

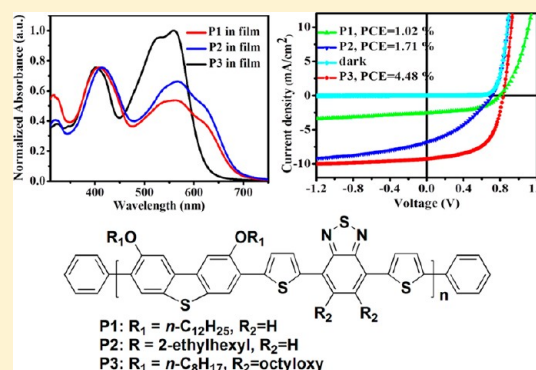
Dibenzothiophene-Based Planar Conjugated Polymers for High Efficiency Polymer Solar Cells

Enquan Jin, Chun Du, Ming Wang, Weiwei Li, Cuihong Li,* Hedi Wei, and Zhishan Bo*

Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Beijing Normal University, Beijing 100875, China

Supporting Information

ABSTRACT: Three D–A alternating copolymers **P1–3** with 3,7-linked 2,8-bis(alkoxy)dibenzothiophene as the donor unit and benzothiadiazole (**P1** and **P2**) or 3,4-bis(octyloxy)benzothiadiazole (**P3**) as the acceptor unit have been designed and synthesized. **P1–3** show two broad absorption peaks in the visible region, and the internal charge transfer (ICT) absorptions at about 530 nm in solutions and 560 nm in films of **P3** are much stronger than that of **P1** and **P2**. All the polymers show narrow band gaps below 2.0 eV and the low-lying HOMO energy levels of approximately -5.30 eV. The hole mobilities of polymer films spin-cast from 1,2-dichlorobenzene (DCB) solutions are 3.0×10^{-4} , 2.7×10^{-4} , and 2.3×10^{-3} $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ for **P1**, **P2**, and **P3**, respectively. Under simulated solar illumination of AM 1.5G (100 mW/cm^2), a PCE of 4.48% with a V_{oc} of 0.83 V, a J_{sc} of 9.30 mA/cm^2 , and an FF of 0.58 has been achieved for PSCs with the **P3**:PC₇₁BM blend (1:3, by weight) as the active layer in simply processed devices, whereas after the optimization, PCEs of only 1.02% and 1.71% have been obtained for **P1**- and **P2**-based devices, respectively. This is the first report on dibenzothiophene-based conjugated polymers used for high efficiency polymer solar cells, demonstrating that photovoltaic performance can be improved by fine-tuning the conjugated polymer structure.



INTRODUCTION

In recent years, polymer solar cells (PSCs) have attracted considerable attention due to their advantages of lightweight, flexibility, and large-scale manufacturing with low-cost roll-to-roll process.¹ Polymer solar cells have experienced a rapid development since the invention of the bulk-heterojunction (BHJ) device structure, which has been proven to be the most efficient device structure until now.² For polymer solar cells power conversion efficiency (PCE) higher than 7% has been achieved by several groups via the optimization of the polymer and device structure.³ The BHJ structure is a phase-separated bicontinuous network formed by blending electron-donating polymers and electron-accepting fullerene derivatives, such as (6,6)-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) or (6,6)-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM). To achieve highly efficient BHJ polymer cells, polymer donors should have a strong and broad absorption to effectively absorb sunlight, an appropriate highest occupied molecular orbital level (HOMO) and an appropriate lowest unoccupied molecular orbital level (LUMO) to maximize the short-circuit current (J_{sc}) and open-circuit voltage (V_{oc}),^{2f,4} and most importantly the polymer donor and PCBM blends (active layer) should have a balanced hole and electron mobility to promote the continuous generation of electrons without recombination reactions or saturation of charges.^{2f,4a} The electron mobility of PCBM is around $2 \times 10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$,⁵ whereas the hole mobility of

conjugated polymer donors is usually several orders lower than the electron mobility of PCBM. In order to increase the hole mobility of polymer donors, polymer chains are required to have a planar structure and closely pack in films.⁶

