Synthesis and Photovoltaic Properties of Two-Dimensional Copolymers Based on Novel Benzothiadiazole and Quinoxaline Acceptors with Conjugated Dithienylbenzothiadiazole Pendants

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ABSTRACT: Two novel acceptors of benzo[*c*][1,2,5]thiadiazole and quinoxaline with conjugated dithienylbenzothiadiazole pendants were first designed and synthesized for building efficient photovoltaic copolymers. Based on benzo[1,2-*b*;3,4*b'*]dithiophene donors and the two acceptors, two new copolymers have been prepared by Stille coupling polymerization. The resulting copolymers were characterized by ¹H NMR, gel permeation chromatography, and thermogravimetric analysis. UV-Visible absorption and cyclic voltammetry measurements indicated that the two copolymers possessed strong and broad absorption in the range of 300–700 nm, and deep-lying energy

INTRODUCTION Polymer solar cells (PSCs) is a promising photovoltaic technology for clean and renewable energy sources due to its superior properties such as mechanical flexibility, light weight, visible transparency, and large-area manufacturing compatibility.^{1–7} Recently, remarkable progress has been made in this field, and the power conversion efficiencies (PCEs) of PSCs have surpassed 10%.^{8–10} However, the design and synthesis of novel polymeric donor materials with unique structures still plays an important role in understanding the basic rules between molecular structure and performance, which can make great contributions to the commercial applications of PSCs in the future.

In recent years, the donor–acceptor (D–A) copolymers which consist of electron-donating and electron-withdrawing building blocks have been widely used in a number of application, such as PSCs, organic field-effect transistors, and organic light-emitted diodes, due to their superiorities in realizing tunable properties like absorption spectra, molecular energy levels, mobilities, and so forth.^{11–15} Among them, alternating copolymers based on 4,8-*bis*(alkoxyl)-benzo[1,2-*b*;4,5*b'*]dithiophene have attracted considerable interest as levels of highest occupied molecular orbitals. The polymer photovoltaic devices based on benzo[*c*][1,2,5]thiadiazole-based copolymer/phenyl-C₇₁-butyric acid methyl ester exhibited a power conversion efficiency of 2.42%, attributed to its relatively better light-harvesting ability and active film morphology. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2016**, *54*, 668–677

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electron-donating building blocks in PSCs application, due to their excellent features including structural symmetry, planarity as well as rigid and π -extended conjugation, which can enhance electron delocalization and intermolecular interactions to improve charge mobility and PCEs.¹⁶⁻¹⁹ Moreover, benzo[*c*][1,2,5]thiadiazole (**BT**) and quinoxaline (**Q**) were the most promising blocks for building high-performance polymeric donor materials. In most cases, a great number of conjugated polymers were focused on alkoxyl- and fluorinemodified BT and Q. Many PSCs based on BT and Q units showed high PCE values of over 8%.²⁰⁻²³ For instance, Yan and coworkers reported the PSCs based on BT unit exhibited a high PCE over 10%, which is the highest PCE from single junction-based PSCs.⁶ While the **BT**- and **Q**-based copolymers with the two-dimensional (2-D)-conjugated electron-deficient pendants have not yet been explored. Compared with the linear polymers, this type of polymer possesses three distinctive characteristics: (1) extension of the π -conjugation; (2) good solubility owing to the overlapping of the conjugated side chains interactions with the main chains; and (3) the increase of electron affinity and the red-shift of absorption. То develop novel strategies for further improving

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FIGURE 1 Structures of the copolymers PBDT-BT and PBDT-Q.

photovoltaic performance, the effect of different acceptor units on PSCs performance is worthy of being studied.

Herein, we report the design and synthesis of two novel 2-D copolymers, PBDT-BT and PBDT-Q (Fig. 1), with novel benzo[c][1,2,5]thiadiazole (**BT**) and quinoxaline (**Q**) acceptor units modified by conjugated dithienylbenzothiadiazole (DTBT) pendants via vinylene groups, which were used as the donor materials in PSCs for the first time. Moreover, the comparative studies would be carried out to study the effect of different acceptor on their thermal stabilities, optical properties, molecular energy levels, and film morphologies of the two polymers by thermogravimetric analysis (TGA), UV-Visible (UV-Vis) spectroscopy, cyclic voltammetry (CV), and atomic force microscope (AFM), respectively. The results indicated that, the two copolymers exhibited high thermal stability, strong and broad absorption, and deep-lying energy levels of highest occupied molecular orbitals (HOMO). The polymer photovoltaic devices based on PBDT-BT/phenyl-C71-butyric acid methyl ester (PC71BM) exhibited a PCE of 2.42%, attributed to the better light-harvesting ability and active film morphology.

