

Benzodithiophene-Based Poly(aryleneethynylene)s: Synthesis, Optical Properties, and Applications in Organic Solar Cells

Shuguang Wen,¹ Xichang Bao,¹ Wenfei Shen,^{1,2} Chuantao Gu,¹
Zhengkun Du,¹ Liangliang Han,¹ Dangqiang Zhu,¹ Renqiang Yang¹

¹CAS Key Laboratory of Bio-based Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China

²Institute of Hybrid Materials, Laboratory of New Fiber Materials and Modern Textile – The Growing Base for State Key Laboratory, Qingdao University, Qingdao 266071, China

Correspondence to: R. Yang (E-mail: yangrq@qibebt.ac.cn)

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ABSTRACT: The synthesis and characterization of building block of ethynylene-substituted benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT), and its application in the construction of poly(aryleneethynylene)s (PAEs) are described in this article. Alkoxy-substituted BDT and thiazolothiazole are selected as the other copolymerized units, and polymers of PEBBDT and PEBTTZ were synthesized by Pd-catalyzed Sonogashira coupling reaction. These polymers showed intense interchain π - π interaction and deep HOMO levels (≤ -5.50 eV). Bulk heterojunction solar cell fabricated using PEBBDT or PEBTTZ as electron donor and PC₆₁BM

as acceptor display power conversion efficiency of 0.85 and 2.40%, respectively, under the illumination of AM1.5G, 100 mW cm⁻². This study shows good prospect for the application of PAEs-type polymers in organic solar cell. © 2013 Wiley Periodicals, Inc. *J. Polym. Sci., Part A: Polym. Chem.* **2014**, *52*, 208–215

KEYWORDS: bulk-heterojunction; charge transfer; conjugated polymer; heteroatom-containing polymers; organic solar cell; poly(aryleneethynylene)s; structure; property relationships

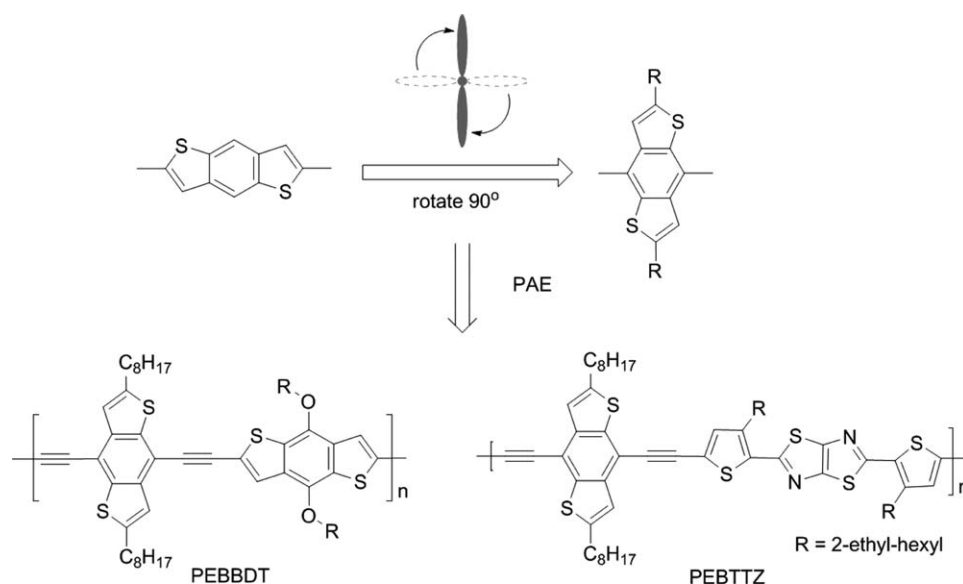
INTRODUCTION In recent several years, polymer solar cells (PSCs) have attracted much attention in both academia and industry, because of their advantages of flexibility, lightweight, and solution processability.^{1–4} With these efforts, several groups have developed some highly efficient photovoltaic polymers, and power conversion efficiencies (PCEs) of up to 9% have been achieved in bulk heterojunction (BHJ) cells devices.^{5–8} As well known, the PCE is proportional to the open circuit voltage (V_{oc}), short circuit current (J_{sc}), and fill factor (FF) of the PSCs. These parameters can be optimized by modifying molecular structures of photovoltaic polymers.⁹ Different strategies have been developed to adjust the relationship of structure–property. For example, the donor–acceptor (D–A) approach is used to construct low-band-gap polymers with tunable energy levels;¹⁰ mobility of conjugated polymers can be improved by increasing regularity of the backbone units. Such modifications promoted the great development of PSCs.

Poly(aryleneethynylene)s (PAEs) are a fascinating class of conjugated polymers. These polymers have rigid backbones for pronounced interchain interactions and are easily synthe-

sized and chemically stable. In recent years, PAEs have attracted much attention in the field of chemical actuators and sensors¹¹ but only a few was reported as a PSCs material.¹² The ethynylene unit in conjugated polymer is characterized as a weak electron-withdrawn group, which is beneficial for lowering the HOMO level and hence increasing V_{oc} of PSCs.¹³ Furthermore, due to containing the rigid backbone of triple bond, PAE is suspected to have high interchain interactions and ordered arrangement, which favors good charge transport characteristic. Given these considerations, we have developed two BDT-based PAE-type polymers. The BDT unit is connected into the conjugated chain directly through the central benzene ring, which is totally different from the conventional approach (Scheme 1). Compared to the usual benzene unit in poly(*p*-phenylenevinylene)s (PPVs), introduction of the vertical BDT to PAE can expand the dimensionality of π -conjugated structure, which will contribute to improving π - π interaction and carrier mobility of the polymer. Thus, ethynylene-substituted BDT monomer (EB, **7**) was used as one copolymerized unit. Alkoxy-substituted BDT (**8**) and thiazolo[5,4-*d*]thiazole (**9**) units were used as the other comonomer, and thus, polymers PEBBDT and PEBTTZ

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**SCHEME 1** Polymer structures of PEBBDT and PEBTTZ.

were synthesized by the Sonogashira coupling reaction. They are characterized as ethynylene-containing donor–donor (D–D) and donor–acceptor (D–A) type copolymer, respectively. Using PEBBDT and PEBTTZ as electron donor materials and PC₆₁BM as the counterpart, solution-processed BHJ solar cells were fabricated and characterized. The relationship between molecular structure, optical property, nanoscale morphology, and PSCs performance was investigated.