Main chain donor–acceptor (D–A) alternating design is a very efficient way to tune the absorption and energy level of conjugated polymers through the intramolecular charge transfer from donor to acceptor unit.^{3g,7} On the one hand, benzothiadiazole is a commonly used acceptor unit in construction of D–A alternating conjugated polymers, and high power conversion efficiency has been achieved for benzothiadiazole containing D–A alternating copolymers.⁸ On the other hand, 2,7-linked fluorene (two benzene ring bridged by carbon atom),^{7e,8a,9} 2,7-linked carbazole (two benzene rings bridged by nitrogen atom),^{2e,10} and 2,7-linked silafluorene (two benzene rings bridged by silicon atom)^{6c,11} have been used as donor units for the construction of the D–A copolymers. However, until now there is no report on using 3,7-linked dibenzothiophene (two benzene rings bridged by sulfur atom) as donor unit in synthesizing D–A alternating copolymers. It is worthy noting that Wang et al. have found that marked chalcogen–chalcogen interactions exist in

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chalcogen-annulated perylene solid films, which may facilitate charge transport.¹² In this work, we design and synthesize three D–A alternating copolymers with 3,7-linked 2,8-bis(alkoxy)-dibenzothiophene as the donor unit and benzothiadiazole or 3,4-bis(octyloxy)benzothiadiazole as the acceptor unit. We attached two alkoxy substituents on the 2,8-positions of dibenzothiophene to ensure that the two alkoxy chains do not hinder the π – π stacking of polymer backbones in solid films and generates soluble polymers. For the first time, we demonstrate that 2,8-bis(alkoxy)-substituted dibenzothiophene can be a useful donor unit for constructing main chain D–A alternating narrow band gap conjugated polymer for high efficiency polymer solar cells. In addition, we have found that conjugated polymers (**P3**) with 2,8-bis(alkoxy)-dibenzothiophene as the donor unit and 5,6-bis(octyloxy)-substituted benzothiadiazole as the acceptor unit show a strong internal charge transfer (ICT) absorption in the long wavelength region, whereas copolymers (**P1** and **P2**) with 2,8-bis(alkoxy)dibenzothiophene as the donor unit and benzothiadiazole as the acceptor unit show a relative weak ICT absorption. As expected, the strong absorbed **P3**-based polymer solar cells show higher PCE than the weak absorbed **P1**- and **P2**-based polymer solar cell devices. Under simulated solar illumination of AM 1.5G (100 mW/cm²), a PCE of 4.48% has been achieved for PSCs with **P3**:PC₇₁BM blend as the active layer in simply processed devices. The devices illustrate a considerably high V_{oc} of 0.83 V, a J_{sc} of 9.30 mA/cm², and a comparable fill factor (FF) of 0.58. The hole mobility of **P3** reached 2.3×10^{-3} cm² V⁻¹ s⁻¹. The above result demonstrates that the absorption and photovoltaic performance can be improved by fine-tuning the conjugated polymer structure.

■ EXPERIMENTAL PART

Materials and Instruments. Unless otherwise noted, all chemicals were purchased from Aldrich or Acros and used without further purification. The catalyst precursor Pd(PPh₃)₄ was prepared according to the literature and stored in a Schlenk tube under a nitrogen atmosphere.¹³ 2,8-Dibromodibenzothiophene was synthesized according to the literature procedure.¹⁴ Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium with benzophenone as an indicator under a nitrogen atmosphere. Hexane and dichloromethane (DCM) were distilled from CaH₂. 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 ¹³C NMR spectra were recorded on a Bruker AV 400 spectrometer. Fluorescence spectra were recorded on a FluoroMax-4 spectrofluorometer. UV–vis absorption spectra were obtained on a PerkinElmer UV–vis spectrometer model Lambda 750. 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 PerkinElmer Diamond DSC instrument, respectively, under a nitrogen atmosphere at a heating rate of 10 °C/min to record TGA and DSC curves. The gel permeation chromatography (GPC) measurements were performed at 150 °C on a PL-220 (Polymer Laboratories) chromatograph connected to a differential refractometer with 1,2,4-trichlorobenzene as an eluent. Atomic force microscopy (AFM) measurements were performed under ambient conditions using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode. The thickness of the blend films was determined by a Dektak 6 M surface profilometer. The powder X-ray diffraction (XRD) patterns were collected using a PANalytical X'Pert PRO MPD diffractometer with Cu K α radiation. The electrochemical behavior of the polymers was investigated using cyclic voltammetry (CHI 630A electrochemical