EXPERIMENTAL

Materials

All the chemicals were purchased from Alfa Aesar and Chem Greatwall Chemical Company (Wuhan, China). Tetrahydrofuran (THF) and toluene were dried and distilled from sodium/benzophenone. All other solvents and chemicals used in this work were analytical grade and used without further purification. 2,6-Di(trimethyltin)-4,8-di((2-ethylhexy-l)oxy) benzo[1,2-*b*;4,5-*b'*]dithiophene (**M3**)²⁴ and 5-(7-(4-hexylthhiophen-2-yl)benzo[*c*][1,2,5] thiadiazole-4-yl)-3-hexylthiophene-2-carbaldehyde²⁴ were prepared according to literature procedures, respectively.

Instrumentation

Nuclear magnetic resonance spectra were measured with Bruker AVANCE 400 MHz spectrometer. Molecular mass of the compounds was determined by Agilent 5975 GC-MS instrument or Bruker Autoflex III MALDI-TOF measurement. UV-Visible absorption spectra of the polymers were con-



ducted on a Perkin-Elmer Lamada 25 UV-Vis-NIR spectrometer. The average molecular weight and polydispersity index (PDI) of the polymers were determined using Waters 1515 gel permeation chromatography (GPC) analysis with THF as eluent and polystyrene as standard. TGA measurement was conducted on a Netzsch TG 209 analyzer under nitrogen at a heating rate of 20 °C min⁻¹. Electrochemical redox potentials were obtained by CV using a three-electrode configuration and an electrochemistry workstation (ZAHNER ZENNIUM) at a scan rate of 100 mV s⁻¹. CV was conducted on an electrochemistry workstation with the thin film on a Pt plate as the working electrode, Pt slice as the counter electrode, and silver electrode as the reference electrode. The supporting electrolyte is 0.1 M *tetra-n*-butylammonium hexafluorophosphate (Bu₄NPF₆) in anhydrous acetonitrile solution. All AFM measurements were performed on a Digital Instruments Veeco Multimode 8 in a tapping mode.

Fabrication of PSCs

The structure of bulk heterojunction (BHJ) PSCs was indium tin oxide (ITO)/MoO₃ (20 nm)/polymers:phenyl-C₆₁ (or C₇₁)butyric acid methyl ester (PC₆₁BM or PC₇₁BM) (~100 nm)/ LiF (0.5 nm)/Al (100 nm). The PSCs devices were fabricated with ITO glass as a positive electrode and LiF/Al as a negative electrode. The ITO glass was precleaned and then modified by a thin layer of MoO₃, which was deposited on the surface of ITO by vacuum evaporation under 5 \times 10⁻⁴ Pa. The photoactive layer was prepared by spin-coating a blend solution of polymer and PC₆₁BM (or PC₇₁BM) in chlorobenzene (CB) on the surface of ITO/MoO_3 substrate. Then, the LiF/Al cathode was deposited on the polymer layer by vacuum evaporation under 5 imes 10⁻⁴ Pa. The accurate area of every device is 3.8 mm², defined by the overlap of the ITO and metal electrode. The current density-voltage (J-V) curves were measured by a Keithley 2602 Source Meter under 100 mW cm⁻² standard AM 1.5 G spectrum using a Sol 3A Oriel solar simulator. The incident light intensity was calibrated using a standard Si solar cell. The measurement of monochromatic incident photon-to-current conversion efficiencies (IPCE) was performed using a Zolix Solar Cell Scan 100 QE/IPCE measurement system.

Synthesis

5-Methyl-benzo[C][1,2,5]thiadiazole (1)

Triethylamine (14.00 mL, 101.00 mmol) was added to a solution of 3,4-diaminotoluene (5.00 g, 40.31 mmol) and CHCl₃ (150 mL). Then thionyl chloride (7.51 mL, 103 mmol) was added with vigorous stirring in an ice–water bath. After the dropwise addition, the solution was refluxed for 8 h. Evaporation of the solvent and purification by column chromatography on silica gel with petroleum ether/dichloromethane (6:1, v/v) as eluent was performed. Compound **1** was finally obtained as a light yellow oil (4.50 g, 73.2% yield). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 7.89–7.87 (d, *J* = 8.8 Hz, 1H), 7.76 (s, 1H), 7.44–7.42 (d, *J* = 8.8 Hz, 1H), 2.55 (s, 3H); GC-MS (C₇H₆N₂S) *m/z*: calcd. for 150.0; found, 150.1.

4,7-Dibromo-5-methyl-benzo[C][1,2,5]thiadiazole (2)

A solution of compound **1** (2.00 g, 13.31 mmol) in 47% HBr (10 mL) was heated to 120 °C, and then bromine (Br₂) (15 mL) in HBr (3 mL) was slowly added dropwise. The mixture was stirred for 8 h and then cooled to room temperature. A saturated sodium bisulfite aqueous solution was then added to remove the excess bromine. The precipitate was filtered and purified by column chromatography on silica gel with petroleum ether/dichloromethane (8:1, v/v) as eluent to give compound **2** as a white solid (3.11 g, 75.6% yield). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 7.78 (s, 1H), 2.62 (s, 3H); MALDI-TOF MS (C₇H₄Br₂N₂S) *m/z*: calcd. for 307.844; found, 307.861.