EXPERIMENTAL

Materials

All reactions and manipulations were carried out under argon with the use of standard inert atmosphere. Solvents were dried by standard procedures. All column chromatography was performed with the use of silica gel 200–300 mesh. 5-Octylthiophene-3-carboxylic acid (**3**),¹⁴ 2,6-dioctyl-4,8-bis(trimethylsilylethynyl)benzo[1,2-*b*:4,5-*b'*]dithiophene (**6**),¹⁵ and polymers were synthesized according to the literature methods. Unless stated otherwise, the other reagents were purchased from commercial sources, and used without further purification.

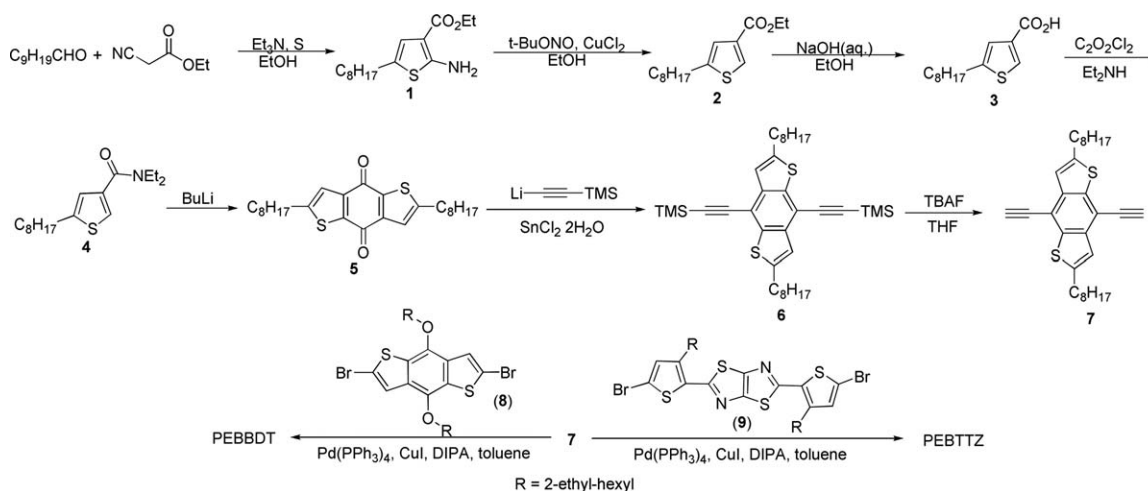
Instrumentation

¹H NMR and ¹³C NMR spectra were performed in a Bruker AVANCE-III 600 MHz spectrometer using solutions in CDCl₃ and chemical shifts were recorded in ppm units with tetramethylsilane (TMS) as the internal standard. Elemental analyses were carried out using a vario EL cube elemental analyzer. UV–vis spectra were recorded on a Lambda25 spectrophotometer. The electrochemical measurements were carried out under nitrogen on a deoxygenated solution of tetra-*n*-butylammonium hexafluorophosphate (*n*-Bu₄NPF₆, 0.1 M) in acetonitrile with a computer-controlled CHI660C electrochemical workstation, a Pt working electrode, a platinum-wire auxiliary electrode, and an SCE as a pseudore-

ference electrode. Potentials were referenced to the ferrocene/ferrocenium (Fc/Fc⁺) couple by using ferrocene as a standard. The HOMO levels of the polymers were determined using the oxidation onset value. Onset potentials are values obtained from the intersection of the two tangents drawn at the rising current and the baseline changing current of the cyclic voltammetry (CV) curves. Differential scanning calorimeter (DSC) and thermal gravimetric analysis (TGA) measurements were performed on STA-409 at a heating rate of 10 °C min^{−1}. All GPC analyses were made using tetrahydrofuran (THF) as eluant and polystyrene standard as reference. Topographic images of the active layers were obtained through atomic force microscopy (AFM) in tapping mode under ambient conditions using an Agilent 5400 instrument.

Photovoltaic Device Fabrication and Characterization

The PSCs were fabricated with a configuration of ITO/PEDOT:PSS/polymers:PC₆₁BM/Ca/Al. A thin layer of PEDOT:PSS [30 nm, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)] was spin-cast on precleaned ITO-coated glass from a PEDOT:PSS aqueous solution (Baytron P VP Al 4083 from H. C. Starck) at 4000 rpm and dried subsequently at 150 °C for 30 min in air, then the device was transferred into glovebox, where the active layer (100 nm) of the blend of the polymer and PC₆₁BM was spin-coated on the PEDOT:PSS layer. Finally, a Ca (10 nm)/Al (100 nm) metal top electrode was thermal evaporated onto the active layer under about 2 × 10^{−4} Pa. The active area of the device was 0.1 cm² defined by shadow mask. The current density–voltage (*J*–*V*) characteristics were measured with a Keithley 2420 source measurement unit under simulated 100 mW cm^{−2} (AM 1.5G) irradiation from a Newport solar simulator. Light intensity was calibrated with a standard silicon solar cell. The external quantum efficiencies (EQE) of solar cells were analyzed using a certified Newport incident photon conversion efficiency measurement system.



SCHEME 2 Synthetic routes of PEBBDT and PEBTTZ.

Synthesis

The synthetic routes of the monomers and polymers were shown in Scheme 2. The detailed synthetic processes are described as follows.