analyzer) with a standard three-electrode electrochemical cell in a 0.1 M tetrabutylammonium tetrafluoroborate solution in CH₃CN at room temperature under an atmosphere of nitrogen with a scanning rate of 0.1 V/s. A Pt plate working electrode, a Pt wire counter electrode, and an Ag/AgNO₃ (0.01 M in CH₃CN) reference electrode were used. The experiments were calibrated with the standard ferrocene/ferrocenium (F_c) redox system and assumption that the energy level of F_c is 4.8 eV below vacuum.

Fabrication and Characterization of Organic Field-Effect Transistors (OFETs). Top-contact devices were fabricated based on Si/SiO₂ substrates (the back low resistance Si as gate, SiO₂ (500 nm) with a capacitance of 7.5 nF cm⁻² as gate insulator). The substrate of Si/SiO₂ was sequentially cleaned with pure water, hot concentrated sulfuric acid–hydrogen peroxide solution (concentrated sulfuric acid:hydrogen peroxide, 2:1 by volume), pure water, pure ethanol, and pure acetone successively and then treated with a monolayer of trichloro(octadecyl)silane (OTS) by the normal vapor deposition method described elsewhere. Polymer or polymer/PC₇₁BM films were cast or spin-coated on the OTS-modified Si/SiO₂ substrate from DCB with the polymer concentration of 10 mg/mL. Electrodes of Au (25 nm) were vacuum-deposited on films with width/length = 50 (channel width = 2.5 mm, channel length = 50 μ m). *J*–*V* characteristics were obtained using an Agilent B2902A source meter with a Micro-manipulator 6150 probe station in a clean and shielded box at room temperature in air.

Polymer Solar Cell Fabrication and Characterization. Polymer solar cells (PSCs) were fabricated with the device configuration of ITO/PEDOT:PSS/Polymer:PC₇₁BM (1:3)/LiF/Al. The conductivity of ITO was 20 Ω/\square . PEDOT:PSS is Baytron AL 4083 from H.C. Starck and was filtered with a 0.45 μ 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 hot plate before transferred into a glovebox. The thickness of the PEDOT:PSS layer was about 40 nm. The blend of polymers and PC₇₁BM was dissolved in ODCB, heated at 90 °C for overnight to ensure the sufficient dissolution, and then spin-coated onto PEDOT:PSS layer. The top electrode was thermally evaporated, with a 0.6 nm LiF layer, followed by 100 nm of aluminum at a pressure of 10⁻⁴ Pa through a shadow mask. Five cells were fabricated on one substrate with an effective area of 0.04 cm². The measurement of devices was conducted in air without encapsulation. Current–voltage characteristics were recorded using an Agilent B2902A source meter under an AM1.5G AAA class solar simulator (model XES-301S, SAN-EI) with an intensity of 100 mW cm⁻² as the white light source, and the intensity was calibrated with a standard single-crystal Si photovoltaic cell. The temperature while measuring the *J*–*V* curves was \sim 25 °C.

Synthesis of 2,8-Dihydroxydibenzothiophene-5,5-dioxide (3). To a solution of 2,8-dibromodibenzothiophene (**1**) (20.0 g, 58.47 mmol) in THF (150 mL) cooled to –78 °C was added *n*-butyllithium (58.47 mL, 2.5 M in hexane, 146.18 mmol) by syringe. The mixture was stirred at –78 °C for 2 h, triisopropyl borate (43.00 mL, 185.17 mmol) was added rapidly, and the mixture was stirred overnight and allowed to warm to room temperature gradually. Dilute hydrochloric acid was added, and the mixture was extracted with ether. The organic layer was separated, washed with brine, and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure, and the residue (crude benzothiophene-5,5-dioxide-2,8-diboronic acid, **2**) was dissolved in acetic acid (150 mL). The solution was cooled to 0 °C with an ice bath, hydrogen peroxide (30%, 80 mL) was added dropwise, and the resulted mixture was stirred at 0 °C overnight. Removal of the solvent under reduced pressure afforded the crude 2,8-dihydroxydibenzothiophene-5,5-dioxide, **3** (13.35 g, 92%), as a colorless solid, which was used for the next step without further purification.

