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Synthesis, Hole Mobility, and Photovoltaic Properties of Cross-Linked Polythiophenes with Vinylene−Terthiophene−Vinylene as Conjugated Bridge

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ABSTRACT: A class of cross-linked polythiophenes with different ratio (2%, 4%, 8%) of vinylene−terthiophene−vinylene (**VTThV**) conjugated bridges (**PT−VTThV2**, **PT−VTThV4**, and **PT−VTThV8**) were synthesized. The cross-linking influenced the absorption spectra of the polymer solutions very little, but it resulted in blue-shift of the absorption spectra of the polymer films by ca. 28−39 nm. Cyclic voltammograms display that the p-doping/dedoping and n-doping/dedoping processes of all the cross-linked polythiophenes are reversible and the electrochemical bandgaps increased a little with the increase of the content of the conjugated bridges. The hole mobility values determined from the space-charge-limited current (SCLC) model reached 4.70×10^{-3} for **PT−VTThV2**, 2.58×10^{-3} for **PT−VTThV4**, and 9.48×10^{-4} cm^2/(V s) for **PT−VTThV8**, respectively. The hole mobility of **PT−VTThV2** with 2% **VTThV** conjugated bridges is about three orders higher than that of the corresponding polymer **P1** without the conjugated bridges. The power conversion efficiency of the polymer solar cell based on the blend of **PT−VTThV2** and PCBM (1:1, w/w) reached 1.72% under the illumination of AM 1.5, 100 mW/cm^2, which is two times of that of the device based on **P1**. The results indicate that the cross-linking with the **VTThV** conjugated bridges obviously improved charge transportation the photovoltaic properties of the conjugated polymers.

1. Introduction

Polythiophenes are a class of important π-conjugated polymers, which can be used in many organic optoelectronic devices such as polymer solar cells (PSCs),[1] light-emitting diodes (LEDs),[2] and field-effect transistors (FETs).[3] Among the polythiophene derivatives, the most familiar and important one is regioregular poly(3-hexylthiophene) (rr-P3HT), which has been investigated widely for optoelectronic application, especially as donor material in the field of PSCs. P3HT can be blended with many acceptors, such as fullerene derivatives,[4] conjugated polymers,[5] inorganic nanocrystals,[6] small organic molecules,[7] dye,[8] and even chlorophyll.[9] At present, the highest power conversion efficiency (PCE) of the PSCs has reached 5%[10] which is based on P3HT and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) by thermal annealing after the device fabrication.

The better photovoltaic properties of P3HT should be attributed to two major aspects: better absorption in the visible region and the higher charge mobility.[11] In order to synthesize new efficient photovoltaic materials, improving absorption spectrum and charge mobility is necessary and important. In order to make the polymers absorb more photons, many low band gap polymers[12] and side-chain conjugated polymers[13] have been synthesized and applied to the PSCs. However, it is comparatively difficult to improve the charge mobility of the conjugated polymers in comparison with improving the absorption spectrum. For the rr-P3HT, it is commonly accepted that the higher hole mobility is mainly due to the regular arrangement of side chain allowing efficient $\pi-\pi$-stacking of the polythiophene backbones and form thin film with nanocrystalline lamellae.[14] Thus, there is no too many good methods to increase its hole mobility except for increasing the molecular weight and decreasing the polydispersity index.[15] The change of side chain might decrease the $\pi-\pi$-stacking of the polythiophene backbones and hinder the hole transportation.

Recently, Weder et al.[16] found that the network structure of cross-linked conjugated polymers can have significant benefits for the electronic communication between chains and thus have higher hole mobility. On the polymer−fullerene bulk-heterojunction PSC structure, the conjugated bridges in the cross-linked polymers should have good role on the charge transportation between the backbones (see Figure 1). In our early works, we have also synthesized a class of cross-linked polythiophenes by conjugated bridges of vinylene−phenylene−vinylene (**VPV**) and found the cross-linked polythiophenes with suitable cross-linking degree show higher hole mobility and thus improved power conversion efficiency (PCE) of the PSC based on the polymer.[17] However, the cross-linked polythiophenes with the **VPV** conjugated bridges show blue-shifted absorption due probably to the distortion of the polymer main chains caused by the short rigid bridge. In order to avoid the negative effect of the short **VPV** conjugated bridges on the polymers, in this paper, we synthesized a new class of cross-linked polythiophenes with longer vinylene−terthiophene−vinylene (**VTThV**) as conjugated bridge. We investigated the effect of content of the conjugated bridges on the optical, electrochemical, hole mobility, and photovoltaic properties in detail. These results will help us to design and synthesize more promising photovoltaic materials with higher hole mobility.