Ethyl 2-amino-5-octylthiophene-3-carboxylate (1)

Decanal (16.07 g, 103 mmol), ethyl cyanoacetate (10.5 mL, 99 mmol), and sulfur (3.3 g, 103 mmol) were dissolved in EtOH (100 mL). Triethylamine (20 mL) was added and the reaction was stirred at 60 °C overnight. The solvent was removed under vacuum and the product was purified by column chromatography on silica, eluting with petroleum ether/ethyl acetate (10:1). The product was obtained as a yellow oil (28.0 g, 100%).

^1H NMR (600 MHz, CDCl_3) 6.54 (s, 1H), 5.72 (s, 2H), 4.18 (q, $J = 7.2$ Hz, 2H), 2.49 (t, $J = 7.4$ Hz, 2H), 1.49 (m, 2H), 1.27–1.20 (m, 13H), 0.81 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 164.4, 160.2, 126.0, 120.3, 105.3, 58.5, 30.8, 30.1, 28.7, 28.3, 28.2, 28.0, 21.6, 13.5, 13.1; IR (film) ν_{max} 3440, 3334, 2926, 1675, 913, 745 cm^{-1} . Anal. Calcd. for $\text{C}_{15}\text{H}_{25}\text{NO}_2\text{S}$: C, 63.56; H, 8.89; N, 4.94; S, 11.31. Found: C, 67.61; H, 8.78; N, 5.07; S, 11.18.

Ethyl 5-octylthiophene-3-carboxylate (2)

Ethyl 2-amino-5-octylthiophene-3-carboxylate (14.3 g, 50 mmol) was added to a suspension solution of *t*-BuONO (10 mL, 75.8 mmol, 1.5 equiv) and CuCl_2 (7.1 g, 53 mmol, 1.05 equiv) in EtOH (100 mL). The reaction mixture was stirred for 0.5 h then saturated aqueous ammonium chloride (50 mL) was added, and the mixture was stirred for a further 15 min. The solvent was removed under vacuum and the residue partitioned between EtOAc and water. The organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography to give light yellow oil (9.4 g, 70%).

^1H NMR (600 MHz, CDCl_3) 7.80 (d, $J = 1.2$ Hz, 1H), 7.11 (d, $J = 1.0$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 2.71 (t, $J = 7.6$ Hz, 2H), 1.59 (m, 2H), 1.30–1.17 (m, 13H), 0.81 (t, $J = 7.1$ Hz,

3H); ^{13}C NMR (150 MHz, CDCl_3) δ 161.9, 145.5, 132.3, 129.3, 123.4, 59.5, 30.8, 30.4, 28.9, 28.3, 28.2, 28.0, 21.6, 13.3, 13.1; IR (film) ν_{max} 2927, 2855, 1717, 1228, 913, 743 cm^{-1} . Anal. Calcd. for $\text{C}_{15}\text{H}_{24}\text{O}_2\text{S}$: C, 67.12; H, 9.01; S, 11.95. Found: C, 67.26; H, 8.86; S, 11.87.

5-Octylthiophene-3-carboxylic acid (3)

A mixture of ester 2 (20.6 g, 71.5 mmol) and NaOH (5.95 g, 148.7 mmol) in EtOH (200 mL) was heated to reflux for 3 h. After TLC indicated the absence of starting material, the solvent was removed *in vacuo*. Water (100 mL) was added to the residue, and the pH was adjusted to 1 with 12 M hydrochloric acid. The precipitate was collected by filtration and recrystallized from hexane to yield acid 3 as a white solid (13.8 g, 80%).

^1H NMR (600 MHz, CDCl_3) 8.02 (d, $J = 1.1$ Hz, 1H), 7.22 (s, 1H), 2.80 (t, $J = 7.6$ Hz, 2H), 1.68 (m, 2H), 1.37–1.27 (m, 10H), 0.81 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 168.3, 147.0, 132.6, 132.3, 124.5, 31.8, 31.4, 29.9, 29.3, 29.2, 29.0, 22.7, 14.1; IR (film) ν_{max} 2926, 2853, 1663, 1468, 911, 732 cm^{-1} . Anal. Calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_2\text{S}$: C, 64.96; H, 8.39; S, 13.34. Found: C, 65.15; H, 8.19; S, 13.56.

N,N-Diethyl-5-octylthiophene-3-carboxamide (4)

5-Octylthiophene-3-carboxylic acid (5.87 g, 244 mmol) and 50 mL of methylene chloride were put into a 150-mL flask. The mixture was cooled by ice-water bath, and then oxalyl chloride (4.3 mL, 489 mmol) was added in one portion. The reactant was stirred overnight at ambient temperature, and a clear solution was obtained. After removing the solvent and unreacted oxalyl chloride by rotary evaporation, the corresponding thiophene-3-carbonyl chloride was obtained. It was dissolved into 50 mL of methylene chloride and used for the next step.

In a 150-mL flask in ice-water bath, diethylamine (5.1 mL, 489 mmol) and 50 mL of methylene chloride were mixed, and the solution of thiophene-3-carbonyl chloride was added into the flask slowly. After all of the solution was added, the

ice bath was removed, and the reactant was stirred at ambient temperature for 30 min. Then, the reactant was washed by water several times, and the organic layer was dried over anhydrous Na_2SO_4 . After removing solvent, the crude product was purified by column chromatography to give pale yellow oil (6.5 g, 90%).

^1H NMR (CDCl_3 , 600 MHz): 7.22 (d, $J = 1.4$ Hz, 1H), 6.85 (d, $J = 1.0$ Hz, 1H), 3.43 (br, 4H), 2.78 (t, $J = 7.7$ Hz, 2H), 1.66 (m, 2H), 1.37–1.19 (m, 16 H), 0.88 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 166.9, 146.3, 137.0, 123.8, 122.4, 31.8, 31.5, 29.9, 29.3, 29.2, 29.0, 22.7, 14.1; IR (film) ν_{max} 2928, 2855, 1628, 1463, 913, 743 cm^{-1} . Anal. Calcd. for $\text{C}_{17}\text{H}_{29}\text{NOS}$: C, 69.10; H, 9.89; N, 4.74; S, 10.85. Found: C, 69.19; H, 10.02; N, 4.85; S, 10.74.

