

Synthesis and photovoltaic behaviors of benzothiadiazole- and triphenylamine-based alternating copolymers

Ming Wang^a, Cuihong Li^{b,**}, Aifeng Lv^a, Zhaohui Wang^a, Zhishan Bo^{a,b,*}, Fengling Zhang^{c,***}

^a State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^b College of Chemistry, Beijing Normal University, Beijing 100875, China

^c Department of Physics, Chemistry and Biology, Linköping University, SE-58183, Linköping, Sweden

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ABSTRACT

A series of donor–acceptor (D–A) alternating copolymers (**P1**, **P2** and **P3**) with thiophene–benzothiadiazole–thiophene–triphenylamine main chain have been synthesized by Suzuki polycondensation. **P1**, **P2**, and **P3** possess medium optical band gaps of 1.99, 1.97 and 1.93 eV, respectively. Bulk heterojunction polymer solar cells (BHJ PSCs) with these polymers as donor and PC₇₁BM as acceptor showed power conversion efficiency (PCE) in the range of 2.1–2.8%. The highest PCE of 2.8 % was achieved for **P1** with short circuit current (J_{sc}) of 7.8 mA/cm². This study offers a useful and important insight for designing triphenylamine derivative-based polymers used for efficient PSCs.

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1. Introduction

Green and renewable solar energies are regarded as promising energy sources to solve the world energy crisis. Polymer solar cells (PSCs) have been attracting considerable attention over the past 15 years because of their unique advantages of light-weight, low cost, and potential for making flexible and large area devices using roll-to-roll process [1–6]. PSCs based on the concept of bulk heterojunction (BHJ) have been intensively investigated worldwide and have become the most successful active layer structure in organic photovoltaic devices to date [7]. BHJ PSCs are generally fabricated with a light-absorption blending layer containing an electron-donating conjugated polymer as a donor and an electron-accepting fullerene derivative as an acceptor. 6,6-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) and 6,6-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) are still the most widely used and efficient acceptors in BHJ PSCs so far [8–11]. Thus, much research efforts have been focused on the molecular engineering of electron-donating conjugated polymers [12–14].

The overlapping of polymer absorption spectrum with the solar photon flux peak is required for harvesting more solar photons to generate photocurrent. Polymers with a band gap of 1.5–1.8 eV are considered suitable for high efficiency PSCs [15]. However, decreasing the band gap of polymers will result in either lower open circuit voltage (V_{oc}) or lower driving force for exciton dissociation as V_{oc} is mainly governed by the energy level difference between the lowest unoccupied molecular orbital (LUMO) of the acceptor and the highest occupied molecular orbital (HOMO) of the donor and short circuit current (J_{sc}) depends on LUMO energy level difference between the donor and the acceptor [16,17]. For a given acceptor, HOMO and LUMO energy levels of polymers must be matched with those of the acceptor to balance V_{oc} and J_{sc} . Noticeably, a high V_{oc} is more readily obtained through medium band gap (1.7–2.0 eV) polymers with a low-lying HOMO energy level while keep properly high LUMO energy level. Based on this design strategy, great progress has been made in synthesis and application of medium band gap polymers in BHJ PSCs. Power conversion efficiencies (PCEs) of 5.2%, 6.1%, and 7.1% have been reached for PBDTTTz (2.0 eV), [18] PCDTBT (1.9 eV) and PBnDT-FTAZ (2.0 eV) [19,20], respectively, indicating their great potential for the next generation high performance PSCs. Thus, the seemingly overlooked medium band gap polymers warrant further exploration.

Triphenylamine (TPA) derivative has been regarded as a promising unit for efficient photovoltaic materials due to excellent

* Corresponding author. State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. Tel./fax: +86 01062206891.

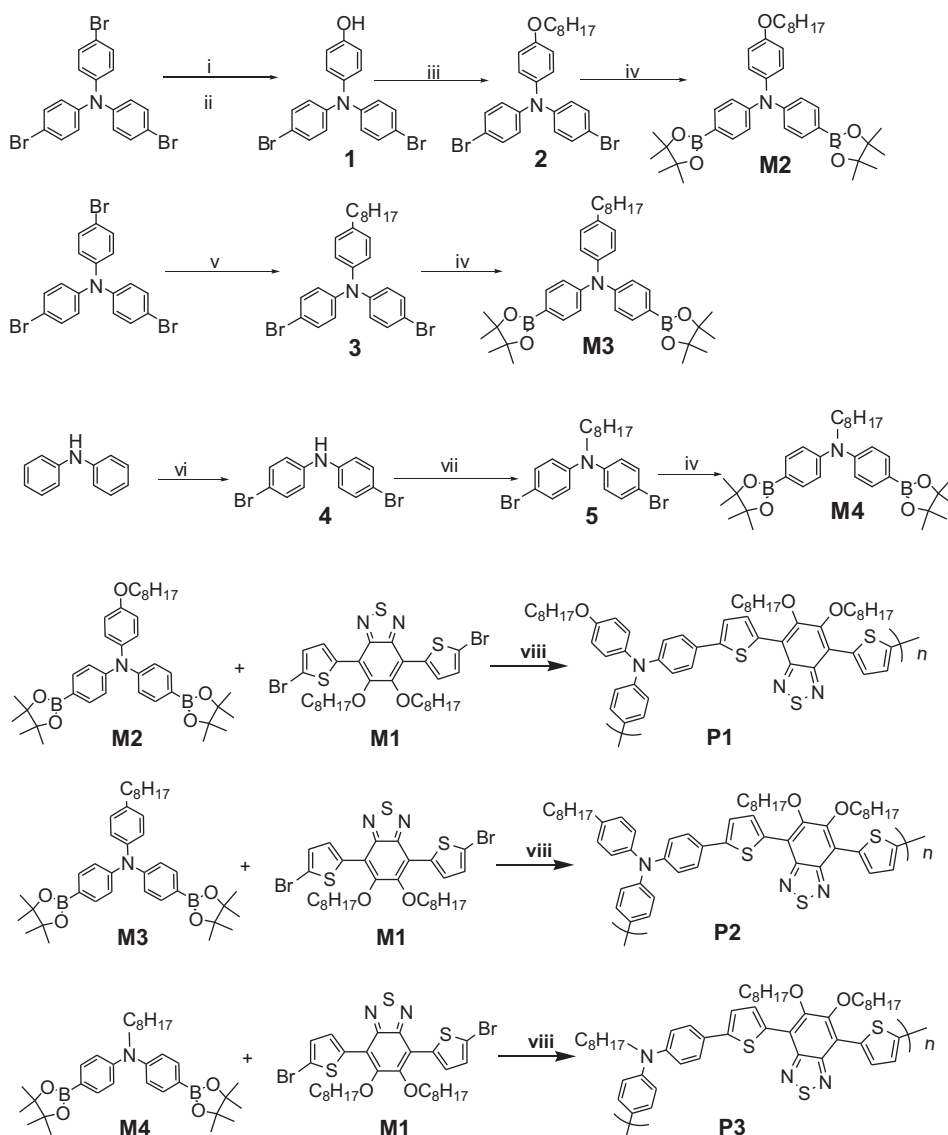
** Corresponding author.