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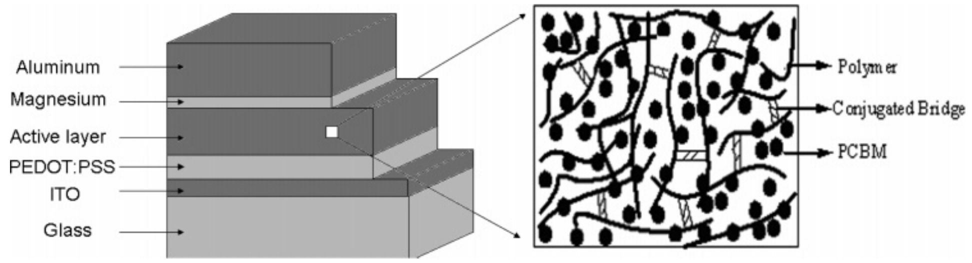
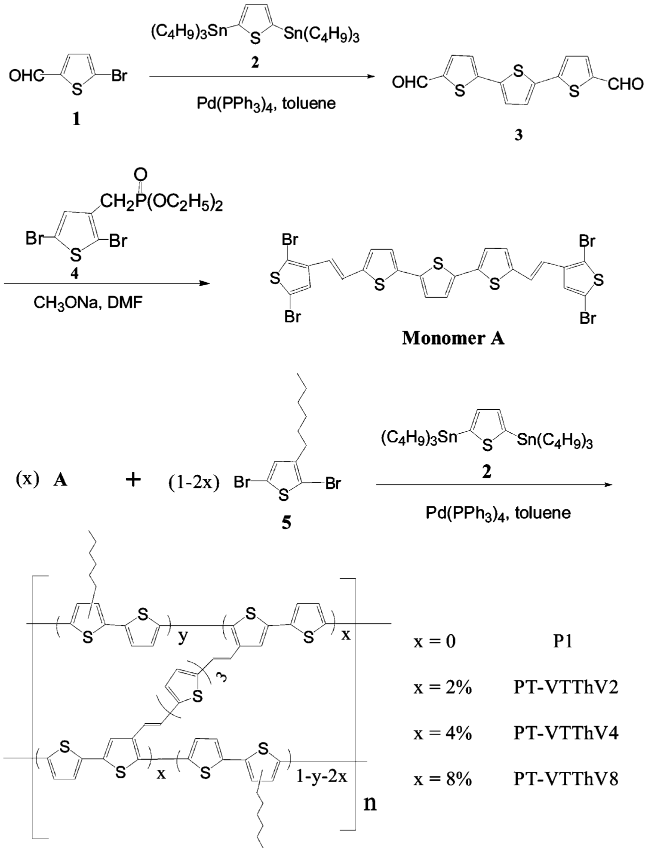


Figure 1. Sketch diagram of the bulk-heterojunction polymer solar cells based on the blend of the cross-linked polythiophenes and fullerene for improving the hole transportation.

Scheme 1. Synthetic Routes of the Monomer A and the Cross-Linked Polythiophene Derivatives PT−VTThV



2. Results and Discussions

2.1. Material Synthesis and Structural Characterization. The synthetic routes of the monomer A and polymers are shown in Scheme 1. Monomer A was synthesized by the Wittig−Hornor reaction. The ^{1}H NMR spectrum of monomer A is shown in Figure 2, where all the peaks were assigned to their corresponding hydrogen atoms according to the chemical shift, integral area, coupling constant, and experience. Like many monomers synthesized by this method,[13] there is no cis-isomer of the compound.

The cross-linked polythiophene were synthesized by Stille coupling reaction[17,18] by adding different ratio of cross-linker A (2%, 4%, 8%) as seed. The ^{1}H NMR spectra of the three polymers are shown in Figure 3, The regioregularity of the three cross-linked polythiophenes can be calculated from the ratio of the integral area of the peaks at 2.5−2.8 ppm.[17,19] We measured the differential scanning calorimetry (DCS) of the three cross-linking polymers for determining the glass transition temperature (T_g) of the polymers, but the DSC thermograms of the polymers only show small peaks at 138, 140, and 144 °C for **PT−VTThV2**, **PT−VTThV4**, and **PT−VTThV8**, respectively (see Figure S1, Supporting Information). If the small DSC peaks could be ascribed to the T_g, then the glass transition temperature of **PT−VTThV2**, **PT−VTThV4**, and **PT−VTThV8** was 138, 140, and 144 °C, respectively, and it increased with the increase of the cross-linking degree of the polymers.

2.2. Optical Properties. Figure 4 shows the UV−visible absorption spectra of the cross-linked polythiophenes with the conjugated bridges of vinylene−terthiophene−vinylene (**VTThV**). When the content of the cross-linker **VTThV** is 2% (**PT−VTThV2**), the absorption peak of the polymer solution was at 476 nm, which is the same as that of poly(3-hexylthiophene-*co*-thiophene) (**P1**).[17] When the content of the cross-linker doubles to 4% (**PT−VTThV4**) and doubles again to 8% (**PT−VTThV8**), the absorption peaks of the **PT−VTThV** solutions blue-shifted to 472 and 459 nm respectively. For the polymer films, the absorption peaks of **PT−VTThV2−8** blue-shifted about 28−39 nm than that of **P1**. Compared with the vinylene−phenylene−vinylene (**VPV**) conjugated bridge,[17] the longer **VTThV** conjugated bridge influenced less (less blue-shifted) on the absorption spectra of the polymers. Perhaps the cross-linking of the conjugated bridges makes the polymer main chains distorted at some extent, so resulting in the blue shift of the absorption. The distortion of the main chains should be less for the polymers with the longer **VTThV** conjugated bridges than that with *VPV* conjugated bridges. The detailed optical data of the polymers are listed in Table 1.