2,6-Dioctyl-4,8-dihydrobenzo[1,2-b:4,5-b']dithiophene-4,8-dione (5)

Compound **4** (2.95 g, 10.0 mmol) was put into a well-dried flask with 100 mL of THF under an inert atmosphere. The solution was cooled down by an ice-water bath, and 7.0 mL of *n*-butyllithium (11.2 mmol, 1.6 M) was added into the flask dropwise. Then, the reactant was stirred at ambient temperature for 30 min. The reactant was poured into ice water and stirred for several hours. The mixture was filtrated, and the yellow precipitate was washed by water, methanol, and hexane successively. The product was obtained as a yellow solid (1.6 g, 72%).

^1H NMR (CDCl_3 , 600 MHz): 7.30 (s, 2H), 2.89 (t, $J = 1.6$ Hz, 4H), 1.74 (m, 4H), 1.41–1.27 (m, 20 H), 0.90 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (150 MHz, CDCl_3) δ 174.6, 155.7, 143.1, 141.9, 123.6, 31.8, 31.2, 30.6, 29.2, 29.1, 29.0, 22.6, 14.1; IR (film) ν_{max} 2920, 2853, 1645, 1452, 908, 732 cm^{-1} . Anal. Calcd. for $\text{C}_{26}\text{H}_{36}\text{O}_2\text{S}_2$: C, 70.22; H, 8.16; S, 14.42. Found: C, 70.43; H, 8.09; S, 14.39.

2,6-Dioctyl-4,8-bis(trimethylsilylethynyl)-benzo[1,2-b:4,5-b']dithiophene (6)

Under an atmosphere of argon, *n*-butyllithium (7.57 mL, 1.6 M in hexane, 12 mmol) was added dropwise to a solution of (trimethylsilyl)acetylene (1.67 mL, 12 mmol) in THF (15 mL) at 0 °C. The mixture was then kept at 0 °C for another 40 min before it was transferred to a solution of quinone **5** (2.15 g, 4.8 mmol) in THF (30 mL) at 0 °C. The mixture was warmed to room temperature and stirred overnight. The reaction was quenched with 9 mL of 10% HCl and then subjected to a $\text{CHCl}_3/\text{H}_2\text{O}$ workup. The solvent was removed and the crude residue was dissolved in 48 mL of acetone. Then a solution of tin (II) chloride dihydrate (2.46 g, 10.9 mmol) in 50% of acetic acid (48 mL) was added dropwise. This mixture was stirred at room temperature for another 24 h, and the resulting solid product was filtered. The solid was then dissolved in CHCl_3 , washed with water and sodium bicarbonate solution, and then dried by Na_2SO_4 . The CHCl_3 was removed *in vacuo* and the residue was purified by column chromatography on silica to give the product **6** as a white solid (0.92 g, 32%).

^1H NMR (600 MHz, CDCl_3) 7.23 (s, 2H), 2.96 (t, $J = 7.6$ Hz, 4H), 1.81 (m, 4H), 1.46–1.28 (m, 20H), 0.91 (t, $J = 7.0$, 6H), 0.39 (s, 18H); ^{13}C NMR (150 MHz, CDCl_3) 148.4, 139.9, 138.2, 119.6, 110.4, 104.1, 101.1, 31.9, 31.3, 31.2, 31.1, 29.4, 29.2, 22.3, 14.1, 0.1; IR (film) ν_{max} 2952, 2928, 2151, 1249, 842, 758 cm^{-1} . Anal. Calcd. for $\text{C}_{36}\text{H}_{54}\text{S}_2\text{Si}_2$: C, 71.22; H, 8.97; S, 10.56. Found: C, 71.06; H, 8.73; S, 10.78.

2,6-Dioctyl-4,8-diethynyl-benzo[1,2-b:4,5-b']dithiophene (7)

Compound **6** (143 mg, 0.23 mmol) was dissolved in dry THF (3 mL). The solution was cooled to 0 °C and Bu_4NF (142 μL , 1 M in THF, 0.14 mmol) was added dropwise. After 30 min, the reaction was quenched with water and extracted with CHCl_3 . The organic phase was washed with saturated brine, dried with Na_2SO_4 and concentrated. The residue was purified by column chromatography with hexane to give the compound **7** as white solid (98 mg, 81%).

^1H NMR (600 MHz, CDCl_3) 7.28 (s, 2H), 3.80 (s, 2H), 2.96 (t, $J = 7.6$ Hz, 4H), 1.81 (m, 4H), 1.46–1.29 (m, 20H), 0.91 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (150 MHz, CDCl_3) 148.7, 140.0, 138.7, 119.5, 109.6, 86.0, 80.0, 31.9, 31.2, 31.0, 29.3, 29.2, 29.1, 22.3, 14.1; IR (film) ν_{max} 3289, 2924, 2848, 2102, 1172, 665 cm^{-1} . Anal. Calcd. for $\text{C}_{30}\text{H}_{38}\text{S}_2$: C, 77.98; H, 8.28; S, 13.86. Found: C, 77.86; H, 8.30; S, 13.67.

Synthesis of Polymer PEBBDT

A mixture of diyne monomer **7** (73.9 mg, 0.160 mmol), dibromo monomer **8** (96.6 mg, 0.160 mmol, 1.0 equiv), $\text{Pd}(\text{PPh}_3)_4$ (9.2 mg, 0.008 mmol, 0.05 equiv), and CuI (2.4 mg, 0.013 mmol, 0.08 equiv) are placed in a Schlenk flask equipped with a magnetic stirrer. Contents are evacuated and back-filled with argon five times. Degassed toluene (3 mL) and diisopropylamine (1 mL) are introduced, and after five more quick vacuum/back-fill cycles, the resulting mixture is stirred at room temperature for 30 min, followed by 48 h at 65 °C and 24 h at 75 °C. After cooling to room temperature, contents are precipitated in MeOH, and isolated by centrifugation. Then, the crude polymer is extracted with MeOH, acetone, hexane, and CHCl_3 in a Soxhlet extractor successively. The fraction from chloroform was concentrated under reduced pressure and precipitated into methanol to give the polymer as a red solid (108 mg, 74%). GPC: $M_n = 18.5$ K; $M_w/M_n = 1.5$.