*** Corresponding author.

E-mail addresses: licuihong@bnu.edu.cn (C. Li), zsbo@iccas.ac.cn (Z. Bo), fenzh@ifm.liu.se (F. Zhang).

electron-donating and high hole-transporting properties [21–24]. It has been reported that the TPA derivative has become an efficient building block as donor units in small molecular solar cells and dye sensitized solar cells [25,26]. Moreover, the two-dimensional conjugated structures by combining TPA with linear π -conjugated systems may improve the isotropic charge transportation [27], which is extremely important for PSCs. Cao et al. have reported a series of two-dimensional conjugated donor–acceptor (D–A) copolymers based on TPA [28–30]. They have shown that such two-dimensional conjugated polymers gave promising photovoltaic performance with PCE of 2–4%. Different from their TPA-containing D–A copolymers, in which the acceptor positioned at the end of TPA units, there are only few reports on TPA-containing main chain donor acceptor alternating copolymers utilized in BHJ PSCs [31,32]. Since benzothiadiazole (BT) has been proved to be an excellent electron-deficient unit in polymer solar cells with PCEs of

5–6% [19,33,34], we report here the synthesis of a series of intermediate band gap D–A copolymers based on TPA derivatives and BT segments. As shown in Scheme 1, alkoxy or alkyl side chains are attached to the TPA unit (**P1** and **P2**) to not only ensure the polymer's solubility in common organic solvents but also get more insight into the influence of substituents on the photovoltaic performances. Besides, diphenylamine unit is also introduced to polymer backbones (**P3**) to investigate the structure–property relationships. Meanwhile, BT unit carrying two octyloxy chains was used to improve the solubility and processability of the resulting polymers [34–36]. The results indicate **P1**, **P2**, and **P3** possess medium band gaps of 1.99, 1.97 and 1.93 eV, respectively. The devices based on the blend of each polymer and PC₇₁BM showed the best photovoltaic performance with PCE of 2.1–2.8%. Among these three polymers, **P1** exhibits the highest PCE of 2.8% with V_{oc} of 0.68 V, J_{sc} of 7.8 mA/cm², and fill factor (FF) of 0.53.



Scheme 1. Synthesis of the monomers and the copolymers. Reagents and reaction conditions: (i) *n*-BuLi, -78°C , 1 h, and then tri-*iso*-propyl borate, overnight to room temperature; (ii) KOH/H₂O, H₂O₂, 50°C for 3 h, and HCl, pH = 2, 53% yield; (iii) 1-bromooctane, butanone, K₂CO₃, reflux for 20 h, 69% yield; (iv) PdCl₂(dppf), potassium acetate, bis(pinacolato)diboron, DMF, 80°C for 72 h; (v) *n*-BuLi, -78°C for 1 h, then 1-iodooctane, overnight, 26% yield; (vi) NBS, 0°C for 6 h, 99% yield. (vii) NaH, 1 h, and then 1-bromooctane, reflux for 24 h, 95% yield; (viii) Pd(PPh₃)₄, NaHCO₃, THF/H₂O, reflux.

2. Experimental section

2.1. Materials and instruments

Unless otherwise noted, all chemicals were purchased from commercial suppliers and used without further purification. Solvents were dried using standard procedures. The catalyst precursor $\text{Pd}(\text{PPh}_3)_4$ was prepared according to the literature [37] and stored in a Schlenk tube under nitrogen. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium with benzophenone as an indicator under nitrogen atmosphere. Hexane and dichloromethane (CH_2Cl_2) were distilled from CaH_2 . Chloroform was distilled before use. All reactions were performed under an atmosphere of nitrogen and monitored by thin layer chromatography (TLC) on silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200–300 mesh). ^1H and ^{13}C NMR spectra were recorded on a Bruker DM 300 or AV 400 spectrometer in CDCl_3 . UV–vis absorption spectra were obtained on a SHIMADZU UV-visible spectrometer model UV-1601PC. Elemental analyses were performed on a Flash EA 1112 analyzer. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on TA2100 and Perkin–Elmer Diamond DSC instrument, respectively, under a nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$ to record TGA and DSC curves. Matrix-assisted laser desorption ionization time of flight (MALDI-TOF) mass spectra were recorded on a BIFLEXIV mass spectrometer. Elemental analysis was performed on a Vario EL elemental analysis instrument. Number-average (M_n) and weight-average (M_w) molecular weights were measured by gel permeation chromatography (GPC) on a PL-GPC 50 with THF as an eluent and calibrated with polystyrene standards. Atomic force microscopy (AFM) images of blend films were obtained on a Nanoscope IIIa Dimension 3100 operating in the tapping mode. The film thickness was determined by a Dektak 6M surface profilometer. Electrochemical measurements were performed on a CHI 630A Electrochemical Analyzer with a standard three-electrode electrochemical cell in a 0.1 M tetrabutylammonium tetrafluoroborate solution in CH_3CN at room temperature with a scanning rate of 0.1 V/s^{-1} . A glassy carbon working electrode, a Pt wire counter electrode, and an Ag/AgNO_3 (0.01 M in CH_3CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (Fc) redox system and assumption that the energy level of Fc is 4.8 eV below vacuum.

2.2. Organic field-effect transistors characteristics

The thin film organic field-effect transistors (OFET) of all three polymers were investigated by spin-coating method. Each polymer with the concentration of 10 mg/mL in 1,2-dichlorobenzene (1,2-DCB) was spun on OTS-treated Si/SiO_2 substrates. Au electrodes were thermally deposited through a multiple finger configuration mask with channel length $50\text{ }\mu\text{m}$ and width $2500\text{ }\mu\text{m}$ separately. Measurements were performed in air using a Keithley 4200-SCS semiconductor parameter analyzer and a Micromanipulator 6150 probe station in a clean and shield box.

2.3. Fabrication and characterization of PSCs

PSCs were fabricated with the device configuration of ITO/PEDOT:PSS/Polymer:PC₇₁BM (1:3)/LiF/Al. The conductivity of ITO is $20\text{ }\Omega/\square$. PEDOT:PSS is Baytron Al 4083 from H.C.Starck and was filtered with a $0.45\text{ }\mu\text{m}$ PVDF film before use. A thin layer of PEDOT:PSS was spin-coated on top of cleaned ITO substrate at 3000 rpm/s for 60 s and dried subsequently at 130°C for 15 min on

a hotplate before transferred into a glove box. The active layer was prepared by spin-coating the solution of polymers and PC₇₁BM on the top of ITO/PEDOT:PSS. The top electrode was thermally evaporated, with a 0.6 nm LiF layer, followed by 80 nm of aluminum at a pressure of 10^{-6} Torr through a shadow mask. Four cells were fabricated on one substrate with an effective area between $0.04\text{--}0.05\text{ cm}^2$. The measurement of devices was conducted in air. Current–voltage characteristics were recorded using a Keithley 2400 Source Meter under AM 1.5 illumination with an intensity of $100\text{ mW}/\text{cm}^2$ from a solar simulator (Model SS-50A, photo Emission Tech., Inc.). The temperature while measuring the $J\text{--}V$ curves was approximately 25°C .