2.3. Electrochemical Properties. The electrochemical properties of the three **PT−VTThV** polymer films on Pt electrode were investigated by cyclic voltammetry (CV). As shown in Figure 5, the three cross-linked polythiohenes show similar reversible p-doping/dedoping (oxidation/rereduction), and n-doping/dedoping (reduction/reoxidation) processes. The HOMO energy level, the LUMO energy level, and the electrochemical bandgaps (E_g^{EC}) of the polymers were calculated from onset oxidation potentials (E_{on}^{ox}) and onset reduction potentials (E_{on}^{red}), respectively, according to the following equations:[20]

$$\mathrm{HOMO} = -e(E_{on}^{ox} + 4.71)\ (\mathrm{eV})$$

$$\mathrm{LUMO} = -e(E_{on}^{red} + 4.71)\ (\mathrm{eV})$$

$$E_g^{EC} = e(E_{on}^{ox} - E_{on}^{red})\ (\mathrm{eV})$$

where the potentials are referred to an Ag/Ag$^+$ reference electrode. The results of the electrochemical measurements of **PT−VTThV2−8** together with **P1** (for comparison) are also listed in Table 1.

It is interesting that the HOMO and LUMO energy levels of **PT−VTThV2** are entirely the same as those of **P1**, which indicates that small amount of 2% **VTThV** bridges influences little on the electrochemical properties of the polymers. When the content of the conjugated bridges increases further, the HOMO energy level raised and the LUMO energy level dropped

