germany) using polymer film on platinum disk as the working electrode, platinum wire as the counter electrode and Ag/Ag^+ (0.1 M) as the reference electrode with a nitrogen-saturated acetonitrile (CH_3CN) solution containing 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6).

The structures of the polymer films were investigated by a SPI 3800N atomic force microscope (AFM) in contacting mode with a 1 μm scanner. X-ray diffraction (XRD) measurements of the thin film were carried out with a 2-kW Rigaku X-ray diffraction system. XRD patterns were obtained using Bragg-Brentano Geometry (θ-2θ) with Cu Kαradiation as an X-ray source in the reflection mode at 45 kV and 300 mA.

Fabrication of OFET Devices

Thin-film OFETs were fabricated with top-contact configuration. An n-doped Si wafer with a 450 nm thick thermally grown silicon dioxide layer (capacitance of 10 nF/cm^2) was used as the substrate. The substrates were cleaned in water, alcohol, acetone, and rinsed in deionized water, and then modified by OTS. Thin polymer films were prepared by spin coating of a 0.3 wt% solution of **PTZV-PT** in chloroform onto the OTS-modified SiO_2/Si substrates at a speed of 2500 rpm (revolutions per minute) for 40 s at room temperature. After dried at 80℃ and annealed at 155℃ under N_2 for half an hour, gold film (50 nm) was deposited on the organic layer to form the drain and source electrodes, for a typical device, the drain-source channel length (L) and width (W) are 50 μm and 3000 μm respectively. OFET measurements were performed at room temperature using a HP 4140B semiconductor parameter analyzer under ambient conditions.

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a TOC Graphic for *Macromolecules*

ma071402v	Polythiophene Derivative with Phenothiazine-Vinylene Conjugated Side Chain: Synthesis and its Application in Field-Effect Transistors Yingping Zou^{1,2}, Weiping Wu, ^{1,2} Guangyi Sang^{1,2},Yi Yang^{1,2}, Yunqi Liu^{*1}, Yongfang Li^{*1}