2.4. Monomer and polymer synthesis

2.4.1. Monomer synthesis

2.4.1.1. 4-(Bis(4-bromophenyl)amino)phenol (1). *n*-Butyllithium (*n*-BuLi) (9 mL, 2.5 M in hexane, 21 mmol) was added dropwise over 30 min under a nitrogen atmosphere to a stirred solution of tris(4-bromophenyl)amine (10 g, 21 mmol) in anhydrous THF (300 mL) at -78°C . The solution was stirred at -78°C for 1 h, and then tri-*iso*-propyl borate (5.9 mL, 25 mmol) was added in one portion. The reaction mixture was stirred overnight and allowed to slowly warm to room temperature. After quenched by water (100 mL), the organic layer was separated and the aqueous layer was extracted by diethyl ether ($50\text{ mL} \times 3$). The combined organic layer was dried over magnesium sulfate (MgSO_4) and the solvents were removed by rotary evaporator. The crude product of boronic acid was obtained as a residue, which was directly used in the next step without purification. To a mixture of the boronic acid crude product, KOH (2.5 g, 45 mmol), and water (50 mL) was added dropwise H_2O_2 (30%, 7.6 g, 68 mmol) at 0°C . After the addition of H_2O_2 , the mixture was heated to 50°C and stirred for 3 h. Dichloromethane (100 mL) was added and the aqueous layer was acidified by hydrochloric acid (HCl) to $\text{pH} = 2$. The organic layer was separated and dried over MgSO_4 and the solvents were removed by rotary evaporator. The crude product was purified on silica gel column eluting with petroleum ether/dichloromethane (2:1 v/v) followed by 1:2 v/v) to afford the title compound as a colorless solid (4.6 g, 53%). The compound was unstable under ambient condition, so only NMR characterizations were performed. ^1H NMR (400 MHz, CDCl_3): δ 7.30 (m, 4H), 6.98 (m, 2H), 6.88 (m, 4H), 6.78 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 152.9, 147.0, 140.1, 132.4, 127.8, 124.5, 116.8, 114.8.

2.4.1.2. 4-Bromo-N-(4-bromophenyl)-N-(4-(octyloxy)phenyl)amine (2). Compound **1** (4.6 g, 10.9 mmol), 1-bromooctane (2.54 g, 13.1 mmol), and butanone (50 mL) were added into a flask and degassed. Potassium carbonate (K_2CO_3) (3.03 g, 22 mmol) was added under nitrogen atmosphere, and the reaction mixture was refluxed for 20 h and then was filtered off. The solid was washed with dichloromethane ($200\text{ mL} \times 3$) and the combined filtrate was concentrated and purified on silica gel column to afford the title compound as a colorless oil (4 g, 69%). ^1H NMR (400 MHz, CDCl_3): δ 7.30 (d, 4H), 7.00 (d, 2H), 6.88 (d, 4H), 6.83 (d, 2H), 3.93 (t, 3H), 1.44 (m, 2H), 1.30 (m, 10H), 0.87 (t, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 156.6, 147.1, 139.7, 132.4, 127.7, 124.5, 115.8, 114.7, 68.5, 32.1, 29.6, 29.5, 29.4, 26.3, 22.9, 14.3. Anal. calcd. for $\text{C}_{26}\text{H}_{29}\text{Br}_2\text{NO}$: C, 58.77; H, 5.50; N, 2.64; found: C, 58.65; H, 5.54; N, 2.39.

2.4.1.3. 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-N-(4-(octyloxy)phenyl)amine (M1). A mixture of compound **2** (2.0 g, 3.77 mmol), bis(pinacolato)diboron (2.2 g, 8.7 mmol), potassium acetate (2.6 g, 26.5 mmol), and DMF (20 mL) was carefully degassed before and

after [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) chloride (PdCl₂(dppf)) (31 mg, 0.038 mmol) was added under nitrogen atmosphere. The reaction mixture was stirred at 80 °C for 72 h and then ethyl acetate (200 mL) and water (100 mL) were added. The organic layer was separated, washed with brine (50 mL × 3), dried over anhydrous MgSO₄, and evaporated to dryness. The crude product was purified on silica gel column eluting with petroleum ether/ethyl acetate (3:1, v/v) increasing to 1:1 (v/v) to give the title compound as a colorless oil (1.46 g, 62%). ¹H NMR (400 MHz, CDCl₃): δ 7.65 (d, 4H), 7.04 (m, 6H), 6.83 (m, 2H), 3.94 (t, 2H), 1.47 (m, 2H), 1.33 (m, 34H), 0.90 (t, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 156.6, 150.6, 139.9, 136.0, 128.3, 122.0, 115.6, 83.8, 68.5, 32.1, 29.6, 29.5, 29.3, 25.1, 22.9, 14.3. Anal. calcd. For C₃₈H₅₃B₂NO₅: C, 72.97; H, 8.54; N, 2.24; found: C, 72.89; H, 8.46; N, 2.12.

2.4.1.4. 4-Bromo-N-(4-bromophenyl)-N-(4-octylphenyl)phenylamine (3). *n*-BuLi in hexane (9 mL, 2.5 M in hexane, 21 mmol) was added dropwise over 30 min to a stirred solution of tris(4-bromophenyl)amine (10 g, 21 mmol) in anhydrous THF (300 mL) at –78 °C under a nitrogen atmosphere. The solution was stirred for 1 h at –78 °C, and then 1-iodooctane (6 g, 25 mmol) was added in one portion. The reaction mixture was stirred overnight and allowed to slowly warm to room temperature. After the reaction mixture was filtered, the solid was washed with petroleum ether (200 mL). The combined organic layers were washed with water (100 mL), dried over Mg₂SO₄, and evaporated to dryness. The crude product was purified on silica gel column eluting with petroleum ether to give the title compound as a colorless oil (2.8 g, 26%). ¹H NMR (400 MHz, CDCl₃): δ 7.32 (m, 4H), 7.08 (d, 2H), 6.98 (d, 2H), 6.92 (m, 4H), 2.57 (t, 3H), 1.61 (m, 2H), 1.30 (m, 10H), 0.90 (t, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 146.8, 144.5, 138.9, 132.3, 132.2, 129.6, 125.1, 115.1, 35.5, 32.0, 31.6, 29.6, 29.5, 29.4, 22.8, 14.2. Anal. calcd. for C₂₆H₂₉Br₂N: C, 60.60; H, 5.67; N, 2.72; found: C, 62.03; H, 5.83; N, 2.64.

2.4.1.5. 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-N-(4-octylphenyl)phenylamine (M2). **M2** was synthesized using the same procedure as **M1** as a colorless oil in a yield of 51%. ¹H NMR (400 MHz, CDCl₃): δ 7.66 (d, 4H), 7.03 (m, 8H), 2.57 (t, 2H), 1.58 (m, 2H), 1.30 (m, 34H), 0.88 (t, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 146.7, 144.4, 138.9, 132.2, 129.5, 124.9, 124.5, 114.9, 35.4, 31.9, 31.5, 29.5, 29.4, 29.3, 22.7, 14.1. Anal. calcd. for C₃₈H₅₃B₂NO₄: C, 74.89; H, 8.77; N, 2.30; found: C, 75.06; H, 8.78; N, 2.26.

2.4.1.6. Bis(4-bromophenyl)amine (4). A solution of *N*-bromo-succinimide (NBS) (10.53 g, 59.2 mmol) in DMF (50 mL) was added dropwise over 30 min to a stirred solution of diphenylamine (5 g, 29.6 mmol) in DMF (50 mL) at 0 °C. The resulting solution continued to be stirred at 0 °C for 6 h. Water was added and the precipitate was filtered and dried under vacuum to afford the title compound as a colorless solid (9.6 g, 99%). ¹H NMR (400 MHz, CDCl₃): δ 7.37 (d, 4H), 6.91 (d, 4H), 5.63 (s, NH); ¹³C NMR (100 MHz, CDCl₃): δ 141.8, 132.4, 119.6, 113.5. Anal. calcd. for C₁₂H₉Br₂N: C, 44.07; H, 2.77; N, 4.28; found: C, 44.26; H, 2.89; N, 4.02.