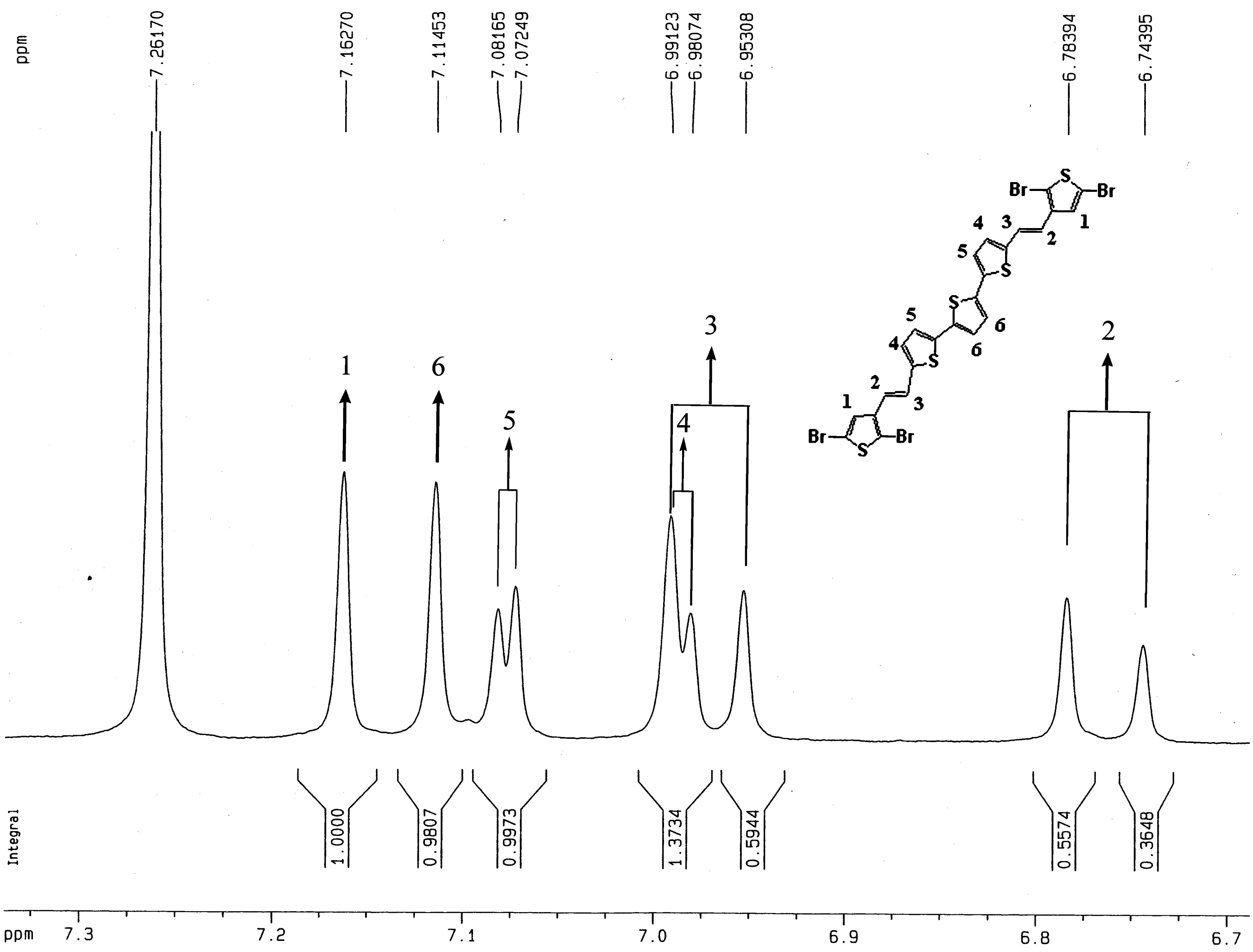


Figure 2. ^{1}H NMR spectrum of monomer **A**.

for some extent and thus leads to an increased electrochemical bandgaps. These results are in accordance with the results of optical measurements.

2.4. Hole Mobility. As mentioned above, the hole mobility is a very important parameter for photovoltaic application of the conjugated polymers, and the main purpose of synthesizing the cross-linked polythiophenes with conjugated bridges is for improving the hole mobility of the polymers. Here the hole mobility of the **PT−VTThV** polymers was determined from the space-charge-limited current (SCLC) model[21] with a device structure of ITO/PEDOT:PSS/polymer/Au. The film thickness of **PT−VTThV2, PT−VTThV4**, and **PT−VTThV8** is 124, 118, and 115 nm, respectively. The current−voltage data are shown in Figure 6a. According to the following eq 1[21]

$$J \cong (9/8)\epsilon\epsilon_0\mu_0 V^2 \exp(0.89\sqrt{V/E_0L})/L^3 \qquad (1)$$

we can get eq 2

$$Ln(JL^3/V^2) \cong 0.89(1/E_0)^{0.5}(V/L)^{0.5} + Ln(9\epsilon\epsilon_0\mu_0/8) \qquad (2)$$

where μ_0 is the zero-field mobility, E_0 is the characteristic field, J is the current density, ϵ is the dielectric constant of the polymer, ϵ_0 is the permittivity of the vacuum, L is the thickness of the polymer layer, $V = V_{\mathrm{appl}} - V_{\mathrm{bi}}$, V_{appl} is the applied potential, and V_{bi} is the built-in potential (in this device structure, $V_{\mathrm{bi}} = 0.2$ V). According to eq 2, from the plots of $\ln(JL^3/V^2)$ vs $(V/L)^{0.5}$, as shown in Figure 5b, hole mobility can be calculated from the intercept of the corresponding lines on the axis of $\ln(JL^3/V^2)$. The hole mobility calculated is 4.70×10^{-3} cm^2/(V s), 2.58×10^{-3} cm^2/(V s) and 9.48×10^{-4} cm^2/(V s) for **PT−VTThV2**, **PT−VTThV4**, and **PT−VTThV8** respectively, which is greatly higher than that (5.23×10^{-6} cm^2/(V s)) of **P1** without the conjugated bridges.[17] Compared with the cross-linked polythiophenes with **VPV** conjugated bridges, the hole mobility of the polymer with 2% conjugated bridges (**PT−VTThV2**) is higher than that of the cross-linked polymer with 2% **VPV** conjugated bridges, probably because that the longer **VTThV** conjugated bridges make the backbone distorted less and benefit the hole transportation at the small amount conjugated bridges. The hole mobilities of the **PT−VTThV** polymers decreased with the further increase of the content of the **VTThV** conjugated bridges, due probably to the increased disorder of the morphology of the polymers at the higher content of the **VTThV** conjugated bridges.

2.5. Photovoltaic Properties. The higher hole mobility of the **PT−VTThV** polymers would benefit the charge transportation in the polymer solar cells (PSCs), and thus may improve the photovoltaic properties of the polymers. The bulk heterojunction-typed PSCs were fabricated with a structure of ITO/PEDOT:PSS (30 nm)/polymer:PCBM (1:1 wt %)/Mg (10 nm)/Al (150 nm), for studying the photovoltaic properties of the polymers. The photovoltaic data of poly(3-hexylthiophene-*co*-thiophene) (**P1**) without the conjugated bridges were also measured for comparison.

