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Poly(thienylene-benzothiadiazole-thienylene-vinylene): A narrow bandgap polymer with broad absorption from visible to infrared region

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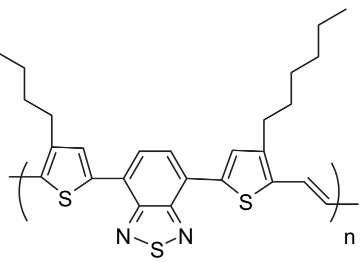
ABSTRACT

Poly(thienylene-benzothiadiazole-thienylene-vinylene) (PTBTV) has been synthesized by Pd-catalyzed Stille-coupling method. The polymer shows broad absorption from visible to infrared region. The maximum absorption of PTBTV in solution and film state is at 600 nm and 614 nm, respectively. The absorption edge of PTBTV film is at 813 nm, indicating a narrow bandgap of 1.50 eV. The HOMO and LUMO energy levels of PTBTV are −4.99 eV and −3.49 eV, respectively. Polymer solar cell based on the blend of PTBTV as donor and [70] PCBM as acceptor was fabricated, the power conversion efficiency of the device is 0.51% under the illumination of AM1.5, 100 mW/cm^2.

1. Introduction

In the past decades, conjugated organic and polymer materials have been the focus of great research activity, mainly due to their interesting electronic and optoelectronic properties. They are being investigated for a variety of applications, including organic field-effect transistors (OFETs) [1–4], organic light-emitting diodes (OLEDs), polymer solar cells (PSCs) [5–8] etc. Poly(thienylenevinylene) derivatives (PTVs) are one important class of conjugated polymers, which possess smaller bandgap (below 1.8 eV) [9,10] than polythiophene (PT) derivatives [11]. The smaller bandgap of PTVs makes the polymer absorption spectra red-shifted and matching well with the solar spectrum, which is attractive for the application as photovoltaic polymers. But at present, the power conversion efficiency (PCE) of the PSCs based on PTVs is quite low [12,13], probably due to the nonluminescent characteristic of PTVs. Obviously, the structure modification of PTVs could be an efficient way to look for new conjugated polymers for the application in PSCs.

For broadening the absorption spectrum of PTVs, Hou et al. synthesized poly(thienylenevinylene) with thienylene-vinylene conjugated side chain, biTV-PTV3 [14]. The polymer film shows a broad absorption band covering the whole visible region from 350 nm to 780 nm, with two absorption peaks at 488 nm and 605 nm, respectively. The absorption edge of the biTV-PTV3 film is at 790 nm [14]. The copolymers of alkylthiophene-benzothiadiazole-alkylthiophene or alkoxylthiophene-benzothiadiazole-alkoxylthiophene also show broad absorption bands [15–19]. For further improving the absorption spectrum of PTVs and regulating the HOMO and LUMO energy levels of the polymers for the application as photovoltaic materials, here we synthesized a novel PTV derivative, poly(thienylene-benzothiadiazole-thienylene-vinylene) (PTBTV, see Scheme 1) with D-A-D-π structure by Pd-catalyzed Stille-coupling method. The polymer film possesses a broad absorption from visible to infrared region, peaked at 614 nm with an absorption edge of 813 nm. The HOMO and LUMO energy levels of PTBTV are −4.99 eV and −3.49 eV respectively. The power conversion efficiency of the polymer solar cells based on PTBTV as donor is 0.51% under the illumination of AM1.5, 100 mW/cm^2.



PTBTV

Scheme 1. Molecular structure of the polymer PTBTV.

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2. Experimental section

2.1. Materials

The monomer 4,7-bis (5-bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazole was synthesized as reported in literature [20]. (E)-1,2-bis (tributylstannyl) ethane was synthesized according to the method in the literature [14]. The other materials were common commercial level and used as received.