4,7-Dibromo-5-bromomethyl-benzo[C][1,2,5]thiadiazole (3)

A mixture of compound **2** (1.51 g, 4.87 mmol), benzoyl peroxide (BPO) (0.10 g), and *N*-bromosuccinimide (NBS) (1.04 g, 5.84 mmol) in *tetra*-chloromethane (50 mL) was heated at reflux for 24 h under an argon atmosphere. The solution was filtered and the filtrate concentrated by rotary evaporation. The residues were purified by column chromatography on silica gel with petroleum ether/dichloromethane (8:1, v/v) as eluent to give compound **3** as a white solid (1.20 g, 63.7% yield). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.42 (s, 1H), 7.27 (s, 2H); MALDI-TOF MS (C₇H₃Br₃N₂S) *m/z*: calcd. for 385.755; found, 385.870.

(4,7-Dibromo-benzo[C][1,2,5]thiadiazole-5ylmethyl)Phosphonic Acid Diethyl Ester (4)

A solution of compound **3** (1.20 g, 3.10 mmol) in triethyl phosphite (30 mL) was heated at reflux for 24 h under an argon atmosphere. Excess triethyl phosphite was removed by vacuum distillation. The residue was purified by column chromatography on silica gel with petroleum ether/acetic ether (2:1, v/v) as eluent to give compound **4** as a white solid (0.71 g, 51.2% yield). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 7.96 (s, 1H), 4.17–4.10 (m, 4H), 3.60–3.54 (d, J = 22.4 Hz, 2H), 1.33–1.29 (t, J = 7.0 Hz, 6H); MALDI-TOF MS (C₁₁H₁₃Br₂N₂O₃PS) *m/z*: calcd. for 443.873; found, 443.961.

4-(4-Hexyl-2-thienyl)-7-[2-(4,7-dibromo-5benzo[C][1,2,5]thiadiazole-vinyl)-4-hexyl-2-thienyl]benzo[C][1,2,5]thiadiazole (M1)

5-(7-(4-Hexylthhiophen-2-yl)benzo[c][1,2,5] thiadiazole-4-yl)-3-hexylthiophene-2-carbaldehyde (0.84 g, 1.70 mmol) and compound **4** (0.62 g, 1.40 mmol) were dissolved in THF (40 mL), and the solution was stirred for 30 min under an argon atmosphere. Then the solution of potassium *tert*-butoxide (0.28 g, 2.50 mmol) and THF (15 mL) was added dropwise. The reaction mixture was stirred at room temperature for 1 h, and then heated to reflux for 15 h. After cooling to room temperature, the reaction mixture was extracted with dichloromethane and washed with dilute aqueous HCI solution. The organic phase was dried over anhydrous MgSO₄, and then the solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel with petroleum ether/dichloromethane (1:1, v/v) as eluent to give **M1** as a red solid (0.78 g, 70.8% yield). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.13 (s, 1H), 8.01–8.00 (d, *J* = 6.8 Hz, 2H), 7.88–7.82 (m, 2H), 7.45 (s, 2H), 7.06 (s, 1H), 2.85–2.82 (t, *J* = 7.6 Hz, 2H), 2.72–2.68 (t, *J* = 7.6 Hz, 2H), 1.76–1.35 (m, 16H), 0.94–0.91 (m, 6H); ¹³C NMR (400 MHz, CDCl₃, δ , ppm): 154.04, 152.58, 152.49, 151.90, 145.32, 144.47, 139.15, 138.84, 138.32, 136.66, 130.58, 130.10, 129.34, 126.68, 125.88, 125.78, 125.24, 124.97, 124.00, 121.95, 113.49, 113.04, 31.74, 31.72, 31.00, 30.67, 30.47, 29.70, 29.17, 29.07, 28.85, 22.66, 22.64, 14.12, 14.09; MALDI-TOF MS (C₃₄H₃₄Br₂N₄S₄) *m/z*: calcd. for 786.001; found, 786.068.

1-Bromo-2,3-butanedione (5)

A solution of 2,3-butanedione (2.01 g, 23.23 mmol) in CHCl₃ (8 mL) was cooled to 0 °C, and then Br₂ (3.97 g, 24.85 mmol) in CHCl₃ (7 mL) was slowly added dropwise. The mixture was stirred for 3 h. A saturated sodium bisulfite aqueous solution was then added to remove the excess bromine. The reaction mixture was extracted with dichloromethane and washed with water. The organic phase was dried over anhydrous MgSO₄, and then the solvent was removed by rotary evaporation to give compound **5** as a light yellow solid (2.01 g, 52.2% yield). GC-MS (C₄H₅BrO₂) m/z: calcd. for 163.9; found, 163.9.

