



A benzo[1,2-*b*:4,5-*b'*]dithiophene-based copolymer with deep HOMO level for efficient polymer solar cells

Shanpeng Wen, Qingfeng Dong, Weidong Cheng, Pengfei Li, Bin Xu, Wenjing Tian*

State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, PR China

ARTICLE INFO

Article history:

Received 3 November 2011

Received in revised form

18 January 2012

Accepted 19 January 2012

Available online 7 February 2012

Keywords:

Conjugated polymer

Polymerization

Photovoltaic devices

ABSTRACT

A new D-A conjugated polymer containing a benzo[1,2-*b*:4,5-*b'*]dithiophene donor unit and bisthieryl-s-tetrazine acceptor unit, PBDT-TTz, was synthesized by Stille cross-coupling polymerization and was characterized by ¹H NMR, elemental analysis and GPC. The copolymer shows good thermal stability with decomposition temperature of 276 °C and broad absorption band from 350 to 700 nm. Cyclic voltammetric measurement shows that the HOMO energy level of the copolymer is deep-lying (−5.42 eV), which implies that the copolymer has good stability in the air and assures a higher open circuit potential when it is applied in photovoltaic cells. Bulk-heterojunction polymer solar cells were fabricated using PBDT-TTz blended PC₇₁BM as the active layer. The power conversion efficiency of the PSC is 3.32% under 100 mW/cm² AM 1.5 illumination, indicating that PBDT-TTz is a potential candidate for polymer solar cells.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Polymer solar cells (PSCs) have great potential as the future energy source due to the advantages of low cost, easy processing, light weight, being mechanically flexible, and suitable for large-area fabrication [1–7]. So far, the most efficient architecture of PSCs is the bulk heterojunction (BHJ) structure formed by blending a conjugated polymer as donor and electron-deficient fullerene derivative as acceptor [8–12]. As we know, region-regular poly(3-hexylthiophene) (P3HT) is one of the most representative donor and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) is the popular acceptor material, and the power conversion efficiency (PCE) of the PSCs based on P3HT/PC₆₁BM has reached 4–5% [13–16]. However, the absorption of P3HT film locates in a short-wavelength region with a maximum at ~510 nm and onset at ~630 nm [17], which cover only a small part of the solar spectrum. Further improvement on PCE entails new conjugated polymers with broader and longer wavelength absorption within solar spectrum. The other drawback of P3HT is its high-lying highest occupied molecular orbital (HOMO) energy level at −4.9 eV, which limits the open circuit voltage (*V*_{oc}) around 0.6 V resulting in the limited PCE of P3HT based solar cells [18]. According to the BHJ solar cell model and experimental results, the *V*_{oc} is determined by the energy difference between the HOMO level of the donor and the lowest unoccupied molecular

orbital (LUMO) level of the acceptor [19]. Therefore, new conjugated polymers with deeper HOMO energy level are pursued in recent years for improving the *V*_{oc} of the PSCs.

Recently, benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) based molecules have shown very promising properties in organic electronic devices, especially in PSC devices, due to their relatively large and planar conjugated structure, which would greatly promote facial π – π stacking of the molecules, and thus benefit charge transportation and red shift of the absorption spectra [20–36]. For photovoltaic applications, BDT was shown to be a good electron donor unit and has been copolymerized with various electron acceptor units, including 2,1,3-benzothiadiazole [20], 4,7-dithien-2-yl-2,1,3-benzothiadiazole (DTBT) [21–23], thieno[3,4-*b*]thiophene [24–27], 3,6-diaryl-2,5-dihydropyrrolo[3,4-*c*]pyrrole-1,4-dione (DPP) [28], thieno[3,4-*c*]pyrrole-4,6-dione (TPD) [29–31], and thieno[3,4-*b*]pyrazine units [20]. Among these copolymers, poly(DBT-thieno[3,4-*b*]thiophene) (PTBx series) showed a rather synergistic combination of the desired properties, e.g., low bandgap (1.7–1.8 eV), relatively high carrier mobility, proper orientation of the π -system, and controllable morphology [37]. PTBx-based solar cells exhibited very promising photovoltaic properties, including a high short-circuit current (*J*_{sc}) and fill factor (FF). However, the *V*_{oc}s of these devices were only ~0.6 V, which was the limiting factor of the device's PCE. In order to improve the *V*_{oc}, Yu and co-workers [25,27] introduced an electron-withdrawing group of the fluorine atom into the thieno[3,4-*b*]thiophene ring. By reducing the HOMO energy level of copolymer, the *V*_{oc} substantially improved to 0.76 V and the device achieved the highest PCE over 7% [38]. It implies that the introduction of a strong electron-withdrawing

* Corresponding author. Tel.: +86 431 85166368; fax: +86 431 85193421.
E-mail address: wjtian@jlu.edu.cn (W. Tian).

unit in a D-A copolymer can effectively reduce the HOMO energy level of copolymer and thus improve the V_{oc} of the copolymer-based PSC.

Here, we introduced bisthienyl-s-tetrazine (TTz) as an acceptor unit to synthesize a BDT-based copolymer, poly(4,8-bis-ethylhexyloxybenzo(1,2-*b*:4,5-*b'*)dithiophene-alt-5,5'-(3,6-bis(4-ethylhexylthienyl-2-yl)-s-tetrazine)) (PBDT-TTz). Bisthienyl-s-tetrazine has a very high electron affinity and should behave as a strong electron-withdrawing unit, leading to the lower the HOMO energy level, the high air stability of the polymer and the increase of V_{oc} in PBDT-TTz based BHJ solar cells [17,39]. UV-vis absorption spectrum displayed that the PBDT-TTz thin film covered a rather broad absorption range from 350 to 700 nm, which is an extremely desirable absorption spectrum for photovoltaic applications. PBDT-TTz showed a deeper HOMO energy level at -5.42 eV and the PCE of the PSC with PBDT-TTz as donor and [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM) as acceptor reached 3.32% with large open circuit potential of 0.92 V under the illumination of AM 1.5(100 mW/cm²).

2. Experimental section

2.1. Characterization

¹H NMR and ¹³C NMR spectra were recorded on Bruker AVANCE 300-MHz spectrometer with chloroform-*d* as solvent and tetramethylsilane (TMS) as internal standard. The elemental analysis was carried out with a Thermoquest CHNS-Ovelemental analyzer. The gel permeation chromatographic (GPC) analysis was carried out with a Waters 410 instrument with tetrahydrofuran as the eluent (flowrate: 1 mL/min, at 35 °C) and polystyrene as the standard. The thermogravimetric analysis (TGA) was performed on a Perkin Elmer Pyris 1 analyzer under nitrogen atmosphere (100 mL/min) at a heating rate of 10 °C/min. UV-vis absorption spectra were measured using a Shimadzu UV-3600 spectrophotometer. Electrochemical measurements of these derivatives were performed with a Bioanalytical Systems BAS 10 B/W electrochemical workstation. Atomic force microscopy (AFM) images of blend films were carried out using a Nanoscope IIIa Dimension 3100.