2.2. Measurement and characterization

All new compounds were characterized by ^{1}H NMR. Nuclear magnetic resonance (NMR) spectra were taken on a Bruker DMX-400 spectrometer. Chemical shift of ^{1}H NMR was reported in ppm relative to the singlet of $CDCl_3$ at 7.26 ppm. Splitting patterns were designated as s (singlet), d (doublet), t (triplet), m (multiplet), and br (broaden). Absorption spectra were taken on a Hitachi U-3010 UV–vis spectrophotometer. Photoluminescence (PL) spectra were measured using a Hitachi F-4500 spectrophotometer. Absorption and PL spectra were measured for the polymer solutions in chloroform (analytical reagent) at 25 °C or for the polymer films spin-coated from the polymer solutions in chloroform on quartz plates. Molecular weight of the polymers was measured by GPC method, and polystyrene was used as a standard. TGA measurement was performed on a Perkin–Elmer TGA-7. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e 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.

2.3. Fabrication of photovoltaic devices

Polymer solar cells were fabricated with ITO glass as a positive electrode, Ca/Al as a negative electrode and the blend film of the polymer/[70] PCBM between them as a photosensitive layer. The ITO glass was pre-cleaned and modified by a thin layer of PEDOT: PSS which was spin-cast from a PEDOT: PSS aqueous solution (Bayer) on the ITO substrate, and the thickness of the PEDOT: PSS layer is about 60 nm. The photosensitive layer was prepared by spin-coating a blend solution of the polymer and [70] PCBM with a weight ratio of 1:1 in *o*-dichlorobenzene at 1000 rpm on the ITO/PEDOT: PSS electrode. Then the Ca/Al cathode was deposited on the polymer layer by vacuum evaporation under 3×10^{-4} Pa. The device was thermal annealed at 130 °C for 15 min. The thickness of the photosensitive layer is ca. 80 nm, measured on an Ambios Tech. XP-2 profilometer. The effective area of one cell is ca. 4 mm^2. The current–voltage (*I–V*) measurement of the devices was conducted on a computer-controlled Keithley 236 Source Measure Unit. A xenon lamp with AM1.5 filter was used as the white light source, and the optical power at the sample is 100 mW/cm^2.

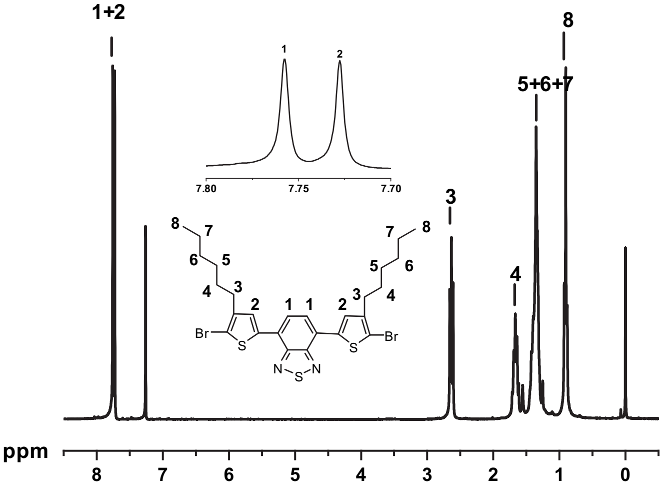
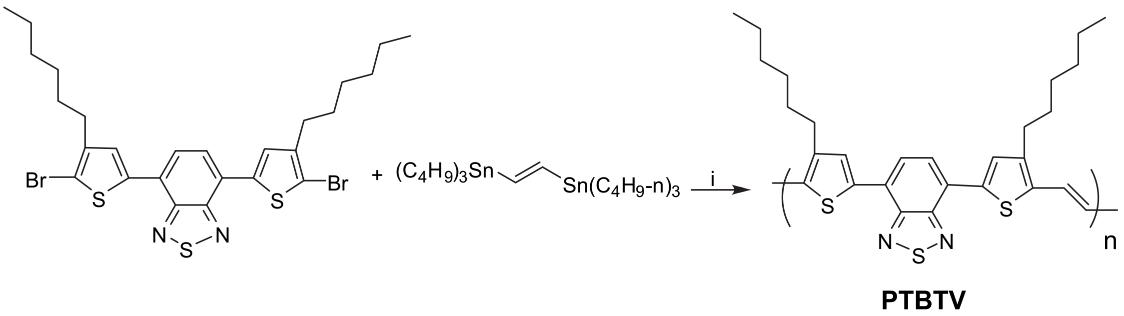


Fig. 1. ^{1}H NMR spectra of monomer.