5,8-Dibromo-2-bromomethyl-3-methyl-quinoxaline (6)

To a suspension of zinc (6.72 g, 102.80 mmol) and 2,7dibromo-benzo[c][1,2,5]thiadiazole (1.51 g, 5.14 mmol) in acetic acid (70 mL), a few drops of water was added. The mixture was stirred at 60 °C for 6 h and the solid residue was removed by filtration. To the filtrate, compound 5 (1.02 g, 6.22 mmol) was added and the resulting solution was stirred at 60 °C overnight under an argon atmosphere. The mixture was transferred to a separatory funnel, extracted with dichloromethane, and then washed with water. The dichloromethane phase was dried over MgSO₄. Removal of the solvent gave a crude product which was purified by column chromatography on silica gel with petroleum ether/dichloromethane (3:1, v/v) as eluent to give compound **6** as a white solid (0.80 g, 39.4% yield). ¹H NMR (400 MHz, CDCl₃, δ, ppm): 7.92-7.87 (m, 2H), 4.82 (s, 2H), 2.97 (s, 3H); ¹³C NMR (400 MHz, CDCl₃, δ , ppm): 155.09, 152.41, 140.41, 139.35, 133.68, 132.90, 123.63, 122.99, 30.77, 22.30; MALDI-TOF MS (C₁₀H₇Br₃N₂) m/z: calcd. for 393.814; found, 393.830.

(5,8-Dibromo-3-methyl-quinoxaline-2-ylmethyl)Phosphonic Acid Diethyl Ester (7)

By following the similar method as for compound **4**, compound **7** was synthesized from compound **6** (0.80 g, 2.03 mmol) and triethyl phosphite (20 mL). The crude product was purified by column chromatography on silica gel with petroleum ether/acetic ether (6:1, v/v) as eluent to give compound **7** as a light yellow solid (0.81 g, 88.4% yield). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.00 (s, 2H), 4.18–4.12 (m, 4H), 3.80–3.74 (d, *J* = 22.8 Hz, 2H), 2.97 (s, 3H), 1.27–1.24 (m, 6H); MALDI-TOF MS (C₁₄H₁₇Br₂N₂O₃S) *m/z*: calcd. for 451.932; found, 452.002.

4-(4-Hexyl-2-thienyl)-7-[2-(5,8-dibromo-3-methyl-2quinoxaline-vinyl)-4-hexyl-2-thienyl]benzo[C][1,2,5]thiadiazole (M2)

By following the similar method as for M1, M2 was synthesized from compound 7 (0.50 g, 1.11 mmol), 5-(7-(4-Hexylthhiophen-2-yl)benzo[c][1,2,5]thiadiazole-4-yl)-3-hexylthiop hene-2-carbaldehyde (0.66 g, 1.33 mmol), THF (40 mL), and potassium tert-butoxide (0.22 g, 2.00 mmol). The crude product was purified by column chromatography on silica gel with petroleum ether/dichloromethane (2:1, v/v) as eluent to give M2 as a purple-red solid (0.62 g, 70.3% yield). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.57–8.53 (d, J = 14.8 Hz, 1H), 8.01-7.99 (d, J = 6.8 Hz, 2H), 7.90-7.53 (m, 4H), 7.28-7.24 (d, J = 14.8 Hz, 1H), 7.07 (s, 1H), 2.97 (s, 3H), 2.93-2.90 (t, J = 7.6 Hz, 2H), 2.72-2.68 (t, J = 7.6 Hz, 2H), 1.80-1.68 (m, 4H), 1.49-0.92 (m, 16H), 0.92-0.90 (m, 6H); ¹³C NMR (400 MHz, CDCl₃, δ, ppm): 154.20, 152.52, 150.77, 147, 28, 144.48, 139.52, 138.83, 136.97, 132.38, 131.87, 130.45, 129.34, 126.68, 125.88, 125.22, 123.51, 122.76, 122.00, 119.47, 31.74, 31.37, 30.67, 30.51, 29.28, 29.10, 28.96, 22.85, 22.74, 22.68, 14.18, 14.15; MALDI-TOF MS (C₃₇H₃₈Br₂N₄S₃) *m/z*: calcd. for 794.060; found, 794.057.