^1H NMR (600 MHz, CDCl_3), δ (ppm): 7.76–7.36 (m, 4H), 4.28–4.19 (m, 4H), 3.03 (br, 4H), 1.88–0.92 (m, 60H). Anal. Calcd. for $\text{C}_{56}\text{H}_{72}\text{O}_2\text{S}_4$: C, 74.29; H, 8.02; S, 14.17. Found: C, 74.13; H, 8.32; S, 14.28.

Synthesis of polymer PEBTTZ

A mixture of diyne monomer **7** (92.4 mg, 0.20 mmol), dibromo monomer **9** (138.0 mg, 0.20 mmol, 1.0 equiv), $\text{Pd}(\text{PPh}_3)_4$ (11.5 mg, 0.010 mmol, 0.05 equiv), and CuI (3.0 mg, 0.016 mmol, 0.08 equiv) are placed in a Schlenk flask equipped with a magnetic stirrer. Contents are evacuated and back-filled with argon five times. Degassed toluene (4.2 mL) and diisopropylamine (1.4 mL) are introduced, and after five more quick vacuum/back-fill cycles, the resulting

TABLE 1 Molecular Weights, Polydispersity Index, and Thermal Properties of Polymers

Polymers	M_w (K)	M_n (K)	PDI	T_d (°C) ^a
PEBBDT	27.7	18.5	1.5	359
PEBTTZ	19.7	8.6	2.3	393

^a The 5% weight-loss temperatures under inert atmosphere.

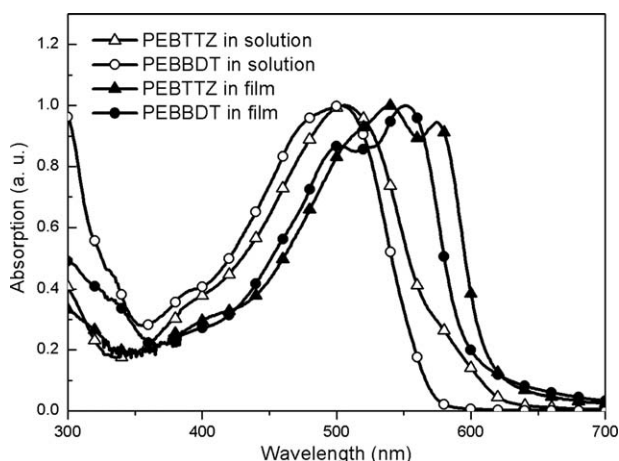
mixture is stirred at room temperature for 30 min, followed by 48 h at 65 °C and 24 h at 75 °C. After cooling to room temperature, contents are precipitated in MeOH, and isolated by centrifugation. Then the crude polymer is extracted with MeOH, acetone, hexane, and CHCl₃ in a Soxhlet extractor successively. The fraction from chloroform was concentrated under reduced pressure and precipitated into methanol to give the polymer as a red solid (53 mg, 26%). GPC: M_n = 8.6 K; M_w/M_n = 2.3.

¹H NMR (600 MHz, CDCl₃), δ (ppm): 7.27–6.94 (m, 4H), 3.03–2.87 (m, 8H), 1.86 (m, 2H), 1.57–1.28 (m, 40H), 0.99–0.89 (m, 18H). Anal. Calcd. for C₅₈H₇₂N₂S₆: C, 70.39; H, 7.33; N, 2.83; S, 19.44. Found: C, 70.52; H, 7.17; N, 2.72; S, 19.58.

RESULTS AND DISCUSSION

Synthesis and Structural Characterization

The polymers PEBBDT and PEBTTZ were synthesized by Pd/Cu-catalyzed Sonogashira coupling copolymerization of alkyne **7** with dibromide compounds **8** and **9**, respectively, in toluene. The comonomer **7** was synthesized from thiophene-3-carboxylic acid **3**, similar to the synthesis of common BDT compound.¹⁵ The 2-alkyl substituted thiophene unit was obtained by a three-component reaction manner of aldehyde, sulfur, and cyanoacetate to produce 2-amino thiophene **1**.¹⁴ Then through the reaction of deamination and hydrolysis the compound **3** was obtained in good yield. PEBBDT was readily soluble in organic solvents [chloroform, THF, chlorobenzene (CB), etc.] at room temperature, whereas PEBTTZ was less soluble in these solvents.

**FIGURE 1** Absorption spectra of PEBBDT and PEBTTZ in dilute chloroform solutions and as thin films.**TABLE 2** Optical Properties and Energy Levels of Polymers PEBBDT and PEBTTZ

Polymers	λ_{\max} ^a (nm)		E_g^{opt} ^b	HOMO ^c (eV)	LUMO ^d (eV)
	Solution	Film			
PEBBDT	503	503, 551	2.08	−5.57	−3.49
PEBTTZ	506	539, 574	2.04	−5.50	−3.46

^a Absorption maxima.

^b Optical band gap estimated from the onset of absorption spectra in solid film.

^c Determined from the onset oxidation based on the reference energy level (ref. 16).

^d Calculated by the equation LUMO = HOMO + E_g^{opt} (eV).

The molecular weights of the polymers were estimated using gel permeation chromatography measured in THF relative to polystyrene standards. The results are summarized in Table 1. PEBTTZ was obtained with lower molecular weights than PEBBDT, which may be caused by the poor solubility of PEBTTZ in the reaction. Thermal stability of the polymers was investigated with TGA under a nitrogen atmosphere. The decomposition temperatures (T_d) of PEBBDT and PEBTTZ are 359 and 393 °C, respectively (Table 1, Supporting Information Fig. 1S), demonstrating their sufficiently high thermal stability for applications in PSCs. DSC measurement of the polymers showed no apparent phase transition up to 250 °C, indicating that the polymers tended to be amorphous.