2.4.1.7. 4-Bromo-N-(4-bromophenyl)-N-octylphenylamine (5). A solution of compound **4** (4 g, 12.2 mmol) in THF (100 mL) was degassed before and after sodium hydride (0.38 g, 15.9 mmol) was added under nitrogen atmosphere. The mixture was stirred for 1 h at room temperature. 1-Bromo-octane (2.83 g, 14.7 mmol) was added and then the reaction was refluxed for 24 h. The reaction was quenched by water and the organic layer was washed with brine (100 mL) and separated. The combined organic layers were dried

over MgSO₄ and evaporated to dryness. The crude product was purified on silica gel column eluting with petroleum ether to give the title compound as a colorless oil (5.1 g, 95%). ¹H NMR (400 MHz, CDCl₃): δ 7.34 (m, 4H), 6.84 (m, 4H), 3.60 (t, 2H), 1.60 (m, 2H), 1.26 (m, 10H), 0.87 (t, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 147.0, 132.6, 123.6, 114.2, 52.7, 32.3, 30.1, 27.9, 27.6, 27.4, 23.0, 14.5. Anal. calcd. for C₂₀H₂₅Br₂N: C, 54.69; H, 5.74; N, 3.19; found: C, 55.20; H, 5.95; N, 2.99.

2.4.1.8. 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-N-octylphenylamine (M3). **M3** was synthesized by the same procedure as **M1**. The title compound was obtained as a colorless oil in a yield of 64%. ¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, 4H), 7.00 (d, 4H), 3.73 (t, 2H), 1.58 (m, 2H), 1.30 (s, 24H), 1.24 (m, 10H), 0.88 (t, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 150.3, 136.2, 120.2, 83.7, 52.3, 32.0, 29.6, 27.6, 27.2, 25.1, 22.9, 14.3. Anal. calcd. for C₃₂H₄₉B₂NO₄: C, 72.06; H, 9.26; N, 2.63; found: C, 72.12; H, 9.28; N, 2.52.

2.4.2. General procedures for the synthesis of polymers **P1**, **P2**, and **P3** by Suzuki polycondensation

A mixture of **M1** (0.25 mmol), **M2** (**M3** or **M4**) (0.25 mmol), NaHCO₃ (0.3 g, 35.7 mmol), H₂O (3 mL) and THF (20 mL) was carefully degassed before and after 0.01 mmol Pd(PPh₃)₄ was added under nitrogen atmosphere. The mixture was stirred and refluxed for 2 days under nitrogen atmosphere. Phenylboronic acid (10 mg, 0.08 mmol) was added; the reaction was further refluxed for 1 h; then 1-bromobenzene (0.05 mL, 0.48 mmol) was added; and the reaction was refluxed for another 1 h. The reaction mixture was then allowed to cool to room temperature, chloroform (100 mL) and water (100 mL) was added. The organic layer was separated and the aqueous layer was extracted with chloroform (50 mL × 2). The combined organic layers were concentrated to 30 mL and poured into acetone (200 mL), and the resulted precipitate was collected by filtration. The crude product was dissolved in chloroform again and precipitated into acetone. This operation was repeated for three times. The precipitate was collected by filtration and dried under high vacuum to afford the aimed polymer.

2.4.2.1. Polymer P1. Dark red solid was obtained (143 mg, 62%). ¹H NMR (400 MHz, CDCl₃): δ 8.46 (m, 8H), 7.35 (m, 4H), 7.13 (m, 4H), 4.14 (m, 4H), 4.06 (m, 2H), 1.91 (m, 6H), 1.48 (m, 14H), 1.21 (m, 16H), 0.81 (m, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 150.6, 150.1, 149.8, 137.9, 133.1, 132.5, 130.7, 129.5, 125.7, 122.6, 116.4, 73.5, 31.5, 30.8, 29.5, 28.6, 25.1, 25.0, 22.1, 21.7, 13.1. Anal. calcd. for C₅₆H₆₇N₃O₃S₃: C, 72.61; H, 7.29; N, 4.54; found: C, 72.64; H, 7.38; N, 4.38.

2.4.2.2. Polymer P2. Dark red solid was obtained (166 mg, 73%). ¹H NMR (400 MHz, CDCl₃): δ 8.51 (m, 2H), 7.61 (m, 4H), 7.38 (m, 2H), 7.16 (m, 8H), 4.18 (m, 4H), 2.61 (m, 2H), 2.00 (m, 4H), 1.64 (m, 4H), 1.33 (m, 22H), 0.85 (m, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 151.6, 150.9, 147.2, 145.5, 144.6, 138.8, 132.9, 131.9, 128.9, 127.8, 126.6, 125.3, 123.9, 123.6, 122.3, 117.4, 35.5, 31.9, 31.8, 31.5, 30.5, 29.6, 29.5, 29.4, 29.3, 29.2, 26.1, 22.7, 14.1. Anal. calcd. for C₅₆H₆₇N₃O₂S₃: C, 73.88; H, 7.42; N, 4.62; found: C, 73.21; H, 7.40; N, 4.41.

2.4.2.3. Polymer P3. Dark red solid was obtained (116 mg, 56%). ¹H NMR (400 MHz, CDCl₃): δ 8.44 (d, 2H), 7.57 (d, 4H), 7.29 (d, 2H), 7.02 (d, 4H), 4.11 (m, 4H), 3.70 (m, 2H), 1.90 (m, 4H), 1.67 (m, 2H), 1.44 (m, 8H), 1.26 (m, 22H), 0.80 (m, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 150.6, 150.0, 146.2, 144.7, 131.7, 130.9, 126.6, 125.8, 121.0, 120.1, 116.4, 73.4, 51.4, 30.8, 29.4, 28.6, 28.4, 28.3, 26.6, 26.1, 25.1, 21.7, 21.6, 13.1. Anal. calcd. for C₅₀H₆₃N₃O₂S₃: C, 71.99; H, 7.61; N, 5.04; found: C, 70.3; H, 7.69; N, 4.89.

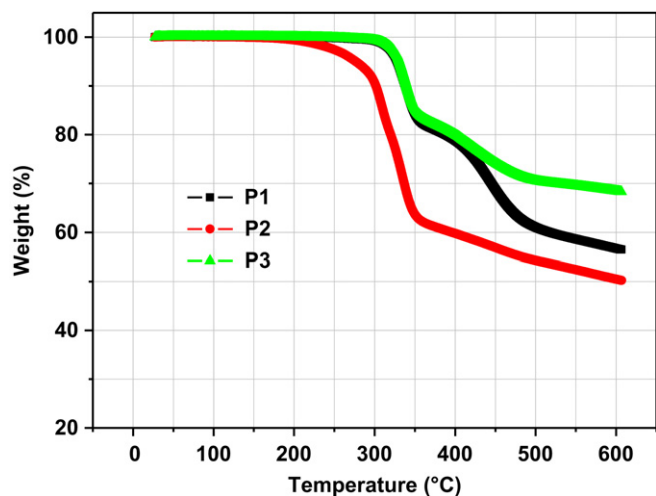


Fig. 1. TGA plots of **P1**, **P2** and **P3** with a heating rate of 10 °C/min in the nitrogen.