Polymerization for PBDT-BT

2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b;3,4b']dithiophene (102.2 mg, 0.130 mmol) (M3) and M1 (100.1 mg, 0.130 mmol) were dissolved in toluene (10 mL). The solution was flushed with argon for 30 min and Pd(PPh₃)₄ (15 mg, 0.01 mmol) was added to the flask. The flask was purged five times by successive vacuum and argon filling cycles. The polymerization reaction mixture was heated at 110 °C with stirring for 48 h under an argon atmosphere. It was then cooled to room temperature and then slowly poured into methanol (200 mL). The precipitate was filtered and washed with methanol and hexane in a Soxhlet apparatus to remove oligomers and catalyst residue. Finally, the polymer was extracted with CHCl₃. The solution was condensed by evaporation and precipitated into methanol. The polymer PBDT-BT was collected as purple-red solid (87.1 mg, 62.8% yield). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.96-7.00 (br, 10H), 4.43-3.22 (br, 4H), 2.90-2.65 (br, 6H), 2.04–0.87 (br, 50H); GPC: $M_{\rm n} = 13.6$ KDa, $M_{\rm w} = 25.3$ KDa.

Polymerization for PBDT-Q

The polymerization process was the same as that for **PBDT-BT**, except that **M1** was used instead of **M2** (103.0 mg, 0.130 mmol) and the polymer **PBDT-Q** was collected as purple-red solid (79.2 mg, 55.8% yield). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.73–6.98 (br, 11H), 4.39–4.12 (br, 4H), 3.08–2.67 (br, 9H), 2.24–0. 56 (br, 50H); GPC: $M_n = 18.2$ KDa, $M_w = 36.2$ KDa.

RESULTS AND DISCUSSION

Syntheses and Characterization

The synthetic routes of monomers **M1**, **M2**, and target copolymers were outlined in Scheme 1. The synthetic route



adopted for the monomer **M1** involved several simple steps. The first was ring cyclized with thionyl chloride in good yield. Compound 2 was prepared by bromination of compound 1 with Br₂ and HBr (45%) according to the procedure used for the synthesis of 4,7-dibromo-benzo[c] [1,2,5]thiadiazole.²⁵ Compound **3** was synthesized from compound 2 by further bromination with NBS using BPO as the radical initiator. Compound 4 was subsequently treated with triethyl phosphite to give phosphonic acid diethyl ester 5. Monomer **M1** was synthesized by the Wittig-Horner reaction by coupling **4** with 5-(7-(4-hexylthiophen-2-yl)benzo[*c*] [1,2,5]thiadiazol-4-yl)-3-hexylthiophe-2-carbaldehyde. Compound 6 was synthesized by reduction reaction and ring cyclized from 4,7-dibromo-benzo[*c*][1,2,5]thiadiazole. The synthesis of monomer M2 involved two steps from compound 6 according to the procedure used for the synthesis of monomer M1. Two copolymers (PBDT-BT and PBDT-Q) were synthesized by Stille coupling polymerization using Pd(0) as catalyst under argon atmosphere. Crude copolymers were purified by extracting with methanol, petroleum ether and chloroform in this order. The structures of the copolymers were confirmed by ¹H NMR.

The copolymers were found to be highly soluble in most of organic solvents such as chloroform, toluene, chlorobenzene, and *o*-dichlorobenzene at room temperature. The number-average molecular weight (M_n) and PDI are 13.6 KDa and 1.85 for **PBDT-BT**, 18.2 KDa and 1.99 for **PBDT-Q** (Table 1), determined by GPC with THF as eluent.

Thermal Properties

The copolymers were analyzed by TGA and the results were summarized in Table 1. The polymers revealed high decomposition temperatures (T_d , 5 wt % loss) of 370 °C and 359 °C for **PBDT-BT** and **PBDT-Q**, respectively (Fig. 2). These results indicated that the copolymers possessed a good thermal and morphology stability, matching well with the requirements of device fabrications.

Optical Properties

Figure 3 shows the UV-Vis absorption spectra of the copolymers in dilute chloroform solutions (0.01 mg mL⁻¹) (a) and in solid films (b), respectively. In chloroform solutions, PBDT-Q showed one broad absorption band covering the wavelength range from 300 to 700 nm, and the maximum absorption wavelength ($\lambda_{s,max}$) was at 517 nm [4.7 \times 10⁴ (g/mL)⁻¹ cm⁻¹], which was attributed to intramolecular charge transfer (ICT) interaction. Note that there was a shoulder peak located around at 420 nm, which should be ascribed to the localized π - π * transition of the polymer backbone.²⁶ While PBDT-BT had two obvious absorption peaks at 381 and 521 nm $[5.6 \times 10^4 \text{ (g/mL)}^{-1} \text{ cm}^{-1}]$. Moreover, PBDT-BT exhibited a slightly broader absorption which was derived from the stronger ICT compared to PBDT-Q. In comparison with the absorptions in solutions, similar profile and red-shift in the solid films were observed, probably due to the increase of intermolecular π - π stacking in the solid state. In addition, compared with the absorption in solutions, the



SCHEME 1 Synthetic routes of monomers and copolymers.