2.2. Photovoltaic device fabrication and characterization

The solar cells were fabricated with a device structure of ITO/PEDOT:PSS/Polymer:PCBM Blend/LiF/Al. The ITO glass substrates were pre-cleaned by detergent, acetone, and boiling in H₂O₂. Highly conducting poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Baytron P, Al4083) was spin-casted (3000 rpm) at a thickness of ~40 nm from aqueous solution (after passing through a 0.45 μm filter). The substrate was annealed at 120 °C for 15 min on hot plate. The active layer contained a blend of copolymer as electron donor and PC₇₁BM as electron acceptor, which was prepared by weight ratio (1:1, 1:2, 1:3, and 1:4 w/w) in chlorobenzene (5 mg/mL) for copolymer. The active layer was obtained by spin coating the blend solutions at 1000 rpm for 50 s and the thickness of films was ~90 nm, as measured with the Ambios Technology XP-2. Subsequently, LiF (0.6 nm) and Al (100 nm) electrodes were deposited via thermal evaporation in vacuum (5×10^{-4} Pa) in thickness of approximately. The active area was about 5 mm². Current-voltage (*J*-*V*) characteristics were recorded using Keithley 2400 Source Meter in the dark and under 100 mW/cm² simulated AM 1.5 G irradiation (Sciencetech SS-0.5K Solar Simulator). All the measurements were performed under ambient atmosphere at room temperature.

2.3. Materials

All starting materials were purchased from either Acros or Aldrich Chemical Co. and used without further purification, unless otherwise noted. In synthetic preparations, diethyl ether and THF were dried by distillation from sodium/benzophenone under nitrogen. Similarly, DMF and dichloromethane were distilled from CaH₂ under nitrogen. 3-ethylhexylthiophene (1) [40] and 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene [20] were prepared according to the known literature procedures.

2.4. Synthesis

2.4.1. 4-Ethylhexylthiophene-2-aldehyde (2) [41]

To a solution of 3-ethylhexylthiophene (1) (7.36 g, 37.5 mmol) in anhydrous THF at -78 °C, 17.2 mL (41.2 mmol) of *t*-butyllithium (2.4 M in hexane) was added by syringe. The mixture was stirred at -78 °C for 2 h. Anhydrous DMF (3.8 mL, 48.7 mmol) was added to the solution, and the resulting mixture was stirred at -78 °C for an hour and warmed to room temperature and stirred for 24 h. It was then hydrolyzed with a saturated aqueous ammonium chloride solution followed by the addition of diethyl ether. The organic layer was washed three times with 150 mL of distilled water and dried over magnesium sulfate. The solvent was evaporated and the residue was purified by silica-gel column chromatograph with 15:1 hexane/ethyl acetate to give a faint yellow oil product (7.19 g, 85%).

¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) 9.89 (s, 1H), 7.59 (d, $J=1.5$ Hz, 1H), 7.37–7.35 (m, 1H), 2.58 (d, $J=6.9$ Hz, 2H), 1.64–1.47 (m, 1H), 1.35–1.23 (m, 8H), 0.92–0.84 (m, 6H). Anal. Calcd for C₁₃H₂₀OS: C, 69.59; H, 8.98. Found: C, 69.30; H, 9.23.

2.4.2. 4-Ethylhexylthiophene-2-carbonitrile (3)

A mixture solution of 4-ethylhexylthiophene-2-carbaldehyde (2) (5.52 g, 24.6 mmol) and hydroxylamine hydrochloride salt (2.80 g, 40.3 mmol) in pyridine/ethanol (50 mL, 1/1 v/v) was stirred at 80 °C overnight. Then the solvent was removed using a rotary evaporator. The residue was dissolved in chloroform (100 mL), and the solution was washed with distilled water (3 × 50 mL) and dried over anhydrous magnesium sulphate. The solvent was removed under vacuum, and the viscous liquid residue was dissolved in acetic anhydride (30 mL) containing potassium acetate (0.1 g) and then refluxed for 5 h. The mixture was poured into distilled water (150 mL) and extracted with hexanes (3 × 50 mL). The organic phase was washed with 5% aqueous sodium hydroxide solution and then water, dried over anhydrous magnesium sulphate before the solvent was removed by a rotate evaporator. The crude product was purified by column chromatography (EtOAc/petroleum ether 1:100) to give a product as light yellow liquid (4.85 g, 89%).

¹H NMR (300 MHz, CDCl₃, TMS): δ (ppm) 7.43 (d, $J=1.5$ Hz, 1H), 7.18–7.16 (m, 1H), 2.56 (d, $J=6.6$ Hz, 2H), 1.57–1.47 (m, 1H), 1.32–1.21 (m, 8H), 0.92–0.84 (m, 6H). Anal. Calcd for C₁₃H₁₉NS: C, 70.54; H, 8.65. Found: C, 70.31; H, 8.82.

2.4.3. 3,6-Bis(4-ethylhexyl-2-thienyl)-1,2,4,5-tetrazine (4)

To a mixture of compound 3 (4.6 g, 23.8 mmol) and sulfur (0.53 g, 16.7 mmol) in anhydrous ethanol (15 mL), hydrazine monohydrate (1.8 g, 35.7 mmol) was slowly added at room temperature. The solution turned into yellow and large amount of gas evolved. The solution was heated up to reflux and stirred for 2 h. The crystal was collected by filtration and rinsed with cold ethanol before dried under vacuum. To a chloroform solution (30 mL) of the obtained solid, isoamyl nitrite (5.58 g, 47.6 mmol) was added and the solution was stirred at room temperature

overnight. After removal of the solvent, the crude product was washed with methanol twice before purified by column chromatography ($\text{CHCl}_3/\text{Hexane}=4/6$, v/v) to yield a red solid (2.12 g, yield: 38%).

^1H NMR (300 MHz, CDCl_3 , TMS): δ (ppm) 8.05 (d, $J=1.5$ Hz, 2H), 7.24 (d, $J=1.5$ Hz, 2H), 2.63 (d, $J=6.6$ Hz, 4H), 1.67–1.58 (m, 2H), 1.38–1.25 (m, 16H), 0.93–0.86 (m, 12H). Anal. Calcd for $\text{C}_{26}\text{H}_{38}\text{N}_4\text{S}_2$: C, 66.34; H, 8.14. Found: C, 66.12; H, 8.43.