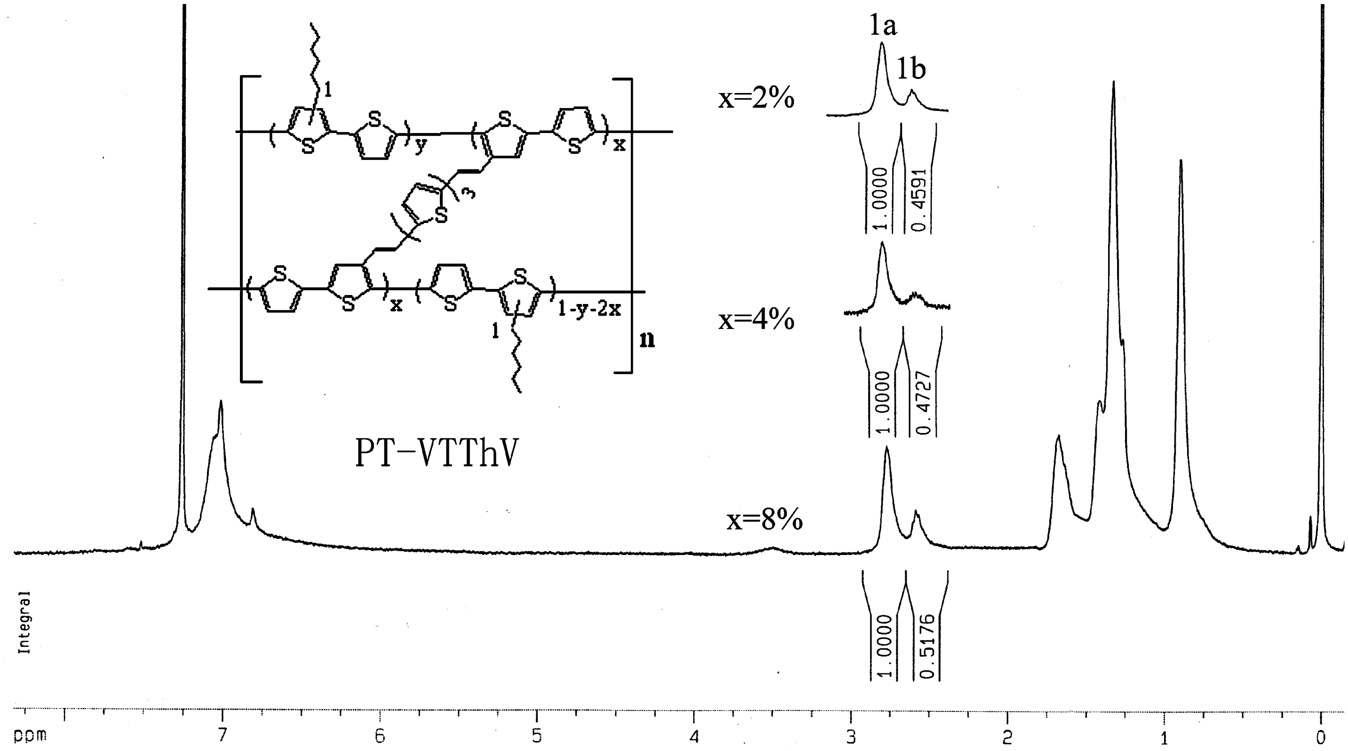


Figure 3. The ^{1}H NMR spectra of the cross-linked polymers **PT−VTThV**.

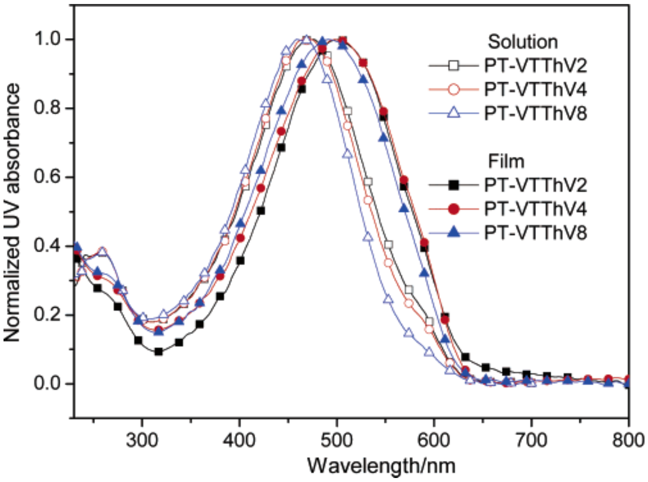


Figure 4. UV−vis absorption spectra of the polymer solutions in $CHCl_3$ and the polymer films on a quartz plate.

Table 1. Optical and Electrochemical Properties of the Cross-Linked PT−VTThV Polymers

	UV-vis absorption data		cyclic voltammetry		
polymers	solution λ_{max} (nm)	film λ_{max} (nm)	p-doping E_{on}^{ox}/HOMO (V/eV)	n-doping E_{on}^{red}/LUMO (V/eV)	E_g^{EC} (eV)
P1	476	530	0.35/−5.06	−1.94/−2.77	2.29
PT−VTThV2	476	502	0.35/−5.06	−1.94 /−2.77	2.29
PT−VTThV4	473	498	0.35/−5.06	−1.96/−2.75	2.31
PT−VTThV8	459	491	0.40/−5.11	−1.97/−2.74	2.37