Optical Properties

The photophysical characteristics of the polymers were investigated by ultraviolet–visible (UV–vis) absorption spectroscopy in dilute chloroform solutions and as spin-coated films on quartz substrates, as shown in Figure 1. Both of the polymers PEBBDT and PEBTTZ show similar absorption band with maximum peak at 503 and 506 nm in solution, respectively (Table 2). The thin film absorption spectrum of PEBBDT has two peaks at 503 and 551 nm, resulting in an absorption edge optical band gap (E_g^{opt}) of 2.08 eV. Similarly, PEBTTZ shows a maximum absorption at 539 nm and a shoulder at 574 nm. The optical band gap of 2.04 eV is slightly reduced compared to PEBBDT. Compared with the absorption spectra of polymers in solution, clear shoulder peaks are formed in the solid film spectra, which indicate that there have strong π – π stacking interchain interactions or aggregation in PEBBDT and PEBTTZ solid films.

Electrochemical Properties

The electrochemical CV (Fig. 2) of PEBBDT and PEBTTZ was performed in acetonitrile at a potential scan rate of 50 mV s^{−1} for determining the HOMO energy levels of the polymer films. And a standard ferrocene/ferrocenium (Fc/Fc⁺) redox system was used as the internal standard. The results are summarized in Table 2. The CV curves of PEBBDT and PEBTTZ films show the oxidation peaks with the onset oxidation potentials (ϕ_{ox}) of 1.16 and 1.09 V versus SCE, corresponding to the HOMO energy level of −5.57 and −5.50 eV,

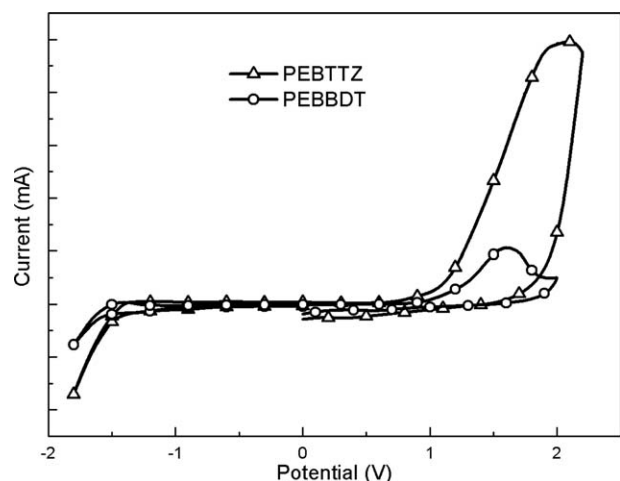


FIGURE 2 Cyclic voltammograms of PEBBDT and PEBTTZ films on Pt electrode in a 0.1 mol L⁻¹ *n*-Bu₄NPF₆ acetonitrile solution at a sweep rate of 50 mV s⁻¹.

respectively. The low-lying HOMO level is attributed to the incorporation of weak electron-withdrawing triple bonds in the conjugated polymer main chains. Note that the HOMO energy level is estimated using the following relation: $\text{HOMO} = -e(E^{\text{ox}}(\text{onset}) - E^{1/2}(\text{ferrocene}) + 4.8)$ (eV), where the unit of $E^{\text{ox}}(\text{onset})$ is V (vs. SCE).¹⁶ The relatively deep HOMO levels of both polymers provide better air stability in ambient conditions and higher V_{oc} of the PSCs because the V_{oc} is usually proportional to the difference between the LUMO level of the acceptor and the HOMO level of the donor.¹⁷ The LUMO energy levels of PEBBDT and PEBTTZ were determined to be -3.49 and -3.46 eV, respectively, which guarantee the charge separation between the donor and acceptor (Table 2).

Photovoltaic Properties

In order to investigate the potential applications of the copolymers in solar cells, the bulk heterojunction PSCs were

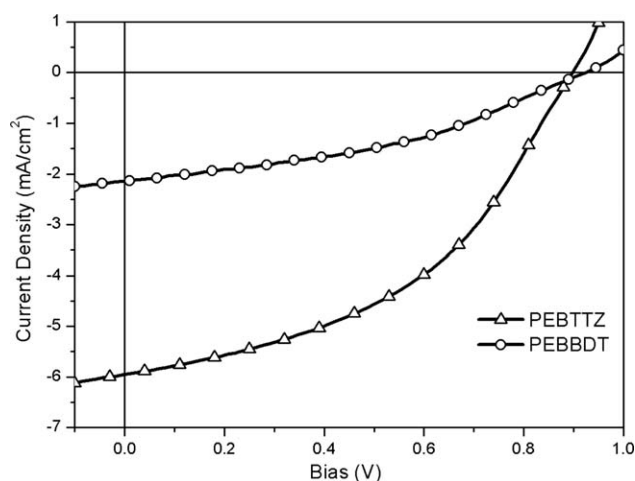


FIGURE 3 Typical J - V curves of the PSCs based on polymers:PC₆₁BM (1:1) under AM1.5G illumination (100 mW cm⁻²).