2.4.4. 3,6-Bis(5-bromo-4-ethylhexyl-2-thienyl)-1,2,4,5-tetrazine (5)

To a suspension solution of compound 4 (1.20 g, 2.55 mmol) in chloroform (20 mL) and acetic acid (20 mL), N-bromosuccinimide (0.95 g, 5.35 mmol) was added at room temperature. The mixture was stirred at RT under dark for 1 h before heated at 80°C for 6 h. Then, the reaction mixture was poured into distilled water (150 mL), and the organic layers were extracted with chloroform (3×50 mL). The organic layer was washed with distilled water, dried over anhydrous magnesium sulphate. After drying over MgSO_4 and removal of organic solvent under reduced pressure, the crude product was purified by column chromatography ($\text{CHCl}_3/\text{hexane}=1/2$, v/v) to provide a product of 1.42 g (87%).

^1H NMR (300 MHz, CDCl_3 , TMS): δ (ppm) 7.92 (s, 2H), 2.58 (d, $J=7.2$ Hz, 4H), 1.72–1.63 (m, 2H), 1.40–1.25 (m, 16H), 0.91 (t, $J=7.5$ Hz, 12H). ^{13}C NMR (125 MHz, TMS): δ (ppm) 161.11, 144.27, 135.26, 132.42, 118.96, 40.34, 34.24, 32.90, 29.20, 26.09, 23.42, 14.51, 11.23. Anal. Calcd for $\text{C}_{26}\text{H}_{38}\text{Br}_2\text{N}_4\text{S}_2$: C, 49.68; H, 5.77. Found: C, 49.41; H, 6.02.

Poly(4,8-bis-ethylhexyloxybenzo(1,2-*b*:4,5-*b'*)dithiophene-*alt*-5,5'-(3,6-bis(4-ethylhexylthienyl-2-yl)-s-tetrazine)) (PBDT-TTz) 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*] dithiophene (0.147 g, 0.191 mmol) and compound 5 (0.120 g,

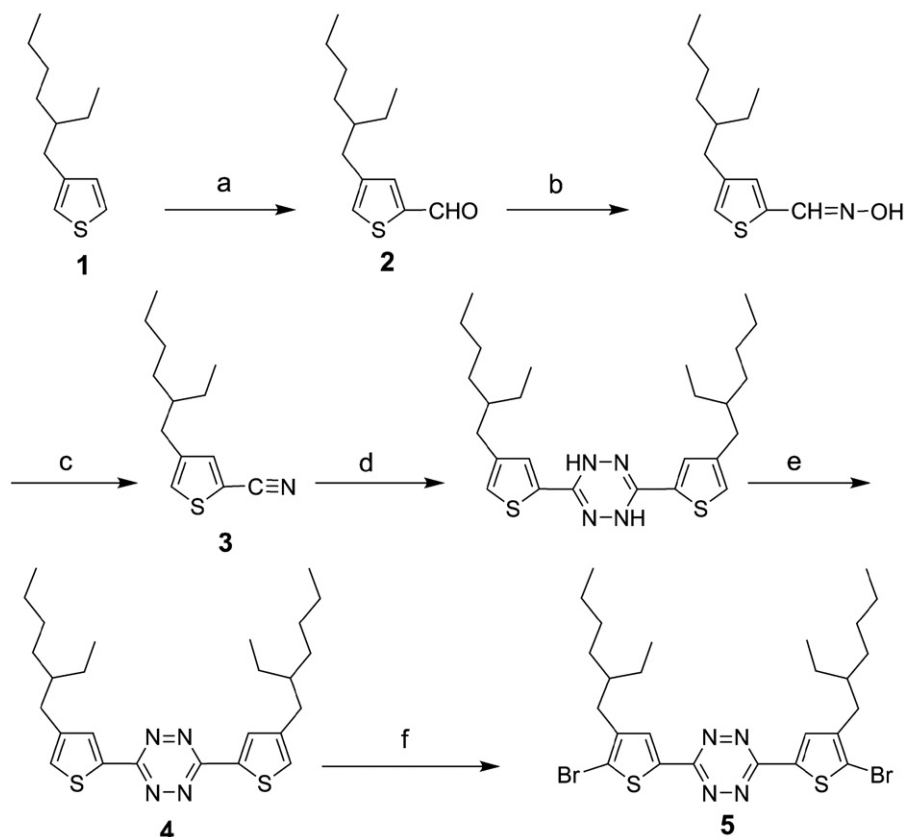
0.191 mmol), and dry toluene (5 mL) and N, N-dimethyl formamide (DMF) (0.5 mL) were added to a 25 mL double-neck round-bottom flask. The reaction container was purged with nitrogen for 30 min to remove O_2 , and then $\text{Pd}(\text{PPh}_3)_4$ (5 mg) was added. The reaction was stirred and refluxed for 16 h under nitrogen. The reactant was cooled down to room temperature and poured into MeOH (150 mL) and then filtered through a Soxhlet thimble, subsequently filter residue was subjected to Soxhlet extraction with methanol, hexane, and chloroform. The fraction from chloroform was concentrated under reduced pressure and precipitated into methanol, collected by filtration. The final product was dried under vacuum overnight to afford PBDT-TTz as a dark solid (110 mg, yield: 73%). GPC: $M_n=56000$, $M_w=149000$, $\text{PDI}=2.67$.

^1H NMR (500 MHz, CDCl_3 , TMS): δ (ppm) 8.10 (br, 2H); 7.63 (br, 2H); 4.26 (br, 4H); 2.93 (br, 4H); 1.98–1.62 (m, 4H), 1.60–1.22 (m, 32H); 1.11–0.80 (m, 24H). Anal. Calcd for $\text{C}_{52}\text{H}_{72}\text{N}_4\text{O}_2\text{S}_4$: C, 68.38; H, 7.95. Found: C, 68.02; H, 8.12.

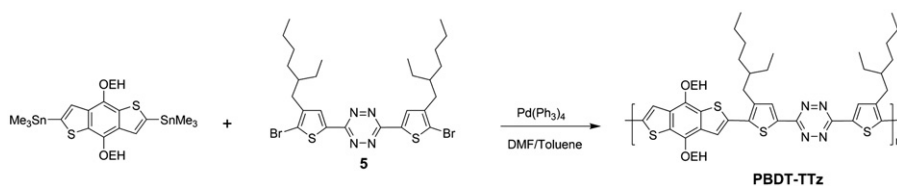
3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes of the bisthieryl-s-tetrazine (TTz) monomer and polymer are shown in Schemes 1 and 2. The TTz monomer synthesis starts from 4-ethylhexylthiophene-2-carbonitrile (**2**), which can be synthesized from 3-ethylhexylthiophene (**1**) by reacting with *n*-butyl lithium and then N,N-dimethylformamide (DMF). 4-ethylhexylthiophene-2-carbonitrile (**3**) was synthesized through a two-step reaction from 4-ethylhexylthiophene-2-carbaldehyde (**2**) with a total yield of 89%. According to well-know Pinner synthesis, the obtained nitrile (**3**) was reacted



Scheme 1. Syntheses of monomer TTz. Reagents and conditions: (a) *n*-Buli, THF, DMF, -78°C to room temperature; (b) $\text{NH}_2\text{OH} \cdot \text{H}_2\text{O}$, pyridine, ethanol, 80°C , overnight; (c) Ac_2O , KOAc, reflux, 5 h; (d) $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$, sulfur, ethanol, reflux, 2 h; (e) isomyl nitrite, chloroform, room temperature, overnight; (f) NBS, chloroform, acetic acid, 80°C , 6h.