maximum absorption peaks of **PBDT-BT** and **PBDT-Q** were red-shifted 23 and 38 nm, respectively. The absorption of **PBDT-Q** was red-shifted more obviously than **PBDT-BT**, probably due to its better planarity. The optical band gaps (E_e^{opt}) for **PBDT-BT** and **PBDT-Q** were calculated from the

TABLE 1 Molecular weights and thermal properties of the copolymers

Polymers	<i>M</i> _n (kg⋅mol ⁻¹) ^a	<i>M</i> _w (kg⋅mol ⁻¹) ^a	PDI	T _d (°C) ^b
PBDT-BT	13.6	25.3	1.85	370
PBDT-Q	18.2	36.2	1.99	359

^a Determined by GPC in THF based on polystyrene standards.

 $^{\rm b}$ Decomposition temperature, determined by TGA in nitrogen, based on 5 wt % loss.

onset wavelengths of the film absorption spectra, which were 1.71 and 1.66 eV, respectively (Table 2).

Electrochemical Properties

The electrochemical properties of the copolymers were studied by CV (Fig. 4 and Table 2). The potentials were referenced to the ferrocene/ferrocenium redox couple (Fc/Fc⁺). The redox potential of Fc/Fc⁺ was assumed an absolute energy level of -4.80 eV relative to vacuum, which was measured under the same condition as polymer sample to be 0.38 V related to the silver electrode. The corresponding HOMO and LUMO energy levels of polymers were calculated according to the equations: $E_{\rm HOMO} = -e (E_{\rm ox} + 4.42)$ (eV) and $E_{\rm LUMO} = -e (E_{\rm red} + 4.42)$ (eV). The HOMO levels of **PBDT-BT** and **PBDT-Q** were -5.51 and -5.48 eV, respectively. The deep and similar HOMO levels were mainly affected by the donor unit of polymers and **DTBT** pendants,²⁷ which were beneficial for a high $V_{\rm oc}$ in PSCs and good air stability. The



FIGURE 2 TGA curves of the copolymers with the scan rate of 20 °C min⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

LUMO levels of **PBDT-BT** and **PBDT-Q** were -3.40 and -3.43 eV, respectively. Note that their LUMO values were >0.3 eV higher than the LUMO energy level of PCBM (PC₆₁BM and PC₇₁BM), which suggested that the energy offsets between the LUMO energy levels of the polymer and PCBM were sufficient to facilitate efficient charge transfer/separation at the interfaces of copolymer donors and PCBM acceptors. The electrochemical band gaps of the copolymers were estimated to be 2.11 eV for **PBDT-BT** and 2.05 eV for **PBDT-Q**, which were larger than their optical band gaps.

Film Morphology

The surface morphology of the active layer was one of the key factors in determining the performance of PSCs.²⁸ Ideal domain size of 10–20 nm of polymer and PCBM with an interpenetrating bicontinuous network has been found to be important for achieving high-performance devices.²⁹ However, both smaller (<10–20 nm) and larger (>10–20 nm) domain sizes of the blend films will limit charge transfer and separation. Figure 5 shows the AFM topographic images of

the films of copolymers/PCBM (1:2, w/w) blends recorded in a tapping mode. All the films exhibited typical cluster structures with many aggregated domains, and root-meansquare (RMS) roughness of 0.45, 0.73, and 1.12 nm were obtained for **PBDT-BT**/PC₆₁BM, **PBDT-BT**/PC₇₁BM and **PBDT-Q**/PC₆₁BM, respectively. The film surface with higher roughness and nanoscaled texture also benefited the internal light scattering and enhanced light absorption.³⁰ Furthermore, a suitable phase separation was observed in Figure 5(f). Hence, it can be tentatively speculated that the more proper phase separation for both exciton dissociation and charge transporting in **PBDT-BT**/PC₇₁BM blend than those of the other two blend systems contributed to its relatively better photovoltaic performance.

Hole Mobility

The charge carrier transport properties of conjugated polymers play a key role in the performance of PSCs.³¹ To understand the influence of charge carrier mobility of the copolymers/PC₆₁BM blend films on the photovoltaic properties, the hole mobility of the target copolymer was measured using a space charge limit current method. Hole-only devices were fabricated with the configuration of ITO/PEDOT:PSS (30 nm)/polymers:PC₆₁BM (1:2, w/w)/MoO₃ (20 nm)/Al (100 nm). The calculated hole mobilities of PBDT-BT and **PBDT-Q** blend films were 1.2×10^{-5} and 3.5×10^{-6} cm² V^{-1} s⁻¹, respectively (Table 3). It is worth noting that these polymers may have good isotropic charge transport ability due to their 2-D conjugated structures, which is desirable for PSCs.⁵ The relatively higher mobility of **PBDT-BT** was enhanced mainly due to the improved intermolecular interactions and ordered alignment of the blend film, which would benefit for the exciton separation and the transport. Therefore, the device based on PBDT-BT would show relatively higher J_{sc} and FF compared to the other device.