2.4. Synthesis of the polymer

The synthesis of the polymer was carried out using palladium-catalyzed Stille-coupling between monomer and (*E*)-1,2-bis-(tributylstannyl)ethane, as shown in Scheme 2. All starting materials, reagents and solvents were carefully purified, and all procedures were performed under Oxide-free atmosphere.

Under the protection of argon atmosphere, monomer (1 mmol) was dissolved in 10 mL dried toluene, (*E*)-1,2-bis (tributylstannyl) ethane (1 mmol) was added to the mixture. The solution was flushed with argon for 10 min, and then 10 mg of Pd $(PPh_3)_4$ was added. After another flushing with argon for 20 min, the reactant was heated to reflux for 12 h. The reaction solution was cooled to room temperature, the reaction mixture was added dropwise to 200 mL methanol, and then filtered through a Soxhlet thimble, which was then subjected to Soxhlet extraction with methanol, hexane, and chloroform. Polymer was recovered from the chloroform fraction by rotary evaporation as solid. The solid was dried under vacuum for 1 day. The elemental analysis result of PTBTV is as follows: Calculated, C: 68.29%; H, 6.45%; S, 19.35; N, 5.65%. Found: C: 67.89%; H, 6.33%; S, 19.32%; N, 5.25%.



Scheme 2. The synthetic route of PTBTV. (i) Pd $(PPh_3)_4$, toluene, Argon, reflux, 12 h.

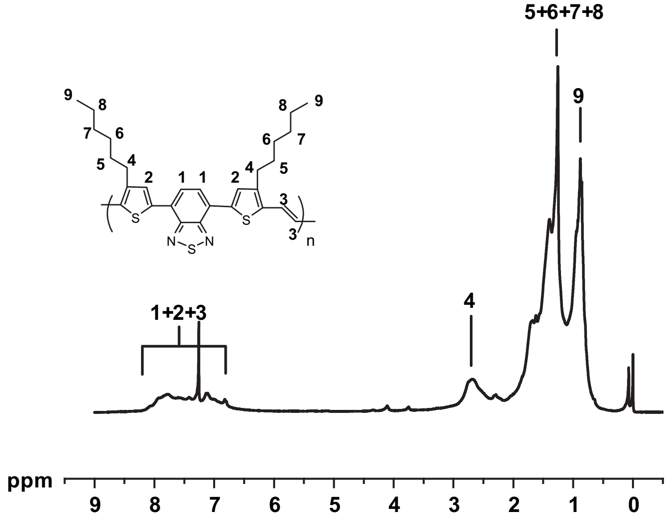


Fig. 2. ^{1}H NMR spectra of PTBTV.

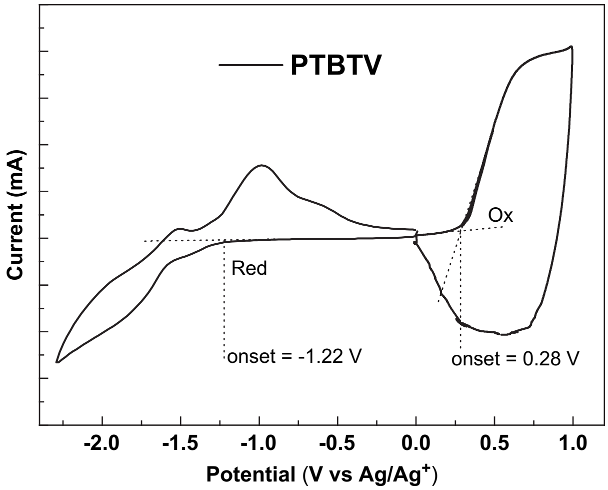


Fig. 4. Cyclic voltammogram of PTBTV film on Pt electrode infilms on Pt electrode 0.1 mol/L Bu_4NPF_6, CH_3CN solution with a scan rate of 100 mV/s.