Scheme 2. Syntheses of copolymer PBDT-TTz.

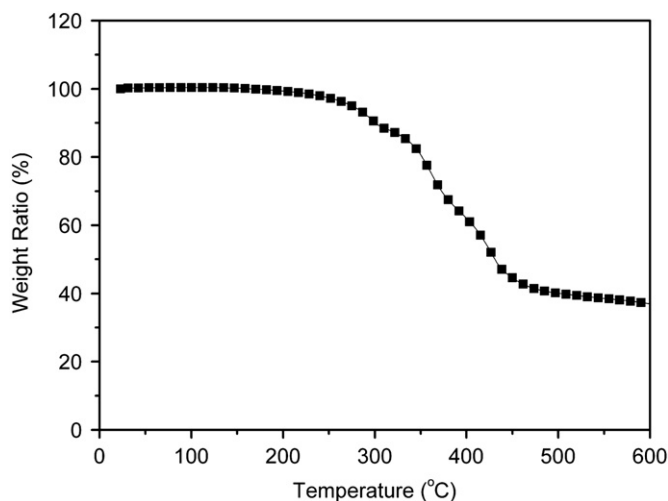


Fig. 1. TGA curve of copolymer PBDT-TTz at the heating rate of 10 °C/min under nitrogen atmosphere.

with hydrazine to form the relatively unstable dihydrotetrazine intermediate, which was not purified and has to be further oxidized into the fully aromatic tetrazine (**4**) with a modest yield of 38%. Bromination of **4** with *N*-bromosuccinimide furnished **5** in a mixture of chloroform and acetic acid with a good yield of 87%.

Benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) has been successfully used to prepare high performance polymer solar cell materials and has been demonstrated as an efficient electron-rich unit; thus, it was chosen as the donor unit in this work. As Stille polycondensation of **5** and 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy) was carried out with Pd(PPh₃)₄ as the catalyst in toluene/DMF to afford polymer PBDT-TTz as a dark solid with a yield of 73%.

The number average molecular weight (Mn) of this polymer is measured to be 56,000 g/mol with a polydispersity (PDI) of 2.67 by gel permeation chromatography (GPC) with THF as the solvent. The thermal property of the polymer was investigated with thermogravimetric analysis (TGA), as shown in Fig. 1. The TGA analysis reveals that the onset temperature with 5% weight loss of PBDT-TTz is 276 °C, which indicates that the thermal stability of the PBDT-TTz is good enough for the application in optoelectronic devices.

3.2. Photophysical properties

Fig. 2 shows the UV–vis absorption spectra of PBDT-TTz in dilute (10^{−5} M) chloroform solution and solid film. The absorption peak wavelengths (λ) of the polymer were summarized in Table 1. In solution, PBDT-TTz shows two absorption peaks at 440 and 516 nm, respectively, covering a broad wavelength range from 350 to 650 nm, which is benefited from its D-A molecular structure. The absorption peak at 440 nm corresponds to the π–π* absorption of conjugated polymer backbone, and the strong absorption peak at ca. 516 nm is attributed to the intramolecular charge transfer (ICT) transition between the BDT donor unit and

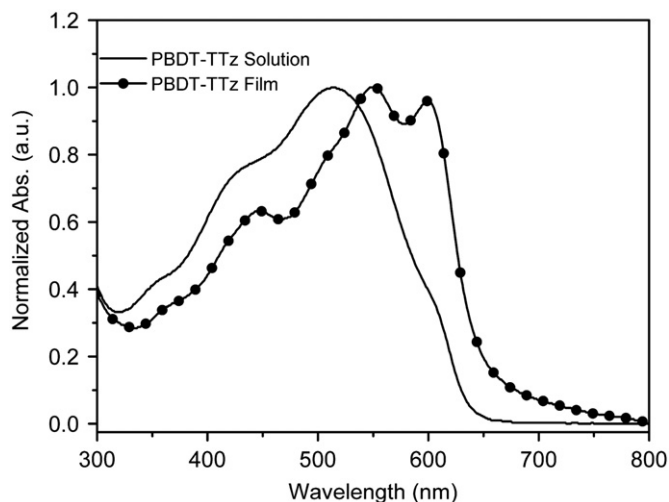


Fig. 2. UV–vis absorption spectra of PBDT-TTz in chloroform solution and in thin film.

Table 1

Summary of optical and electrochemical properties of PBDT-TTz.

$\lambda_{\text{max}}^{\text{abs, sol}}$ (nm)	$\lambda_{\text{max}}^{\text{abs, film}}$ (nm)	$E_{\text{ox}}^{\text{onset}}$ (V)	HOMO (eV)	$E_{\text{red}}^{\text{onset}}$ (V)	LUMO (eV)	E_{g}^{ec} (eV)	$E_{\text{g}}^{\text{opt}}$ (eV)
440/516	451/551	0.68	−5.42	−1.16	−3.58	1.84	1.85

TTz acceptor unit [42]. The absorption spectrum of the polymer film displays an absorption peak at 551 nm, red shifted by 35 nm in comparison with the absorption of polymer solution, indicating a strong intermolecular interaction in the polymer film [43,44]. The optical bandgap ($E_{\text{g}}^{\text{opt}}$) of PBD-TTz, calculated from the absorption edges in the UV–vis spectrum of the thin solid film, was 1.85 eV.

3.3. Electrochemical properties

Electrochemical cyclic voltammetry has been widely employed to investigate the redox behavior of a polymer and to estimate its HOMO and LUMO energy levels. Cyclic voltammetry of the copolymer in films was performed in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte at scan rates of 50 mV/s. Platinum wire electrodes were used as both counter and working electrodes, and silver/silver ion (Ag in 0.1 M AgNO₃ solution, from Bioanalytical Systems, Inc.) was used as a reference electrode. Ferrocene/ferrocenium (Fc/Fc⁺) was used as the internal standard.

The cyclic voltammogram of PBDT-TTz is shown in Fig. 3. On the anodic sweep, PBDT-TTz showed an oxidation with an onset potential of 0.68 V (versus Ag/Ag⁺). In contrast, the cathodic sweep showed an onset reversible reduction potential of −1.16 V (versus Ag/Ag⁺).