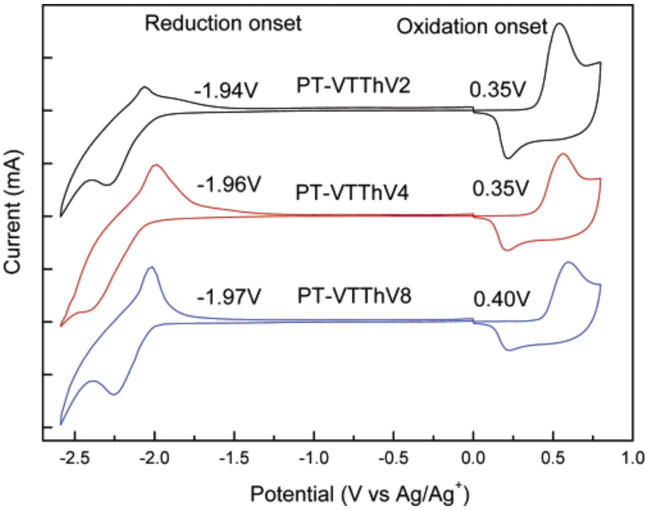


Figure 5. Cyclic voltammograms of the **PT−VTThV** polymer films on platinum plates in an acetonitrile solution of 0.1 mol/L $[Bu_4N]PF_6$ (Bu = butyl) with a scan rate of 0.1 V/s.

Figure 7 shows $I-V$ curves of the devices, and Table 2 lists the corresponding open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), fill factor (FF), and power conversion efficiency (PCE) of the devices under the illumination of AM 1.5, 100 mW/cm^2. The V_{oc} of the devices based on **PT−VTThV2** and **PT−VTThV4** are almost the same as that of **P1**, which could result from the same HOMO energy levels of the three polymers because the V_{oc} is related to the energy difference between the LUMO of the acceptor (PCBM) and the HOMO of the donor (conjugated polymers).[22] The V_{oc} of the device based on **PT−VTThV8** increased to 0.73 V because of its lower HOMO energy level. Benefited from the higher hole mobilities of the **PT−VTThV** polymers, the I_{sc} of the three cross-linked polythiophenes are all higher than that of **P1**. The I_{sc} of **PT−VTThV2** reached 6.82 mA/cm^2, and PCE of the PSC based on **PT−VTThV2** reached 1.72% which is two times of that of the PSC based on **P1** without the conjugated bridges. The improvement of the photovoltaic properties of the cross-linked polymers could result from the increase of their hole mobilities since there is no improvement on the absorption spectra of the polymers. In fact, the absorption spectra of the cross-linked polymers blue-shifted for some extent. If we could improve the absorption

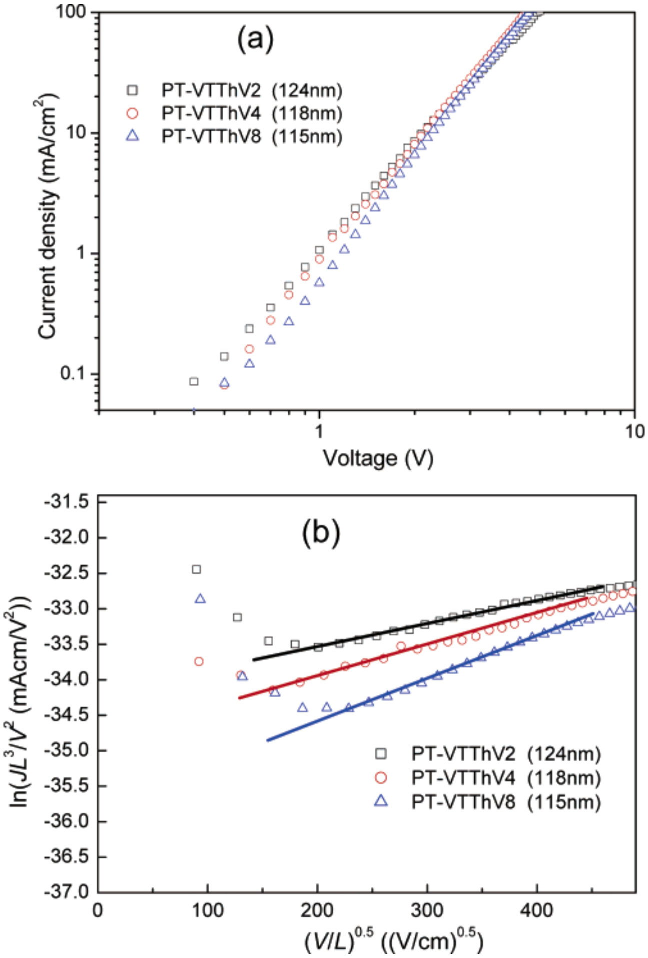


Figure 6. (a) Current−voltage data from the device of ITO/PEDOT:PSS/polymer/Au. (b) Plots of ln(JL^3/V^2) vs $(V/L)^{0.5}$ according to the SCLC model equation. The numbers shown in the plots are the film thickness of the samples.