3. Results and discussion

3.1. Synthesis of the polymer

The synthetic route of the polymer was outlined in Scheme 2. The polymer was prepared by Pd-catalyzed Stille-coupling reaction [21] and the molecular structure was confirmed by ^{1}H NMR spectroscopy and elemental analysis.

Fig. 1 shows the ^{1}H NMR spectrum of the monomer. The hydrogens in thiophene rings and benzothiadiazole are at 7.75 and 7.69 ppm, respectively. The other hydrogen positions are analyzed as shown in Fig. 1. Fig. 2 shows the ^{1}H NMR spectrum of PTBTV, where the double-bond hydrogen 3, the hydrogen 1 and 2 in thiophene rings and benzothiadiazole are in the range from 6.80 ppm to 8.10 ppm. The α-hydrogen linking to the thiophene of PTBTV positions at 2.79 ppm.

The polymer is soluble in common organic solvents, such as chloroform, toluene, and THF at room temperature. The weight-average molecular weight (M_w) and polydispersity index (PDI) of the polymer are 4.3 K and 2.16, respectively. The decomposition temperature of PTBTV determined by TGA in N_2 atmosphere based on 5% weight loss is 215 °C.

3.2. Optical properties of the polymer

Fig. 3(a) shows the absorption spectra of the polymer solution in chloroform and film on quartz plates. PTBTV has broad absorption from visible to infrared region both in solution state and solid film state. The absorption peaks of PTBTV solution and film state are at 600 nm and 614 nm respectively, which are 44 nm and 34 nm red-shifted to that of poly(3-hexylthienylene vinylene) [22]. The broad and longer wavelength absorption of the polymer may be contributed by the inter-molecular electron and energy transfer induced by the structure of D-A-D of the thiophene-benzothiadiazole-thiophene in the polymer [23–26].

Fig. 3(b) shows the photoluminescence (PL) spectrum of PTBTV solution in chloroform. Interestingly, PTBTV shows strong photoluminescence in the wavelength range from 600 to 800 nm peaked at ca. 710 nm, but there is no PL emission of poly(3-hexylthienylene vinylene) solution in chloroform [14,22]. The PL emission of PTBTV could be benefited from the thiophene-benzothiadiazole-thiophene unit in the polymer.

3.3. 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 (CVs).

Fig. 4 shows the cyclic voltammogram of the polymer film on Pt electrode. It can be seen that there are *p*-doping/dedoping (oxidation/

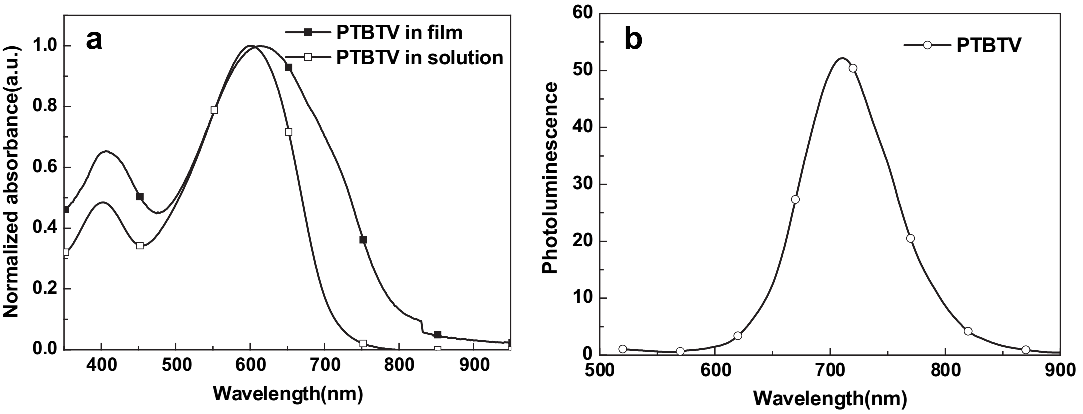


Fig. 3. a) Normalized absorption spectra of PTBTV in chloroform solution and film on quartz plates; (b) Photoluminescence spectrum of PTBTV solution in chloroform.