Table 1
Polymerization results and thermostability of polymers.

Polymer	Yield (%)	M_n (g/mol) ^a	M_w (g/mol) ^a	PDI	T_d (°C) ^b	T_g (°C) ^c
P1	62	97,000	150,000	1.54	329	109
P2	73	5800	13000	2.24	276	53
P3	56	5400	13500	2.49	331	142

^a M_n , M_w and PDI of polymers were determined by GPC using polystyrene standards with THF as eluent.

^b Decomposition temperature determined by TGA in N₂ based on 5% weight loss.

^c Glass transition temperature determined by DSC in N₂ at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routes toward polymers **P1**, **P2**, and **P3** are outlined in Scheme 1. Benzothiadiazole based monomer (**M1**) and TPA-based diboronic ester monomers (**M2**, **M3** and **M4**) were synthesized according to the modified literature procedures [34]. Three polymers were synthesized by Suzuki polycondensation between TPA-based monomer and **M1** in a biphasic mixture of THF/aqueous NaHCO₃ with Pd(PPh₃)₄ as the catalyst precursor. After polymerization, the obtained polymers were dissolved in a small amount of chloroform and precipitated into acetone for three times to remove

low molecular weight oligomers. The purified polymers were obtained as dark red solids in yields of 62% for **P1**, 73% for **P2**, and 52% for **P3**. The polymers display good solubility in chloroform, chlorobenzene (CB), 1,2-dichlorobenzene (DCB), tetrahydrofuran (THF), 1,2,4-trichlorobenzene (TCB), etc. at elevated temperature. Number- and weight-average molecular weights (M_n and M_w) and polydispersity indexes (PDI) of polymers were measured by gel permeation chromatography (GPC) with THF as an eluent and calibrated with polystyrene standards. The M_n of **P1**, **P2** and **P3** were 97,000, 5800 and 5400 kg/mol, with the corresponding PDI of 1.54, 2.24 and 2.49, respectively. The thermal behaviors of the copolymers under nitrogen atmosphere were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). As shown in Fig. 1, all three polymers exhibited good thermal stability and are suitable for application in PSCs. The molecular weights and the thermal properties of the polymers are listed in Table 1.

3.2. Optical and electrochemical properties

The UV–vis absorption spectra of the polymers both in chloroform solution and in the solid state at 20 °C are shown in Fig. 2. In chloroform solutions, the three polymers all exhibit two distinct absorption bands. The band located at about 382 nm is corresponding to the π – π transition of their conjugated backbones. The peaks at longer wavelength are at 525, 515, 525 nm for **P1**, **P2** and **P3**, respectively, which can be attributed to strong intermolecular charge transfer (ICT) interaction between the donor and the acceptor units. Compared with **P2**, the maximum absorption band of **P1** shows a slight red-shift of 10 nm, which might be due to the incorporation of the alkoxy chains in the end of TPA as a stronger donor resulting in stronger ICT interaction. For **P3**, the introduction of diphenylamine units into the polymer backbone has no obvious influence on the absorption spectra in solution in contrast to that of **P1**. The absorption bands of these three polymers all red-shift and become broader when they go from the solutions to the solid states. The maximum absorption bands in films are 558, 550 and 562 nm for **P1**, **P2** and **P3**, respectively. The red shift that occurs from the solution to the film state is attributed to the aggregation of the polymer chains or the orderly π – π stacking formed in the solid states. The absorption red-shifts for **P1**, **P2** and **P3** are 29, 34 and 36 nm, respectively. Larger red-shift for **P3** can be attributed to the replacement of phenyl group in TPA unit by alkyl chains to deduce the twist of the polymer backbone and increase the aggregation effect in solid state. The onsets of the absorption spectra in films are 624, 628

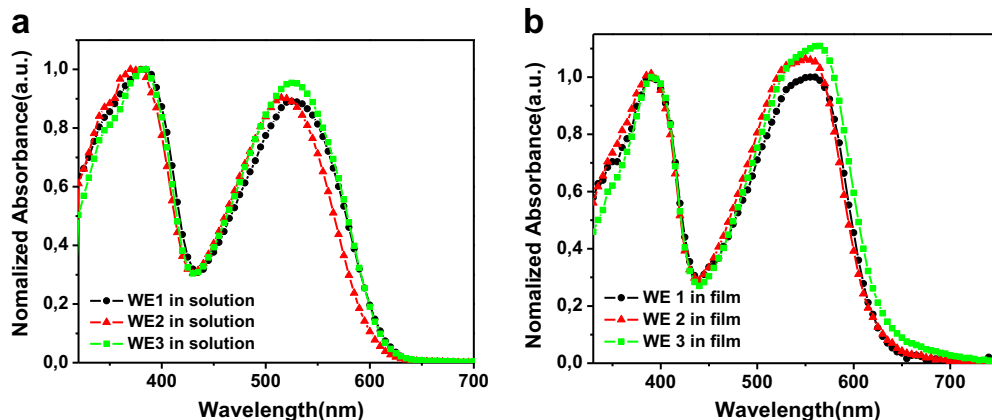


Fig. 2. UV–vis absorption spectra of **P1**, **P2**, and **P3** in chloroform solutions (a) and in films (b).

Table 2
Electrochemical and optical properties of the polymers.

polymer	In solution	In film		$E_{g,opt}$ (eV)	HOMO (eV)	LUMO (eV)
	λ_{max} [nm]	λ_{max} [nm]	λ_{onset} [nm]			
P1	383, 529	388, 558	624	1.99	−5.29	−3.30
P2	378, 516	388, 550	628	1.97	−5.31	−3.34
P3	383, 526	388, 562	640	1.93	−5.13	−3.20

and 640 nm for **P1**, **P2** and **P3**, respectively, corresponding to the optical band gaps of 1.99, 1.97 and 1.93 eV. The absorption maximum in solutions and in films and $E_{g,opt}$ of the polymers are summarized in Table 2.

The positions of the HOMO and LUMO energy levels have pronounced influence on V_{oc} , the driving force for charge separation, and the overall photovoltaic performance. Thus, cyclic voltammetry (CV) was used to determine the electrochemical properties of polymers. From the oxidation potentials obtained in the electrochemical measurements, the HOMO energy level can be estimated according to the equation $E_{HOMO} = -e(E_{ox} + 4.71)$ (eV), where E_{ox} is the onset oxidation potential in volts vs Ag/Ag⁺. For **P1**, **P2** and **P3**, the HOMO energy levels are calculated to be −5.29, −5.31 and −5.13 eV, respectively, according to the onset oxidation potentials. Because the reduction potentials could hardly be obtained, the LUMO energy levels often are difficult to determine. Therefore, with the combination of the optical band gap and the HOMO energy levels, the LUMO energy levels of the resulting polymers can be calculated according to the equation $E_{LUMO} = E_{HOMO} + E_{g,opt}$. The LUMO energy levels of three polymers are −3.30, −3.34 and −3.20 eV for **P1**, **P2** and **P3**,

respectively. The related electrochemical parameters, HOMO and LUMO energy levels are summarized in Table 2. **P2** shows lower lying HOMO energy levels than **P1**, which is attributed to alkyl groups with weaker electron-donating ability than alkoxy groups for **P1**. **P3** exhibited higher HOMO energy level among the three polymers, which was due to the weaker electron delocalization ability of alkyl chains than the phenyl group in **P1** and **P2**. Lower lying HOMO energy levels are expected to a higher V_{oc} , since V_{oc} linearly depends on the difference between the HOMO energy level of the donor polymer and the LUMO energy levels of the acceptor. Therefore, higher V_{oc} for **P2** will be expected in solar cells compared to the other two polymers. Furthermore, three polymers all possess high LUMO energy levels, which can ensure enough driving force for charge separation.