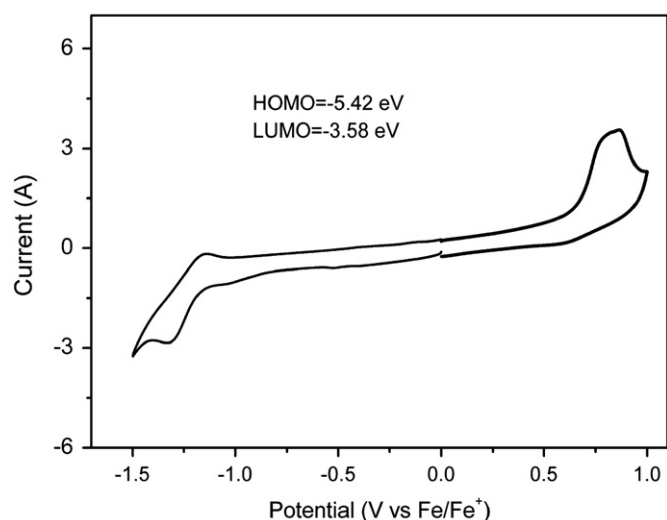


Fig. 3. Cyclic voltammogram of PBDT-TTz film on a platinum electrode measured in 0.1 mol L⁻¹ Bu₄NPF₆ acetonitrile solution at a scan rate of 50 mV s⁻¹.

From the onset oxidation potential ($E_{\text{ox}}^{\text{onset}}$) and the onset reduction potential ($E_{\text{red}}^{\text{onset}}$) of the copolymer, HOMO and LUMO energy levels as well as the energy gap were calculated according to the following equations [45]:

$$\text{HOMO (eV)} = -e(E_{\text{ox}}^{\text{onset}} + 4.74)$$

$$\text{LUMO (eV)} = -e(E_{\text{red}}^{\text{onset}} + 4.74)$$

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

where $E_{\text{ox}}^{\text{onset}}$ and $E_{\text{red}}^{\text{onset}}$ are the measured onset potentials relative to Ag/Ag⁺.

The results of the electrochemical measurements and calculated energy levels of the copolymer are listed in Table 1. The estimated HOMO and LUMO energy levels of PBDT-TTz are -5.42 and -3.58 eV, respectively. Lower HOMO and LUMO levels were observed for PBDT-TTz than those for PTB4 and PTB5 [12]. That means the introduction of TTz unit does result in a lower HOMO as well as a lower LUMO. In addition, the deep HOMO energy level of PBDT-TTz suggested that PBDT-TTz would be more stable against oxidation in air, which will enhance the device stability. And the optical bandgap (1.85 eV) and electrochemical bandgap (1.84 eV) are similar within the experimental error.

3.4. Theoretical calculation

Fig. 4 depicts the electron-state-density distribution of the HOMO and LUMO of geometry optimized structure (DFT B3LYP/6-31G*) of analogous monomer PBDT-TTz using the Gaussium 03 program [46]. To simplify the calculation, only one repeating unit of polymer was subject to the calculation, with alkyl chains replaced by CH₃ groups. The electron density distributions of LUMO level for the polymer is primarily localized on the TTz-based acceptor unit, while the electron density of HOMO is distributed over the entire conjugated molecule (both the acceptor and donor unit), which indicates the acceptor unit significantly affects the LUMO and HOMO level of the resulting polymer. For comparison, the DFT-calculated results of analogous monomers of PTB4 and PTB5 are also shown in Fig. 4. Both the LUMO and HOMO energy levels are slightly lower in PBDT-TTz than those in PTB4 and PTB5, which is in agreement with the experimental results estimated from the cyclic voltammogram.

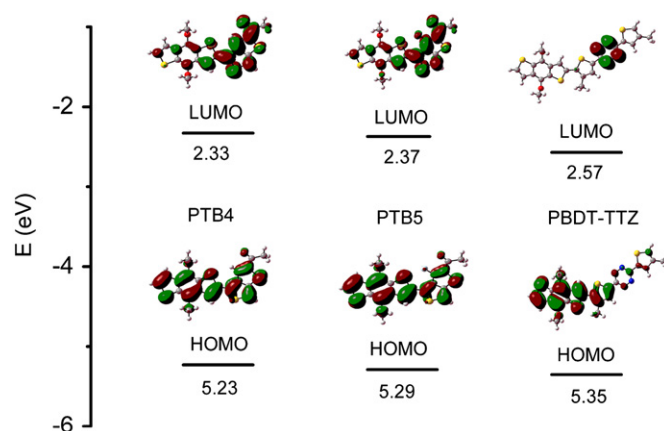


Fig. 4. DFT-calculated LUMO and HOMO of the geometry optimized structures of analogous monomers of PBDT-TTz, PTB4 and PTB5.

Table 2

Photovoltaic properties of polymer solar cells incorporating PBDT-TTz:PC₇₁BM blends prepared at various weight ratios.

PBDT-TTz:PC ₇₁ BM	V _{oc} (V)	J _{sc} (mA cm ⁻²)	FF	PCE (%)
1:1	0.92	4.34	0.42	1.65
1:2	0.91	5.00	0.50	2.31
1:3	0.92	6.21	0.58	3.32
1:4	0.90	4.91	0.59	2.60

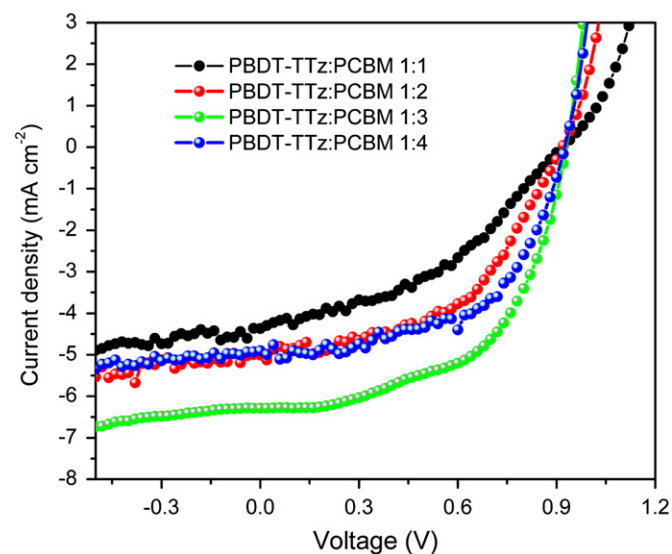


Fig. 5. J-V curve of the polymer solar cells based on PBDT-TTz:PC₇₁BM under the illumination of AM 1.5, 100 mW/cm².