Photovoltaic Properties

To investigate whether the different acceptors of the two copolymers make a contribution to the photoelectric conversion in the PSCs, BHJ solar cells using the copolymers as the



FIGURE 3 UV–Vis absorption spectra of the copolymers (a) in chloroform solution (0.01 mg mL⁻¹) and (b) in solid films. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE 2 Photophysical and electrochemical properties of the polymers

	Solution	Film					
Polymers	$\lambda_{\rm max}$ (nm) (10 ⁴ (g/mL) ⁻¹ cm ⁻¹) ^a	$\lambda_{\max} (nm)^{b}$	$\lambda_{edge} (nm)^{b}$	$E_{\rm g}^{\rm opt}$ (eV) ^c	HOMO (eV) ^d	LUMO (eV) ^d	$E_{\rm e}^{\rm ec}$ (eV) ^e
PBDT-BT	381 (5.2), 521 (5.9)	544	724	1.71	-5.51	-3.40	2.11
PBDT-Q	420 (3.2), 517 (4.7)	555	745	1.66	-5.48	-3.43	2.05

^a Dilute chloroform solution.

 $^{\rm b}$ Thin film spin-cast from chloroform solution.

^c Optical band gap determined from the onset of absorption in the solid state.

^d Determined by CV.

 $e_e E_e^{ec} = - (E_{HOMO} - E_{LUMO})$ (eV).



FIGURE 4 (a) Cyclic voltammograms of the copolymers and (b) Energy levels of the system components. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



FIGURE 5 AFM height images and phase images of the polymers/PCBM blend films (1:2, w/w). (a) and (d): PBDT-BT/PC₆₁BM, (b) and (e): PBDT-BT/PC₇₁BM, (c) and (f): PBDT-Q/PC₆₁BM. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Polymers	PCBM	Polymers/PCBM	$J_{ m sc}$ (mA cm ⁻²)	$V_{ m oc}$ (V)	FF	PCE (%)	$\mu_{\rm h}~({\rm cm^2~V^{-1}~s^{-1}})$
PBDT-BT	PC ₆₁ BM	1:1	4.31	0.88	0.32	1.21	$1.2 imes 10^{-5}$
	PC ₆₁ BM	1:2	5.36	0.88	0.36	1.70	
	PC ₇₁ BM	1:2	6.65	0.88	0.42	2.42	
	PC ₆₁ BM	1:3	5.05	0.87	0.31	1.36	
	PC ₆₁ BM	1:4	3.95	0.87	0.29	1.00	
PBDT-Q	PC ₆₁ BM	1:1	3.38	0.57	0.30	0.57	$3.5 imes10^{-6}$
	PC ₆₁ BM	1:2	4.40	0.60	0.30	0.80	
	PC ₇₁ BM	1:2	4.71	0.60	0.41	1.16	
	PC ₆₁ BM	1:3	2.89	0.55	0.29	0.46	
	PC ₆₁ BM	1:4	2.58	0.55	0.27	0.38	

TABLE 3 Photovoltaic properties and hole mobilities of the two copolymers

donors and PCBM as the acceptor were investigated with the conventional device configuration. The weight ratio of the polymers/PC₆₁BM was optimized from 1:1 to 1:4 and the optimized weight ratio for the two polymers to PC₆₁BM was 1:2 (Table 3). Figure 6(a) displays J-V curves of the devices incorporating both $J_{\rm sc}$ and FF of the PSCs. It was observed that an increase in PC₆₁BM content resulted in no obvious change in V_{oc} . However, the J_{sc} and FF decreased continuously, when the ratio of PBDT-BT to PC₆₁BM changed from 1:2 to 1:4. Therefore, the optimal blend ratio for this polymer was determined to be 1:2. It was found that the changes of the photovoltaic properties for PBDT-Q and optimal blend ratio was the same as PBDT-BT. When the mixing ratio of **PBDT-Q** to PC₆₁BM changed from 1:1 to 1:2, the PCE of the device increased slightly from 0.57% to 0.80% (Table 3). However, when the ratio of PBDT-Q and $PC_{61}BM$ changed from 1:2 to 1:4, the J_{sc} and FF decreased slightly. **PBDT-BT** obtained a high V_{oc} of 0.88 eV, which was attributed to its deep-lying HOMO level. The highest $J_{\rm sc}$ of the devices incorporating the PBDT-BT blends (5.36 mA cm^{-2}) was higher than that of **PBDT-Q** (4.40 mA cm^{-2}). This trend has also been observed for FF.