3.3. Transport properties

The transport properties of these three polymers were investigated by fabricating organic thin film field-effect transistors (OFETs). Typical *p*-channel field-effect transistor behavior was obtained. The hole mobility (μ) was estimated in the saturated regime from the derivative plots of the square root of source–drain current (I_{SD}) versus gate voltage (V_G) through equation $I_{SD} = (W/2L)C_i\mu(V_G - V_T)^2$ where W is the channel width, L is the channel length, C_i is the capacitance per unit area of the gate dielectric layer (SiO₂, 500 nm, $C_i = 7.5$ nF/cm²), and V_T is the threshold voltage. A hole mobility of 8.21×10^{-3} cm²V^{−1}s^{−1} is observed for **P1** based OFETs. The hole mobilities of **P2** and **P3** are 6.20×10^{-4} and 6.98×10^{-4} cm²V^{−1}s^{−1}, respectively, which are one order of magnitude lower than **P1**. The output curves are

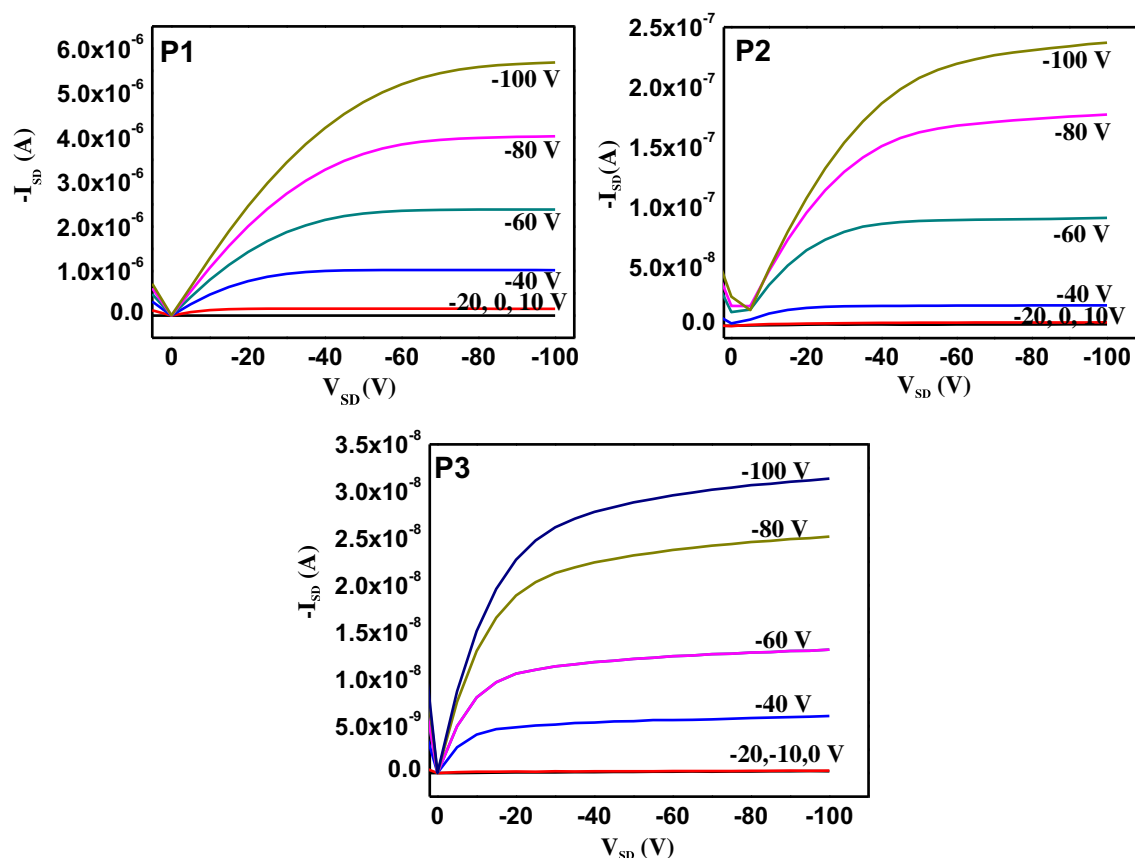


Fig. 3. The output curves at different gate voltages (V_G) for OFETs using spin-coated **P1**, **P2** and **P3** on OTS-treated Si/SiO₂ substrates.

shown in Fig. 3. The transfer curves of the spin-coated film of **P1**, **P2** and **P3** on OTS-treated Si/SiO₂ substrates are shown in Fig S1 in the Supporting Information.

3.4. Photovoltaic properties

Bulk heterojunction photovoltaic devices were fabricated. PC₇₁BM was chosen as the acceptor because it has similar electronic properties as PC₆₁BM, but a higher absorption coefficient in the visible region with a broad peak from 440 to 530 nm, which compensates the absorption valley of the polymers. The solvent used for device fabrication is important because the solubility of the polymers has a pronounced influence on the blend film morphology that affects charge separation and transport in devices. To optimize the morphology of the active layers, solar cells were fabricated from the blends of each polymer and PC₇₁BM in 1,2-DCB, CB, and TCB solutions, respectively. The optimized weight ratio between polymer and PC₇₁BM is 1:3. The photovoltaic parameters of the solar cells and the thicknesses of the corresponding active layers are listed in Table 3.

The devices of **P1**:PC₇₁BM = 1:3 fabricated from TCB or CB solution both show PCE of 2.1% with V_{oc} of 0.76–0.77 V, J_{sc} of 5.4–5.7 mA/cm² and fill factor (FF) of 0.46–0.50. Slightly higher PCE of 2.3% with a V_{oc} of 0.77 V, J_{sc} of 6.9 mA/cm², and FF of 0.43 is achieved by the device fabricated from **P1**:PC₇₁BM = 1:3 in DCB solution. PCEs of solar cells fabricated from **P2**:PC₇₁BM = 1:3 in TCB, CB, and DCB solution are 2.0, 2.1 and 2.1%, respectively. It is striking that the performance of the solar cells are not extremely sensitive to the solvents, which can simplify the preparation of devices and it is unnecessary to select one kind of the solvent strictly. Such insensitivity might be due to the two-dimensional structure of TPA-containing polymers **P1** and **P2**, since the two-dimensional structure can suppress the aggregation of polymer chains to some extent and endow the polymers with better solubility in solutions. PCEs of the devices fabricated from **P3**:PC₇₁BM = 1:3 in CB and DCB solution are 1.7 and 1.8%, respectively. The film spin-coating from **P3**:PC₇₁BM = 1:3 in TCB solution show extremely rough and large visible particles, which might be due to the poor solubility of **P3** in TCB solution. Therefore, the device fabricated from **P3**:PC₇₁BM = 1:3 in TCB solution provided unsatisfactory results. Noticeably, the solar cell fabricated from **P2**:PC₇₁BM = 1:3 in DCB solution exhibits higher V_{oc} of 0.80 V than that of **P1** with 0.77 V and **P3** with 0.71 V, which is consistent with its deeper HOMO energy level among these three polymers. Fig. 4a shows the current density–voltage (J – V) curves of the three polymer devices fabricated from DCB solution. The device fabricated from **P1**:PC₇₁BM = 1:3 in DCB solution shows the highest PCE of 2.3%