3.5. Photovoltaic properties

Photovoltaic properties of PBDT-TTz were investigated by fabricating the PSCs with PBDT-TTz as donor and PC₇₁BM as acceptor. The device structure is ITO/PEDOT:PSS/PBDT-TTz:PC₇₁BM/LiF/Al. Weight ratio of PBDT-TTz:PC₇₁BM was optimized from 1:1, 1:2, 1:3 to 1:4 and the relative photovoltaic parameters are summarized in Table 2. The active layer was spin-coated at 60 °C from chlorobenzene solution because of limited solubility of PBDT-TT at room temperature. The current density-voltage (J-V) characteristic of the device under the illumination of AM 1.5, 100 mW/cm² is shown in Fig. 5. Table 2 summarizes the corresponding data.

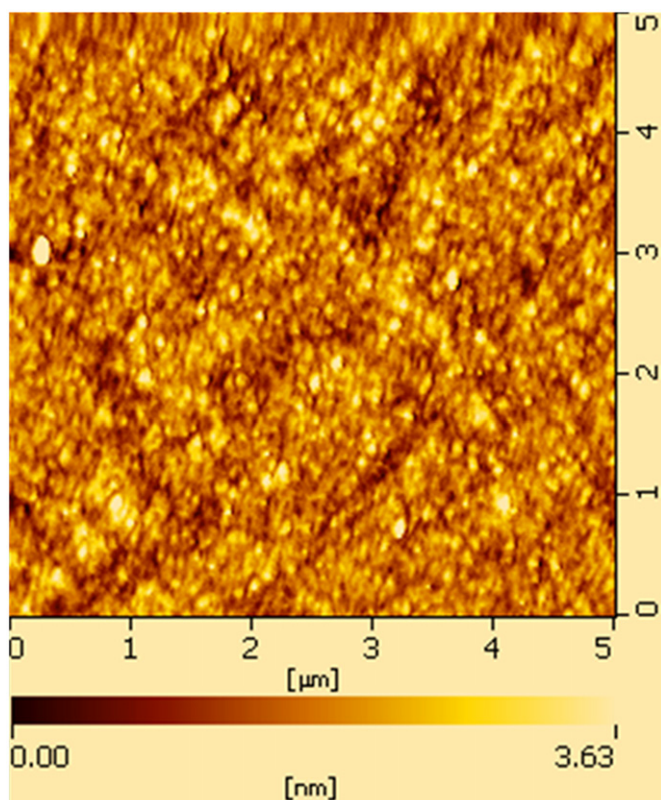


Fig. 6. AFM image ($5 \times 5 \mu\text{m}^2$) of the active layer from PBBDT-TTz:PC₇₁BM (1:3, w/w).

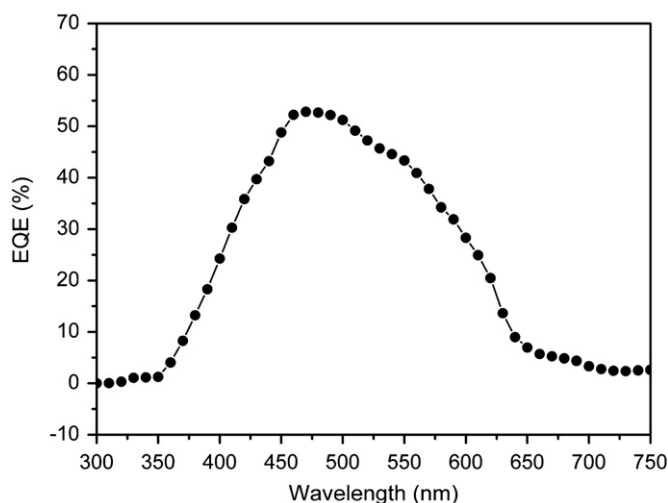


Fig. 7. EQE curve of the PSCs based on PBBDT-TTz:PCBM (1:3, w/w).

The devices fabricated from PBBDT-TTz and PC₇₁BM blends exhibited high values of V_{oc} (0.90–0.92 V). The optimal PBBDT-TTz:PCBM device, prepared at a blend weight ratio of 1:3, exhibited a value of V_{oc} of 0.92 V, a value of J_{sc} of 6.21 mA/cm², an FF of 58.2%, and resulting power conversion efficiency (PCE) of 3.32%. The surface morphology of the blend film of PBBDT-TTz:PC₇₁BM (1:3, w/w) was observed by atomic force microscopy (AFM) in Fig. 6. Its surface is quite smooth. The film shows small roughness with a root-mean-square (rms) of 0.49 nm and no significant aggregation, suggesting that the polymer is highly compatible with PC₇₁BM molecules.

Fig. 7 shows the external quantum efficiency (EQE) spectra of the optimized PSC [PBBDT-TTz:PC₇₁BM (1:3, w/w)] under the

illumination of monochromatic light. The device shows a broad response range from 350 to 650 nm. High IPCE values over 40% are reached in the range of 430–560 nm and the maximum IPCE of almost 50% is reached around 470 nm. The value of J_{sc} obtained through integration of this IPCE (6.24 mA/cm²) was in reasonable agreement with that measured from the J – V curve (6.21 mA/cm²).

4. Conclusion

In conclusion, we have synthesized a new D-A conjugated copolymer PBBDT-TTz containing benzo[1,2-*b*:4,5-*b'*]dithiophene donor unit and bisthienyl-s-tetrazine acceptor unit by the Pd-catalyzed Stille-coupling reaction. PBBDT-TTz exhibited good thermal stability, high molecular weight, and low HOMO energy level. The PCE of the photovoltaic device based on PBBDT-TTz:PC₇₁BM (1:3, w/w) reached 3.32% with V_{oc} =0.92 V, J_{sc} =6.21 mA/cm², and FF=0.58, under the illumination of AM 1.5, 100 mW/cm², which indicates that PBBDT-TTz is a promising polymer donor material for the application in polymer solar cells.

Acknowledgments

This work was supported by the State Key Development Program for Basic Research of China (Grant no. 2009CB623605), the National Natural Science Foundation of China (Grant no. 20874035), the 111 Project (Grant no. B06009), and the Project of Jilin Province (20080305).