TABLE 3 Photovoltaic Properties of PSCs Based on Polymers:PC₆₁BM = 1:1

Polymer ^a	Treatment	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE (%)
PEBBDT	Annealed at 80 °C	0.92	2.38	39.0	0.85
	As cast	0.87	1.51	33.1	0.43
PEBTTZ	Annealed at 80 °C	0.83	3.83	40.0	1.59
	As cast	0.90	5.95	45.0	2.40

^a 10 mg mL⁻¹ of polymer in CB solution.

fabricated with device structure of ITO/PEDOT:PSS/polymers: PC₆₁BM/Ca/Al. Both PEBBDT/PC₆₁BM and PEBTTZ/PC₆₁BM blends were dissolved into CB to make the solutions of the D-A blends for spin-coating, respectively. Photovoltaic devices were tested under the illumination of AM1.5G, 100 mW cm⁻². The performance of the PSCs were strongly affected by the processing parameters, such as the choice of solvent, the blend ratio of the polymer to PC₆₁BM, and the additive effects.¹⁸ The photovoltaic effect of the two polymers were investigated under a variety of conditions. The ratio of polymer to PC₆₁BM was adjusted from 2:1, 1:1 to 1:2 (by weight), and the optimized condition was 1:1 for both of them. Addition of 1,8-diiodooctane gave no improvement on PCEs. Thermal annealing process helps improving the PCE of PEBBDT but decreasing the performance for PEBTTZ. Figure 3 shows the current density versus voltage (J - V) curves of the devices with optimum D-A ratio; the basic photovoltaic data are listed in Table 3. The device based on the PEBBDT:PC₆₁BM blend exhibited a great V_{oc} of 0.92 V, a J_{sc} of 2.38 mA cm⁻², a FF of 39%, delivering a PCE of 0.85%. And the device using PEBTTZ:PC₆₁BM blend exhibited a V_{oc} value of 0.90 V and a larger J_{sc} of 5.95 mA cm⁻² with an improved PCE of 2.40%. High V_{oc} values (≥ 0.90 V) of both polymers were resulted from the deep HOMO level

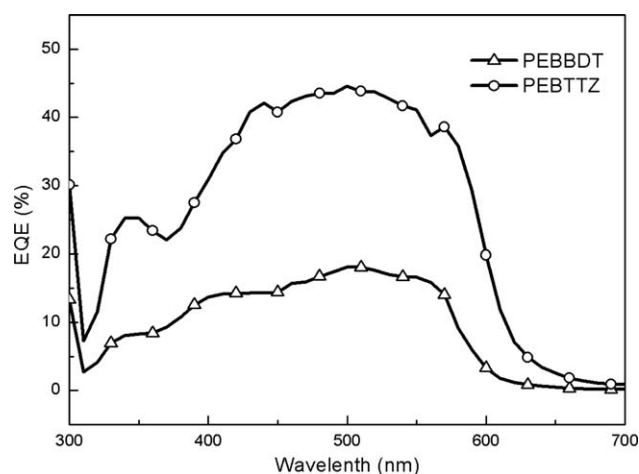


FIGURE 4 EQE curves of the PSCs based on polymers:PC₆₁BM (1:1).

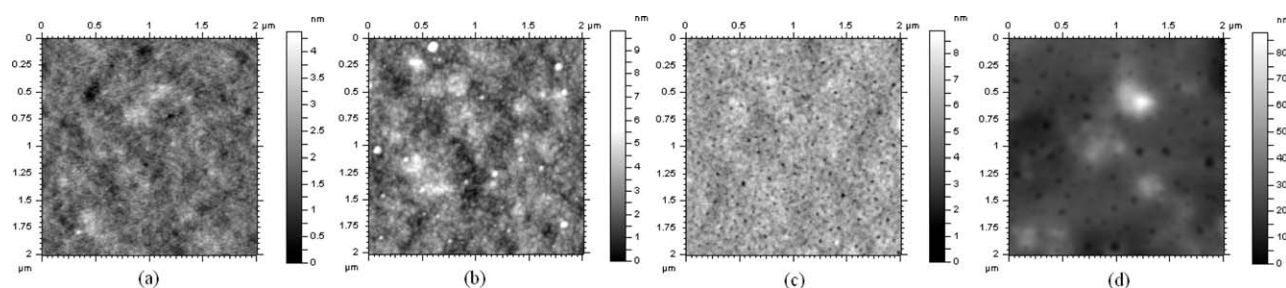


FIGURE 5 AFM height images of polymer:PC₆₁BM (1:1) blend films: (a, b) PEBBDT, (c, d) PEBTTZ, (a, c) as-cast, and (b, d) annealed at 80 °C.

(≤ -5.50 eV). Compared to PEBBDT, PEBTTZ showed higher J_{sc} value, which may be originated from the relatively lower band gap and stronger π - π stacking interaction. Thermal treatment has great influence on PCE especially the J_{sc} . Annealing the blend film at 80 °C for 10 min, all the parameters of PEBBDT was increased and the J_{sc} increased from 1.51 to 2.38 mA cm⁻². However, for PEBTTZ, the parameters of the device were decreased upon thermal annealing. This opposite results may be induced by different transformation of morphologies during the annealing process, which will be discussed later. The relatively low FF values of two polymers indicate unfavorable compatibility between donor and acceptor, which could be optimized by the spin-coating condition, active layer morphology, and device structure.¹⁹

EQE spectra were measured under illumination of monochromatic light (Fig. 4). It is observed that the EQE value of PEBTTZ is higher than that of PEBBDT in the whole spectra (325–600 nm) and the maximum value reaches 43%. It indicates that PEBTTZ has good photo response among the absorption range and PEBBDT is inefficient.

Morphological Characterization

To investigate the effect of nanoscale topography on the performance of PSC, AFM was employed to measure the surface morphology.²⁰ The height images of the blends (polymer:PC₆₁BM = 1:1) prepared from CB solution are shown in Figure 5.

The unannealed blend film of PEBBDT exhibits an organized nanofibrillar structure with a root-mean-squared (rms) surface roughness of 0.44 nm [Fig. 5(a)]. After annealing at 80 °C, the blend film appears small crystallite region [Fig. 5(b)], which is favorable for the charge transferring. Therefore, the J_{sc} and PCE were increased as a result. As for PEBTTZ, the unannealed blend film exhibits a uniform and smooth surface formed by tightly packed small and regular unconnected grains [Fig. 5(c)].^{21,22} This structure is destroyed upon the annealing process and the surface roughness is increased from 0.82 to 5.81 nm [Fig. 5(d)]. The coarsening of morphology reduces the diffusion and separation of excitons and charge transport, leading to lower J_{sc} and FF. Thus, the as-cast device of PEBTTZ shows higher properties. The morphologies of the two blends well support the photovoltaic performance (Fig. 3 and Table 3).