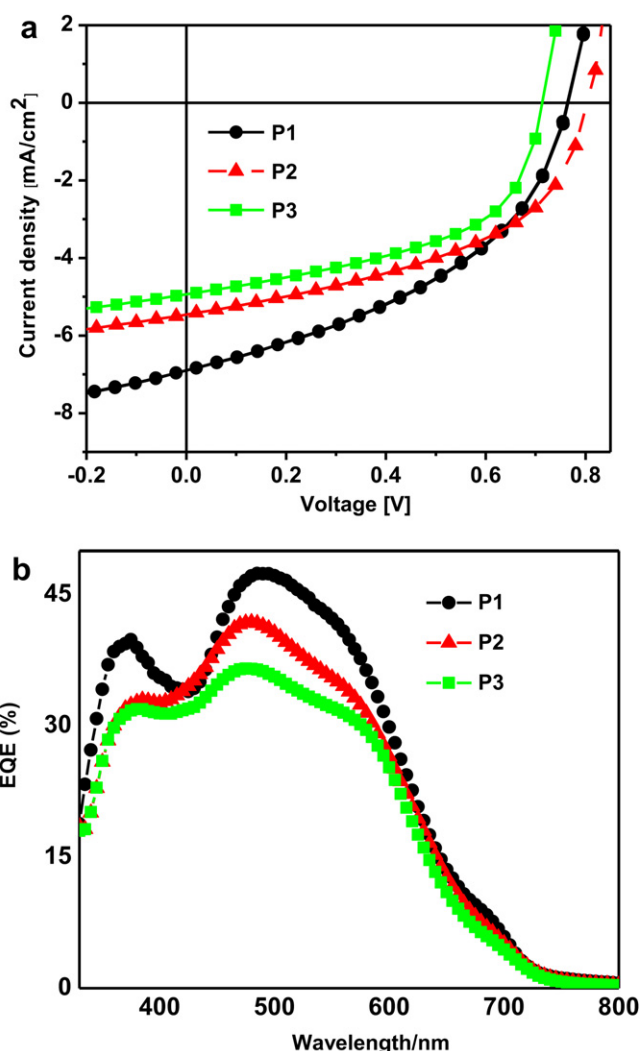


Fig. 4. J – V curves (a) and EQE (b) of PSCs fabricated from **P1**:PC₇₁BM = 1:3, **P2**:PC₇₁BM = 1:3 and **P3**:PC₇₁BM = 1:3 in DCB solutions.

Table 3
Summary of the photovoltaic properties of BHJ PSCs based on **P1**, **P2**, and **P3**.

The active layer	Solvent	Thickness (nm)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
P1 :PC ₇₁ BM	CB	90	0.76	5.7	0.46	2.1
	DCB	75	0.77	6.9	0.43	2.3
	TCB	50	0.77	5.4	0.50	2.1
	DCB (1% DIO)	70	0.68	7.8	0.53	2.8
P2 :PC ₇₁ BM	CB	100	0.83	5.3	0.46	2.1
	DCB	85	0.80	5.5	0.48	2.1
	TCB	60	0.82	4.7	0.52	2.0
	DCB (2% DIO)	75	0.71	5.8	0.61	2.5
P3 :PC ₇₁ BM	CB	80	0.68	5.3	0.48	1.7
	DCB	65	0.71	4.9	0.52	1.8
	DCB (2% DIO)	65	0.68	4.6	0.63	2.0

although **P1** possesses medium V_{oc} of 0.77 V among these three polymers. It is obvious that higher J_{sc} for **P1** accounts for the better photovoltaic performance. J_{sc} can be improved mainly from the increased light absorption, the good hole mobility of the polymer for charge transfer and optimal film nanoscale morphology for charge separation and transport. Obviously, all polymer films have similar absorption spectra and intensity with almost superimposed absorption profiles, higher J_{sc} for **P1** was attributed to, at least partially, the higher hole mobility of **P1** than that of **P2** and **P3**. To evaluate the accuracy of measurements, the external quantum efficiency (EQE) curves of the PSC devices fabricated from the blend of the corresponding polymer and PC₇₁BM in DCB solution were measured. EQE curves are shown in Fig. 4b and present shallower valleys from 400 to 500 nm compared to the corresponding absorption spectra (Fig. 2b), which indicates PC₇₁BM compensates the absorption valley of the polymers and the contribution from PC₇₁BM to the photocurrent is very pronounced. PSC devices based on three polymers all exhibited excellent response in their absorption range from 350 to 750 nm. The highest EQE value of the devices reached 48% at about 490 nm for **P1** based PSCs. All current intensity (J_{sc}) values calculated from the integration of the EQEs of the devices agree well with the J_{sc} values obtained from the J – V measurements.

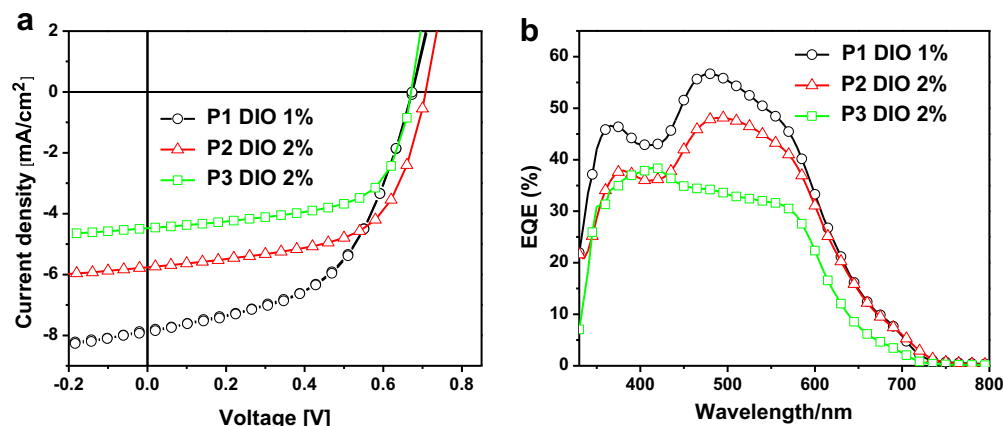


Fig. 5. J – V curves (a) and EQE (b) of the PSCs fabricated from **P1**:PC₇₁BM = 1:3, **P2**:PC₇₁BM = 1:3 and **P3**:PC₇₁BM = 1:3 in DCB solution containing DIO.

Processing additives have considerable influence on the photovoltaic performance. 1,8-Diiodooctane (DIO), which is a commonly used processing additive, was chosen to optimize the morphology and expected to enhance the photovoltaic performance of the resulting PSCs [4,38–40]. The photovoltaic parameters of solar cells are shown in Table 3. With the addition of DIO, the devices fabricated from the blend of each polymer and PC₇₁BM in DCB solution all show slight enhanced photovoltaic performance. For **P1**, the PCE is improved from 2.3 to 2.8% with V_{oc} of 0.68 V, J_{sc} of 7.8 mA/cm^2 and FF of 0.53. PCE of the device from **P2** based PSCs is increased from 2.1 to 2.5%. Both the devices based on **P1** and **P2** exhibit improved PCEs, which is attributed to the increased J_{sc} and

FF with the addition of the additive DIO. For **P3** based PSCs, there is a slight decrease for J_{sc} although the PCE is increased a little from 2.1 to 2.3%. The J – V curves of these devices are shown in Fig. 5a. EQE of the devices fabricated from the blend of each polymer and PC₇₁BM in DCB solution containing the additive DIO is also shown in Fig. 5b. The high EQE of 56% for **P1** was observed at 477 nm, which reflects higher J_{sc} for **P1** based PSCs.