References

- [1] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, Polymer photovoltaic cell: enhanced efficiencies via a network of internal donor–acceptor heterojunctions, *Science* 270 (1995) 1789–1791.
- [2] E. Bundgaard, F.C. Krebs, Low band gap polymers for organic photovoltaics, *Solar Energy Materials and Solar Cells* 91 (2007) 954–985.
- [3] F.C. Krebs, T. Tromholt, M. Jørgensen, Upscaling of polymer solar cell fabrication using roll-to-roll processing, *Nanoscale* 2 (2010) 873–886.
- [4] M.O. Reese, S.A. Gevorgyan, M. Jørgensen, E. Bundgaard, S.R. Kurtz, D.S. Ginley, D.C. Olson, M.T. Lloyd, P. Morvillo, E.A. Katz, A. Elschner, O. Haillant, T.R. Currier, V. Shrotriya, M. Hermenau, M. Riede, K.R. Kirov, G. Trimmel, T. Rath, O. Inganäs, F. Zhang, M. Andersson, K. Tvingstedt, M.L. Cantu, D. Laird, C. McGuinness, S. Gowrisanker, M. Pannone, M. Xiao, J. Hauch, R. Steim, D.M. DeLongchamp, R. Rösch, H. Hoppe, N. Espinosa, A. Urbina, G.Y. Uzunoglu, J.B. Bonekamp, A.J.J.M.V. Breemen, C. Girotto, E. Voroshazi, F.C. Krebs, Consensus stability testing protocols for organic photovoltaic materials and devices, *Solar Energy Materials and Solar Cells* 95 (2011) 1253–1267.
- [5] Y. Kim, K. Lee, N.E. Coates, D. Moses, T.-Q. Nguyen, M. Dante, A.J. Heeger, Efficient tandem polymer solar cells fabricated by all-solution processing, *Science* 317 (2007) 222–225.
- [6] J. Brabec, N.S. Sariciftci, J.C. Hummelen, Plastic solar cells, *Advanced Functional Materials* 11 (2001) 15–26.
- [7] F.C. Krebs, J. Fyenbo, M. Jørgensen, Product integration of compact roll-to-roll processed polymer solar cell modules: methods and manufacture using flexographic printing, slot-die coating and rotary screen printing, *Journal of Materials Chemistry* 20 (2010) 8994–9001.
- [8] G. Yu, A.J. Heeger, Charge separation and photovoltaic conversion in polymer composites with internal donor/acceptor heterojunctions, *Journal of Applied Physics* 78 (1995) 4510–4515.
- [9] J.J.M. Halls, C.A. Walsh, N.C. Greenham, E.A. Marseglia, R.H. Friend, S.C. Moratti, A.B. Holmes, Efficient photodiodes from interpenetrating polymer networks, *Nature* 376 (1995) 498–500.
- [10] R. Qin, W. Li, C. Li, C. Du, C. Veit, H.-F. Schleiermacher, M. Andersson, Z. Bo, Z. Liu, O. Inganäs, U. Wuerfel, F. Zhang, A planar copolymer for high efficiency polymer solar cells, *Journal of the American Chemical Society* 131 (2009) 14612–14613.
- [11] F. Huang, K.-S. Chen, H.-L. Yin, S. Hau, O. Acton, Y. Zhang, J.D. Luo, A.K.-Y. Jen, Development of new conjugated polymers with donor- π -bridge-acceptor side chains for high performance solar cells, *Journal of the American Chemical Society* 131 (2009) 13886–13887.
- [12] X. Zhang, J.W. Shim, S.P. Tiwari, Q. Zhang, J.E. Norton, P.-T. Wu, S. Barlow, S.A. Jenekhe, B. Kippelen, J.-L. Brédas, S.R. Marder, Dithienopyrrole-quinoxaline/pyridopyrazine donor–acceptor polymers: synthesis and