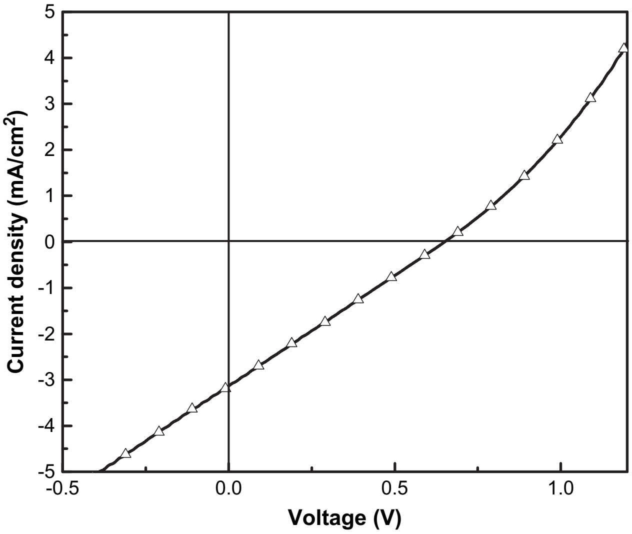


Fig. 5. *I–V* curve of the PSC based on the blend of PTBTV as donor and [70] PCBM as acceptor (1:1, w/w) under the illumination of AM1.5, 100 mW/cm^2.

re-reduction) processes at positive potential range and *n*-doping/dedoping (reduction/re-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 −4.8 eV below the vacuum level [27]. The formal potential of Fc/Fc$^+$ was measured as 0.09 V against Ag/Ag$^+$. The energy gap (E_g^{ec}) of the polymer was calculated from the HOMO and LUMO energy levels. The calculating equations are as follows [28]:

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

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

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

where the units of φ_{ox} and φ_{red} are V vs Ag/Ag$^+$. The φ_{ox} and φ_{red} of PTBTV are 0.28 V and −1.22 V, respectively. The HOMO and LUMO energy levels of PTBTV are −4.99 and −3.49 eV, respectively. The energy bandgap of PTBTV is 1.50 eV.

3.4. *Photovoltaic properties of the polymer*

The motivation of design and synthesis of the polymer are to look for novel poly(thiophene vinylene) derivatives which can be used as donor materials in PSCs. We fabricate the PSCs with the structure of ITO/PEDOT-PSS/PTBTV: [70] PCBM (1:1, w/w)/Ca/Al, where the polymer PTBTV was used as electron donor and [70] PCBM was used as electron acceptor. Fig. 5 shows the *I–V* curve of the PSC under the illumination of AM1.5, 100 mW/cm^2. The V_{oc}, I_{sc} and PCE of the device were 0.66 V, 3.10 mA/cm^2 and 0.51% respectively. Although the efficiency of 0.51% is low, it is improved obviously in comparison with that of the common PTVs.

4. Conclusions

PTBTV was synthesized by the Pd-catalyzed Stille-coupling method. The polymer film shows broad absorption from visible to infrared region with absorption peak at 614 nm and absorption edge at 813 nm which indicates a bandgap of 1.5 eV. The HOMO and LUMO energy levels of PTBTV are −4.99 eV and −3.49 eV respectively. The power conversion efficiency of the PSC based on the blend of PTBTV as donor and [70] PCBM as acceptor was 0.51% under the illumination of AM1.5, 100 mW/cm^2. The results indicate that poly(thienylenevinylene) derivatives with D-A-D-π structure could be a promising photovoltaic material after further structural modification.

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