The morphology of the blend films spin-coated from the polymers and PC₇₁BM in DCB solution without or with DIO was investigated by tapping-mode atomic force microscopy (AFM). DIO has a higher boiling point than the host solvent, PCBM tends to remain in solution (during drying) longer than the blend polymer, since the

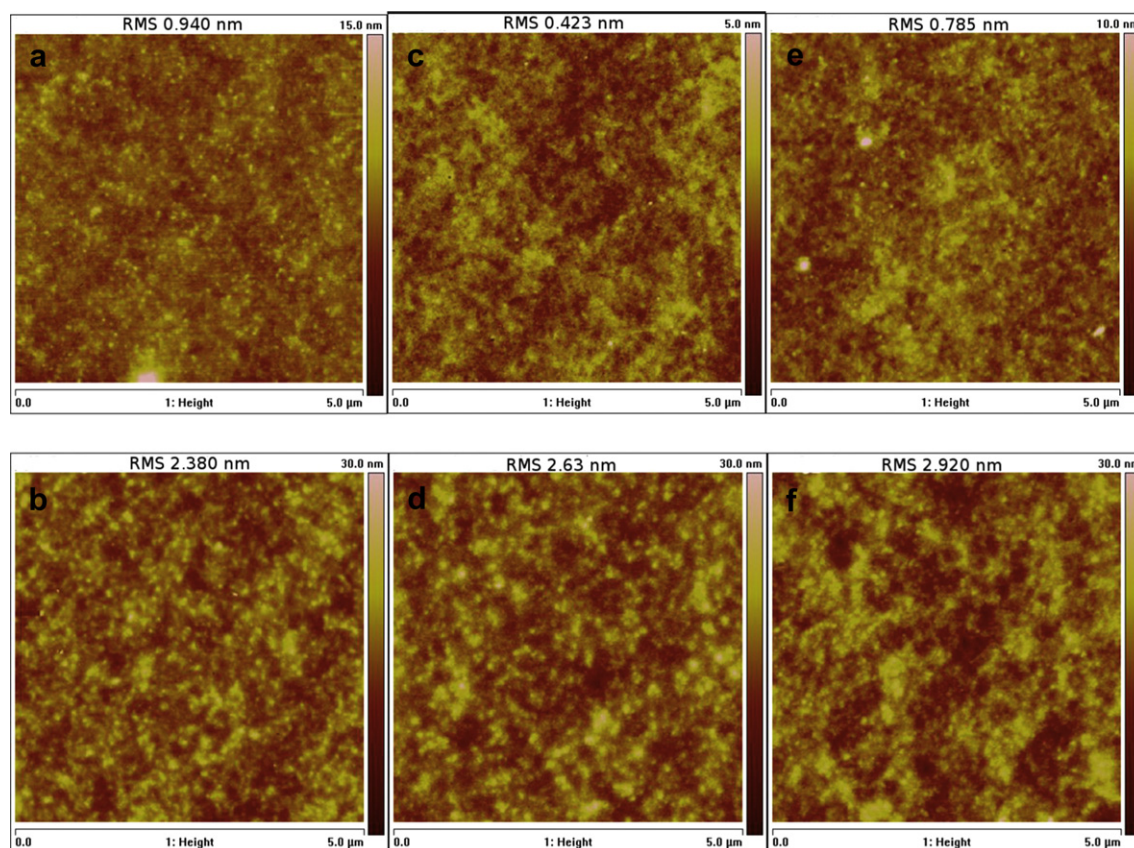


Fig. 6. AFM images ($5 \times 5 \mu\text{m}^2$) of the active layers from the blend of the polymer and PC₇₁BM (polymer: PC₇₁BM = 1:3) without (a for **P1**, c for **P2** and e for **P3**) and with DIO (b for **P1**, d for **P2** and f for **P3**).

fullerenes are selectively dissolved in DIO, which can realize the control of the phase separation and the resulting morphology of the BHJ material [4,38–40]. As shown in Fig. 6, all three blend films from DCB, **P1** (a), **P2** (c) and **P3** (e) show very smooth surfaces and no large domains can be observed, which indicate no obvious phase separations occur. It is well known that a certain degree of phase separation is necessary for providing a percolation pathway for charge transport to the electrodes. The root-mean-square (rms) roughness for the polymers and PC₇₁BM blend films are 0.940, 0.423 and 0.785 nm for **P1**, **P2** and **P3**, respectively. Therefore, it can be concluded that the designed polymers **P1**, **P2** and **P3** possess the optimized geometry. The incorporation of TPA group can construct the two-dimensional architecture and would create large free space between the polymer chains, where fullerene molecules can be distributed well over the polymer network, thus no evident phase separation was observed. With the addition of DIO, the images exhibited rms has been increased to 2.38 and 2.63 nm from 0.94 and 0.423 nm for **P1** (b) and **P2** (d), respectively. The increasing of the roughness indicates the phase separation takes place, which reduces the recombination of charges, leading to higher J_{sc} and FF for **P1** and **P2** based PSCs with the addition of DIO. For **P3** (f), the image of the blend film with DIO exhibited a rougher film with rms of 2.92 nm in contrast to the rms of 0.785 nm without the additive. Such large phase separation can decrease the interface for exciton dissociation, which caused a little drop of J_{sc} . The increase of FF compensates the loss of J_{sc} resulting in the slight improvement of the photovoltaic performance for **P3** based PSCs. An interpenetrating bicontinuous network between polymer and PCBM with an ideal domain size of 10–20 nm is desirable for high-performance PSCs. Both larger and smaller phase separations are not favorable for efficient charge separation and transportation. Large phase separation increases the distance to the nearest interface where the exciton may dissociate before they recombine, which leads to low photocurrent. While, smaller domain sizes between polymer and PCBM increase the possibility of charge recombination. Only appropriate phase separation can balance charge generation and recombination and result in the optimized photovoltaic performance. The influence of DIO on V_{oc} is more pronounced for **P1** and **P2** (V_{oc} decrease almost 0.1 V) than **P3** (only reduced by 0.03 V), which indicates that **P3** is less sensitive to processing additive.

4. Conclusion

We have successfully designed and synthesized a series of alternating copolymers based on benzothiadiazole and triphenylamine (TPA) derivatives: **P1**, **P2** and **P3**. These three polymers all possess medium optical band gaps, which are 1.99, 1.97 and 1.93 eV, respectively. The field-effect hole mobilities are $8.21 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **P1**, $6.20 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **P2**, and $6.98 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for **P3**. PCEs of higher than 2.0% have been obtained for photovoltaic cells fabricated from **P1**, **P2**, and **P3** blended with PC₇₁BM. The highest PCE of 2.8% for **P1** with short circuit current (J_{sc}) of 7.8 mA/cm² was achieved. The photovoltaic performance of **P1** and **P2** is not sensitive to the choice of the blend solvent due to the incorporation of two-dimensional TPA units. This study offers a useful and important insight for designing TPA derivative-based polymers for efficient PSCs.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2011.12.026.

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