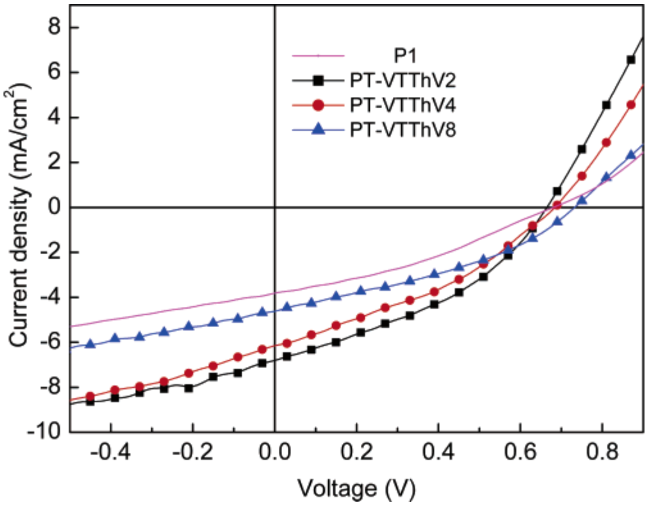


Figure 7. $I-V$ curves of the polymer solar cells based on the **PT−VTThV** polymers under the illumination of AM 1.5, 100 mW/cm^2.

spectra of the cross-linked polymers, which is the next target of our research, the photovoltaic properties could be improved further.

Figure 8 shows the input photon to converted current efficiency (IPCE) of the PSCs based on the **PT−VTThV** polymers. The shape of the IPCE curves of the devices based on the three polymers is very similar to their absorption spectra, which indicate that all the absorption of the polymers contributed to the photovoltaic conversion. The IPCE values decreased from **PT−VTThV2** to **PT−VTThV4** and to **PT−VTThV8**, which should be related to the decrease of the hole mobilities of the polymers with the further increase of the content of the conjugated bridges.

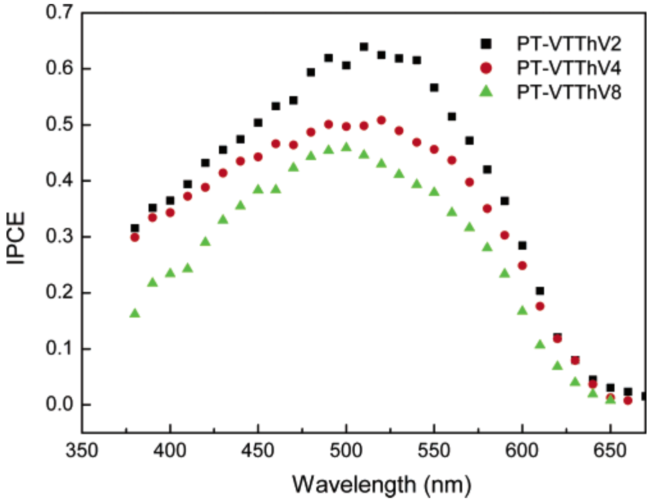


Figure 8. IPCE of the polymer solar cells based on the cross-linked **PT−VTThV** polymers.

Table 2. Photovoltaic Performance of the Polymer Solar Cells Based on the PT−VTThV Polymers

polymer	V_{oc} (V)	I_{sc} (mA/cm^2)	FF (%)	PCE (%)
P1	0.68	3.80	34	0.87
PT−VTThV2	0.67	6.82	38	1.72
PT−VTThV4	0.68	6.14	35	1.47
PT−VTThV8	0.73	4.65	36	1.21

Table 3. Molecular Weight, Elemental Analysis, and Regioregularity of the PT−VTTV Polymers

	mol wt by GPC		elemental analysis calculated[a]/found			
polymers	M_n	PDs	C	H	S	% regio-regularity[b]
PT−VTTV2	25K	1.9	67.38/66.98	6.30/6.18	26.32/26.11	69
PT−VTTV4	33K	2.3	67.08/66.35	6.10/6.01	26.81/26.38	68
PT−VTTV8	38K	2.1	66.50/66.02	5.74/5.43	27.77/27.03	66

[a] Calculated according to the formula $[(C_{14}H_{16}S_2)_{1-2x} + (C_{32}H_{16}S_7)_x]$. [b] Calculated from the ratio of the integral area of peak **1a** to the sum of the integral area of peaks **1a** and **1b** in Figure 3

3. Conclusion

Three cross-linked polythiophene derivatives with different ratio (2%, 4%, 8%) of vinylene−terthiophene−vinylene (**VTThV**) conjugated bridges, **PT−VTThV2, PT−VTThV4** and **PT−VTThV8,** were designed and synthesized in this work. It was found that the cross-linking with the **VTThV** conjugated bridges helped the charge transportation of the polymers, but made the absorption spectrum blue-shifted a little. The maximum hole mobility reached 4.70 × 10^{-3} cm^2/(V s) (SCLC method) for the polymer **PT−VTThV2** with 2% **VTThV** conjugated bridges, which is about three orders higher than that of the corresponding polymer **P1** without the conjugated bridges. The power conversion efficiency of the polymer solar cell based on the blend of **PT−VTThV2** and PCBM (1:1, w/w) reached 1.72% under the illumination of AM 1.5, 100 mW/cm^2, which is two times of that of the device based on **P1**. The photovoltaic performance of the cross-linked polythiophenes can be further improved if we could improve their absorption spectra by proper method.