- electrochemical, optical, charge-transport, and photovoltaic properties, *Journal of Materials Chemistry* 21 (2011) 4971–4982.
- [13] W. Ma, C. Yang, A.J. Heeger, Thermally stable, efficient polymer solar cells with nanoscale control of the interpenetrating network morphology, *Advanced Functional Materials* 15 (2005) 1617–1622.
 - [14] G. Li, V. Shrotriya, Y. Yao, J. Huang, Y. Yang, Manipulating regioregular poly(3-hexylthiophene): [6,6]-phenyl-C61-butyric acid methyl ester blends—route towards high efficiency polymer solar cells, *Journal of Materials Chemistry* 17 (2007) 3126–3140.
 - [15] G. Li, V. Shrotriya, J.S. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, High-efficiency solution processable polymer photovoltaic cells by self-organization of polymer blends, *Nature Materials* 4 (2005) 864–868.
 - [16] S. Ko, R. Mondal, C. Risko, J.K. Lee, S. Hong, M.D. McGehee, J.-L. Bredas, Z.N. Bao, Tuning the optoelectronic properties of vinylene-linked donor–acceptor copolymers for organic photovoltaics, *Macromolecules* 43 (2010) 6685–6698.
 - [17] Z. Li, J.F. Ding, N.H. Song, J.P. Lu, Y. Tao, Development of a new s-tetrazine-based copolymer for efficient solar cells, *Journal of the American Chemical Society* 132 (2010) 13160–13161.
 - [18] M.C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A.J. Heeger, C.J. Brabec, Design rules for donors in bulk-heterojunction solar cells—towards 10% energy-conversion efficiency, *Advanced Materials* 18 (2006) 789–794.
 - [19] S.P. Wen, J.N. Pei, Y.H. Zhou, L.L. Xue, B. Xu, Y.W. Li, W.J. Tian, Synthesis and photovoltaic properties of poly(pphenylenevinylene) derivatives containing oxadiazole, *Journal of Polymer Science Part A: Polymer Chemistry* 47 (2009) 1003–1012.
 - [20] J.H. Hou, M.-H. Park, S.Q. Zhang, Y. Yao, L.-M. Chen, J.-H. Li, Y. Yang, Bandgap and molecular energy level control of conjugated polymer photovoltaic materials based on benzo[1,2-b:4,5-b']dithiophene, *Macromolecules* 41 (2008) 6012–6018.
 - [21] L.J. Huo, J.H. Hou, S.Q. Zhang, H.-Y. Chen, Y. Yang, A polybenzo[1,2-b:4,5-b']dithiophene derivative with deep HOMO level and its application in high-performance polymer solar cells, *Angewandte Chemie International Edition* 49 (2010) 1500–1503.
 - [22] H.X. Zhou, L.Q. Yang, A.C. Stuart, S.C. Price, S.B. Liu, W. You, Development of fluorinated benzothiadiazole as a structural unit for a polymer solar cell of 7% efficiency, *Angewandte Chemie International Edition* 123 (2011) 3051–3054.
 - [23] S.C. Price, A.C. Stuart, W. You, Low band gap polymers based on benzo[1,2-b:4,5-b']dithiophene: rational design of polymers leads to high photovoltaic performance, *Macromolecules* 43 (2010) 4609–4612.
 - [24] Y.Y. Liang, Y. Wu, D.Q. Feng, S.T. Tsai, H.J. Son, G. Li, L.P. Yu, Development of new semiconducting polymers for high performance solar cells, *Journal of the American Chemical Society* 131 (2009) 56–57.
 - [25] Y.Y. Liang, D.Q. Feng, Y. Wu, S.-T. Tsai, G. Li, C. Ray, L.P. Yu, Highly efficient solar cell polymers developed via fine-tuning of structural and electronic properties, *Journal of the American Chemical Society* 131 (2009) 7792–7799.
 - [26] J.H. Hou, H.-Y. Chen, S.Q. Zhang, R.I. Chen, Y. Yang, Y. Wu, G. Li, Synthesis of a low band gap polymer and its application in highly efficient polymer solar cells, *Journal of the American Chemical Society* 131 (2009) 15586–15587.
 - [27] H.-Y. Chen, J.H. Hou, S.Q. Zhang, Y.Y. Liang, G.W. Yang, Y. Yang, L.P. Yu, Y. Wu, G. Li, Polymer solar cells with enhanced open-circuit voltage and efficiency, *Nature Photonics* 3 (2009) 649–653.
 - [28] L.J. Huo, J.H. Hou, H.-Y. Chen, S.Q. Zhang, Y. Jiang, T.L. Chen, Y. Yang, Bandgap and molecular level control of the low-bandgap polymers based on 3,6-dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione toward highly efficient polymer solar cells, *Macromolecules* 42 (2009) 6564–6571.
 - [29] Y.P. Zou, A. Najari, P. Berrouard, S. Beaupre, B.R. Aich, Y. Tao, M. Leclerc, A thieno[3,4-c]pyrrole-4,6-dione-based copolymer for efficient solar cells, *Journal of the American Chemical Society* 132 (2010) 5330–5331.
 - [30] C. Piliego, T.W. Holcombe, J.D. Douglas, C.H. Woo, P.M. Beaujuge, J.M.J. Fréchet, Synthetic control of structural order in N-alkylthieno[3,4-c]pyrrole-4,6-dione-based polymers for efficient solar cells, *Journal of the American Chemical Society* 132 (2010) 7595–7597.
 - [31] Y. Zhang, S.K. Hau, H.-L. Yip, Y. Sun, O. Acton, A.K.-Y. Jen, Efficient polymer solar cells based on the copolymers of benzodithiophene and thienopyrroledione, *Chemistry of Materials* 22 (2010) 2696–2698.
 - [32] M.J. Zhang, H.J. Fan, X. Guo, Y.H. He, Z.-G. Zhang, J. Min, J. Zhang, G.J. Zhao, X.W. Zhan, Y.F. Li, Synthesis and photovoltaic properties of a copolymer of benzo[1,2-b:4,5-b']dithiophene and bithiazole, *Macromolecules* 43 (2010) 8714–8717.
 - [33] L.J. Huo, X. Guo, S.Q. Zhang, Y.F. Li, J.H. Hou, PBDTTTz: a broad band gap conjugated polymer with high photovoltaic performance in polymer solar cells, *Macromolecules* 44 (2011) 4035–4037.
 - [34] H. Pan, Y. Li, Y. Wu, P. Liu, B.S. Ong, S. Zhu, G. Xu, Low-temperature, solution-processed, high-mobility polymer semiconductors for thin-film transistors, *Journal of the American Chemical Society* 129 (2007) 4112–4113.
 - [35] H. Pan, Y. Wu, Y. Li, P. Liu, B.S. Ong, S. Zhu, G. Xu, Benzodithiophene copolymer—a low-temperature, solution-processed high-performance semiconductor for thin-film transistors, *Advanced Functional Materials* 17 (2007) 3574–3579.
 - [36] H. Pan, Y. Li, Y. Wu, P. Liu, B.S. Ong, S. Zhu, G. Xu, Synthesis and thin-film transistor performance of poly(4,8-didodecylbenzo[1,2-b:4,5-b']dithiophene), *Chemistry of Materials* 18 (2006) 3237–3241.
 - [37] H.J. Son, W. Wang, T. Xu, Y.Y. Liang, Y. Wu, G. Li, L.P. Yu, Synthesis of fluorinated polythienothiophene-co-benzodithiophenes and effect of fluorination on the photovoltaic properties, *Journal of the American Chemical Society* 133 (2011) 1885–1894.
 - [38] Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu, For the bright future—bulk heterojunction polymer solar cells with power conversion efficiency of 7.4%, *Advanced Materials* 22 (2010) E135–E138.
 - [39] Z. Li, J.F. Ding, N.H. Song, X.M. Du, J.Y. Zhou, J.P. Lu, Y. Tao, Alternating copolymers of dithienyl-s-tetrazine and cyclopentadithiophene for organic photovoltaic applications, *Chemistry of Materials* 23 (2011) 1977–1984.
 - [40] S.P. Wen, J.N. Pei, P.F. Li, Y.H. Zhou, W.D. Cheng, Q.F. Dong, Z.F. Li, W.J. Tian, Synthesis and photovoltaic properties of low-bandgap 4,7-dithien-2-yl-2,1,3-benzothiadiazole-based poly(heteroarylenevinylene)s, *Journal of Polymer Science Part A: Polymer Chemistry* 49 (2011) 2715–2724.
 - [41] I.H. Jung, Y.K. Jung, J. Lee, J.-H. Park, H.Y. Woo, J.-I. Lee, H.Y. Chu, H.-K. Shim, Synthesis and electroluminescent properties of fluorene-based copolymers containing electron-withdrawing thiazole derivatives, *Journal of Polymer Science Part A: Polymer Chemistry* 46 (2008) 7148–7161.
 - [42] Y. Zhu, R.D. Champion, S.A. Jenekhe, Conjugated donor–acceptor copolymer semiconductors with large intramolecular charge transfer: synthesis, optical properties, electrochemistry, and field effect carrier mobility of thienopyrroazine-based copolymers, *Macromolecules* 43 (2010) 8712–8719.
 - [43] T. Yamamoto, D. Komarudin, M. Arai, B.L. Lee, H. Suganuma, N. Asakawa, Y. Inoue, K. Kubota, S. Sasaki, T. Fukuda, H. Matsuda, Extensive studies on π -stacking of poly(3-alkylthiophene-2,5-diyl)s and poly(4-alkylthiazole-2,5-diyl)s by optical spectroscopy, NMR analysis, light scattering analysis, and X-ray crystallography, *Journal of the American Chemical Society* 120 (1998) 2047–2058.
 - [44] Q. Peng, K. Park, T. Lin, M. Durstock, L.M. Dai, Donor– π -acceptor conjugated copolymers for photovoltaic applications: tuning the open-circuit voltage by adjusting the donor/acceptor ratio, *Journal of Physical Chemistry B* 112 (2008) 2801–2808.
 - [45] S.P. Wen, J.N. Pei, Y.H. Zhou, P.F. Li, L.L. Xue, Y.W. Li, B. Xu, W.J. Tian, Synthesis of 4,7-diphenyl-2,1,3-benzothiadiazole-based copolymers and their photovoltaic applications, *Macromolecules* 42 (2009) 4977–4984.
 - [46] Z.-J. Li, W.-W. Yang, X. Gao, A room-temperature fluorescence study of organofullerenes: cis-1 bisadduct with unusual blue-shifted emissions, *Journal of Physical Chemistry A* 115 (2011) 6432–6437.