PC₇₁BM has commonly led to performance enhancements in BHJ donor-acceptor devices using semiconducting polymers as the electron-donating component due to its stronger visible absorption.³² Compared with the device with **PBDT-BT**/PC₆₁BM (1:2, w/w), the device with **PBDT-BT**/PC₇₁BM (1:2, w/w) show the higher $J_{\rm sc}$ (5.36 mA cm⁻²) and FF (0.42), due to an optimized blend morphology. In addition, there was no change of $V_{\rm oc}$, and the resulting PCE was raised to 2.42%. This trend has also been observed for **PBDT-Q**/PC₇₁BM (1:2, w/w), and the PCE was raised to 1.16%. Additionally, no further improvement was observed when using 1,8-diiodooctane (DIO) as an additive.

To better understand the difference of the photovoltaic performance, the shunt resistances ($R_{\rm sh}$) and series resistances ($R_{\rm s}$) were calculated according to the *J*–*V* curves. Usually, a high-performance PSC requires not only low series resistance ($R_{\rm s}$) but also high-shunt resistance ($R_{\rm sh}$).³³ A large $R_{\rm sh}$ indicates the device possesses low electron-hole recombination and efficient free carriers collection, which is beneficial for obtaining a high $J_{\rm sc}$ and $V_{\rm oc}$.³⁴ Additionally, a smaller $R_{\rm s}$ is helpful to get a higher $J_{\rm sc}$ and FE.³⁵ According to the



FIGURE 6 (a) J-V curves of the photovoltaic cells and (b) IPCE curves of the photovoltaic cells based on the polymers/PC₆₁BM (or PC₇₁BM) (1/2, w/w). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

calculated results, the $R_{\rm sh}$ and $R_{\rm s}$ values were 247 and 12.4 Ω cm² for **PBDT-BT**/PC₆₁BM (1:2, w/w) film, 272 and 9.5 Ω cm² for **PBDT-BT**/PC₇₁BM (1:2, w/w) film, 187 and 21.1 Ω cm² for **PBDT-Q**/PC₆₁BM (1:2, w/w) film, and 256 and 13.2 Ω cm² for **PBDT-Q**/PC₇₁BM (1:2, w/w) film. For the **PBDT-Q**/PC₆₁BM-based solar cells, its $R_{\rm sh}$ value was obviously smaller than those of solar cells and its $R_{\rm s}$ value was the largest, which contributed to its low $V_{\rm oc}$ and further low PCE values. In contrast, **PBDT-BT**/PC₇₁BM-based solar cells showed relatively best $R_{\rm sh}$ and $R_{\rm s}$ value.

The spectra of IPCE were measured for the conventional BHJ cells with the 1:2 blend ratio of the polymers/PC₆₁BM (and PC₇₁BM), and the curves were shown in Figure 6(b). In the polymers/PC₆₁BM-based device, **PBDT-BT** exhibited higher IPCE (330–700 nm) than that of **PBDT-Q** resulting from its obviously better light-harvesting ability (Fig. 2), which was consistent with the higher J_{sc} of the former. The J_{sc} values calculated by integrating the IPCE curves of the devices incorporating the copolymer blends of **PBDT-BT** and **PBDT-Q** with PC₆₁BM (1/2, w/w), were 5.52 and 4.46 mA cm⁻², that agree reasonably with *J–V* measured data (discrepancy <6%). Compared with the copolymers/PC₆₁BM exhibited stronger absorption in the range of 350–650 nm. The broad and high coverage of IPCE of PSCs also ensured a considerable J_{sc} .

CONCLUSIONS

In summary, two novel 2-D-conjugated BT and Q building blocks with conjugated DTBT pendants via vinylene groups had been designed and used to develop efficient photovoltaic polymers. Two new conjugated copolymers (PBDT-BT and **PBDT-Q**) based on **BDT** unit were synthesized by Stille coupling reaction. The results revealed that the copolymers possessed good solubility and thermal properties. UV-Vis measurements indicated that two polymers exhibited strong and broad absorption in the region from 300 to 700 nm. The copolymers showed relatively deep HOMO levels (-5.51 and -5.48 eV for **PBDT-BT** and **PBDT-Q**, respectively), which were beneficial for the stability and the increase of $V_{\rm oc}$ of the fabricated PSCs. While the devices based on PBDT-BT showed relatively better microstructures and higher hole mobility, which benefit for the exciton separation and transport. The PSCs based on PBDT-BT and PBDT-Q/PC₆₁BM (1/2, w/w) exhibited the PCEs of 1.70% and 0.80%, respectively. For the PBDT-BT/ PC71BM and PBDT-Q/PC71BM cells, combined with an increased J_{sc} and FF, the resulting PCEs were raised to 2.42% and 1.16%, respectively. These features in the resulting copolymers provide great interest of using **BT** with a conjugated DTBT pendant as the building block for PSCs and offer new insight into designing a new class of 2-D π -extended polymers.

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