4. Experimental Section

Materials. All reagents and chemicals were purchased from Alfa and Aldrich. Toluene and DMF were freshly distilled prior to use. The other materials were used without further purification. The following compounds were synthesized according to the literature procedure: 5-bromothiophene-2-carbaldehyde (**1**),[23] 2,5-bis(tributylstannyl)thiophene (**2**),[24] 5,5′′-diformyl-2,2′:5′,2′′-terthiophene (**3**),[24] (2,5-dibromothiophen-3-ylmethyl)phosphonic acid diethyl ester (**4**).[13] 2,5-dibromo-3-hexylthiophene (**5**),[25] [6,6]-phenyl-C61-butyric acid methyl ester (**PCBM**).[26]

Characterization. ^{1}H NMR (400 MHz) spectra were measured on a Bruker spectrometer. Absorption spectra were taken on a Hitachi U-3010 UV−vis spectrophotometer. The molecular weight of polymers was measured by GPC method, and polystyrene was used as a standard. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e electrochemical workstation. A Pt plate coated with a thin polymer film was used as the working electrode. A Pt wire and an Ag/Ag^+ electrode were used as the counter electrode and reference electrode respectively.

Fabrication and Characterization of Polymer Solar Cells. The PSCs were constructed in the traditional sandwich structure through several steps. Poly(3,4-ethylene dioxythiophene)−poly(styrene sulfonate) (PEDOT:PSS, from Bayer AG) was spin-coated from an aqueous solution on a precleaned indium tin oxide (ITO)/glass substrate giving a thickness of about 30 nm as measured by Ambios Technology XP-2 surface profilometer, and was dried subsequently at 150 °C for 10 min. The photosensitive blend layer of polymer and PCBM was prepared by spin-coating the chlorobenzene solution of the polymers and PCBM (1:1 w/w) with the polymer concentration of 12 mg/mL on the ITO/PEDOT:PSS electrode, and dried at 80 °C for 30 min, in a nitrogen-filled glove box. The cathode of devices, consisting of 10 nm of magnesium and 150 nm of aluminum, was thermally deposited on the top of polymer film at 5×10^{-5} Pa. The active area of the device is 4 mm^2. Current density−voltage ($I-V$) characteristics were measured by a computer-controlled Keithley 236 source measurement unit (SMU) in dark and under the illumination of AM 1.5, 100 mW/cm^2 from the ITO side. The light intensity at each wavelength was calibrated with a calibrated Silicon photovoltaic cell. All these measurements were performed under ambient atmosphere at room temperature.

Synthesis of (*E*,*E*)-5,5′′-Di[2-(2,5-dibromothiophen-3-yl)vinyl]-2,2′:5′,2′′-terthiophene (Monomer A). The synthetic route of Monomer A is shown in Scheme 1. Under an ice−water bath, 5,5′′-diformyl-2,2′:5′,2′′-terthiophene (**3**) (1.52 g, 5 mmol) and (2,5-dibromothiophen-3-ylmethyl)phosphonic acid diethyl ester (**4**) (3.92 g, 10 mmol) were dissolved in 50 mL of DMF, and then CH_3ONa (0.65 g, 12 mmol) in 20 mL of DMF was added dropwise to the solution. After reaction for 2 h at room temperature, the solution was poured into cold CH_3OH, filtered and purified by column chromatography (silica gel, PE/CH_2Cl_2, 10:1) to give 1.25 g (32%) of monomer **A** as a red powder. GC−MS: $m/z = 776$. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.16 (s, 2H, Th−H), 7.11 (s, 2H, Th−H), 7.07 (d, 2H, Th−H), 6.99 (d, 2H, Th−H), 6.97 (d, 2H, CH═CH), 6.76 (d, 2H, CH═CH). Anal. Calcd for $C_{24}H_{12}Br_4S_5$: C, 36.94; H, 1.55; Br, 40.96; S, 20.55. Found: C, 36.52; H, 1.64; Br, 40.59; S 20.43.

Synthesis of the Polymers via Stille Coupling Reaction. These three cross-linked polythiophenes were prepared with same coupling procedure (see Scheme 1) by adding different ratio of cross-linker **A** (x = 2%, 4%, 8%). The detailed synthesis processes are as follows.

Cross-linker **A** (x mmol), compound **4** ((1 − 2x) mmol), and compound **2** (0.67 g; 1.0 mmol) were put into a three-neck flask. Then 15 mL of toluene was added and then the mixture was flushed with argon for 10 min. $Pd(PPh_3)_4$ (50 mg) was added and another flushing with argon for 10 min was done. Under 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 molecular weight, elemental analysis, and regioregularity of the three polymers are shown in Table 2.

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Supporting Information Available: Figure S1, showing the DSC thermograms of the cross-linking polymers. These materials are available free of charge via the Internet at http://pubs.acs.org.

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