CONCLUSIONS

We have successfully synthesized two novel polymers PEBBDT and PEBTTZ by Pd-catalyzed Sonogashira coupling reaction. The polymers are characterized as ethynylene-containing D-D- and D-A-type structures, respectively. The investigation of optical properties shows that PEBBDT and PEBTTZ have similar optical band gap with 2.08 and 2.04 eV and HOMO level of -5.57 and 5.50 eV, respectively. Both copolymers were applied as electron-donating materials with PC₆₁BM as acceptor in conventional BHJ photovoltaic devices. The PSC based on PEBBDT:PC₆₁BM = 1:1 (w/w) reached a PCE of 0.85% with $J_{sc} = 2.38$ mA cm⁻², $V_{oc} = 0.92$ V, and FF = 39.0%, and the PSC based on PEBTTZ:PC₆₁BM = 1:1 (w/w) reached a PCE of 2.40% with $J_{sc} = 5.95$ mA cm⁻², $V_{oc} = 0.90$ V, and FF = 45.0%, under the illumination of AM1.5G, 100 mW cm⁻². High V_{oc} values of over 0.90 V were achieved for both polymers, which were attributed to the deep HOMO levels. Although two polymers possess similar band gaps and energy levels, the D-A-type polymer PEBTTZ exhibits even higher photovoltaic performance.

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REFERENCES AND NOTES

- 1 Y. J. Cheng, S. H. Yang, C. S. Hsu, *Chem. Rev.* **2009**, *109*, 5868–5923.
- 2 Y. F. Li, *Acc. Chem. Res.* **2012**, *45*, 723–733.
- 3 G. Dennler, M. C. Scharber, C. J. Brabec, *Adv. Mater.* **2009**, *21*, 1323–1338.
- 4 J. W. Chen, Y. Cao, *Acc. Chem. Res.* **2009**, *42*, 1709–1718.
- 5 H. Y. Chen, J. H. Hou, S. Q. Zhang, Y. Y. Liang, G. W. Yang, Y. Yang, L. P. Yu, Y. Wu, G. Li, *Nat. Photonics* **2009**, *3*, 649–653.
- 6 S. C. Price, A. C. Stuart, L. Yang, H. Zhou, W. You, *J. Am. Chem. Soc.* **2011**, *133*, 4625–4631.

- 7 T.-Y. Chu, J. Lu, S. Beaupre, Y. Zhang, J. Pouliot, S. Wakim, J. Zhou, M. Leclerc, Z. Li, J. Ding, Y. Tao, *J. Am. Chem. Soc.* **2011**, *133*, 4250–4253.
- 8 Z. He, C. Zhong, S. Su, M. Xu, H. Wu, Y. Cao, *Nat. Photonics* **2012**, *6*, 591–595.
- 9 P. M. Beaujuge, J. M. J. Fréchet, *J. Am. Chem. Soc.* **2011**, *133*, 20009–20029.
- 10 C. Kitamura, S. Tanaka, Y. Yamashita, *Chem. Mater.* **1996**, *8*, 570–578.
- 11 U. H. F. Bunz, *Macromol. Rapid Commun.* **2009**, *30*, 772–805.
- 12 (a) R. S. Ashraf, M. Shahid, E. Klemm, M. Al-Ibrahim, S. Sensfuss, *Macromol. Rapid Commun.* **2006**, *27*, 1454–1459; (b) C. Du, W. Li, C. Li, Z. Bo, *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 383–393; (c) Y. Hou, Y. Chen, Q. Liu, M. Yang, X. Wan, S. Yin, A. Yu, *Macromolecules* **2008**, *41*, 3114–3119; (d) Y. P. Zou, Z. Tan, L. J. Huo, Y. F. Li, *Polym. Adv. Technol.* **2008**, *19*, 865–871.
- 13 J. Cremer, P. Bauerle, M. M. Wienk, R. A. J. Janssen, *Chem. Mater.* **2006**, *18*, 5832–5834.
- 14 S. P. Webster, J. R. Seckl, B. Walker, P. R. Ward, T. D. Pallin, H. J. Dyke, T. R. Perrior, PCT Intl WO/2009/074789 **2009**.
- 15 Q. Shi, H. Fan, Y. Liu, W. Hu, Y. Li, X. Zhan, *Macromolecules* **2011**, *44*, 9173–9179.
- 16 J. L. Bredas, R. Silbey, D. S. Boudreaux, R. R. Chance, *J. Am. Chem. Soc.* **1983**, *105*, 6555–6559.
- 17 B. C. Thompson, J. M. J. Fréchet, *Angew. Chem., Int. Ed.* **2008**, *47*, 58–77.
- 18 L.-M. Chen, Z. Hong, G. Li, Y. Yang, *Adv. Mater.* **2009**, *21*, 1434–1449.
- 19 J. Kim, M. H. Yun, G.-H. Kim, J. Y. Kim, C. Yang, *Polym. Chem.* **2012**, *3*, 3276–3281.
- 20 M. Campoy-Quiles, T. Ferenczi, T. Agostinelli, P. G. Etchegoin, Y. Kim, T. D. Anthopoulos, P. N. Stavrinou, D. D. C. Bradley, J. Nelson, *Nat. Mater.* **2008**, *7*, 158–164.
- 21 E. Zhou, J. Cong, K. Hashimoto, K. Tajima, *Energy Environ. Sci.*, **2012**, *5*, 9756–9759.
- 22 M.-S. Su, C.-Y. Kuo, M.-C. Yuan, U.-S. Jeng, C.-J. Su, K.-H. Wei, *Adv. Mater.* **2011**, *23*, 3315–3319.