General Procedure for the Synthesis of 2,8-Bis(alkoxy)-dibenzothiophene-5,5-dioxide (4). A mixture of compound **3**, alkyl bromide, potassium carbonate, and butanone was heated to reflux and stirred under a nitrogen atmosphere for 2 days. The solvent was removed under reduced pressure, the residue was partitioned between

methylene dichloride and water, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 . The combined organic layers were dried over anhydrous MgSO_4 and evaporated to dryness. The residue was purified by flash column chromatography on silica gel eluted with petroleum ether (60–90 °C)/dichloromethane (1:2, v/v) to give 3,6-bis(alkoxy)dibenzothiophene-*S,S*-dioxide (4) as colorless solids.

Synthesis of 2,8-Bis(dodecyloxy)dibenzothiophene-*S,S*-dioxide (4a). 3,6-Dioxybenzothiophene-*S,S*-dioxide (3) (6.00 g, 24.17 mmol), dodecyl bromide (15.06 g, 60.43 mmol), potassium carbonate (10 g, 72.5 mmol), and butanone (250 mL) were used. 4a was obtained in a yield of 89% (12.58 g). ^1H NMR (400 MHz, CDCl_3) δ : 7.64–7.61 (d, 2H), 7.10–7.09 (d, 2H), 6.90–6.88 (dd, 2H), 4.00–3.97 (t, 4H), 1.79–1.72 (m, 4H), 1.44–1.37 (m, 4H), 1.27–1.20 (m, 32H), 0.82–0.79 (t, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ : 163.65, 133.70, 130.48, 123.49, 115.77, 107.46, 68.80, 31.91, 29.65, 29.62, 29.58, 29.54, 29.34, 29.03, 25.94, 22.68, 14.11. Anal. Calcd for $\text{C}_{36}\text{H}_{56}\text{O}_4\text{S}$: C, 73.93; H, 9.65. Found: C, 73.75; H, 9.38.

Synthesis of 2,8-Bis(2-ethylhexyloxy)dibenzothiophene-*S,S*-dioxide (4b). 3,6-Dioxybenzothiophene-*S,S*-dioxide (3) (6.00 g, 24.17 mmol), 2-ethylhexyl bromide (11.67 g, 60.43 mmol), potassium carbonate (10.00 g, 72.46 mmol), and butanone (150 mL) were used. 4b was obtained in a yield of 76% (8.68 g). ^1H NMR (400 MHz, CDCl_3) δ : 7.61–7.59 (d, 2H), 7.11–7.10 (d, 2H), 6.89–6.86 (dd, 4H), 3.87–3.86 (d, 4H), 1.45–1.41 (m, 2H), 1.40–1.20 (m, 18H), 0.89–0.85 (t, 6H), 0.84–0.80 (t, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ : 163.85, 133.67, 130.38, 123.36, 115.86, 107.41, 71.18, 65.26, 41.96, 39.30, 30.43, 30.12, 29.11, 29.05, 23.80, 23.34, 23.08, 23.00, 14.06, 11.11, 11.09. Anal. Calcd for $\text{C}_{28}\text{H}_{40}\text{O}_4\text{S}$: C, 71.15; H, 9.53. Found: C, 71.77; H, 9.92.

Synthesis of 2,8-Bis(octyloxy)dibenzothiophene-*S,S*-dioxide (4c). 3,6-Dioxybenzothiophene-*S,S*-dioxide (3) (8.40 g, 33.8 mmol), *n*-octyl bromide (16.34 g, 84.6 mmol), potassium carbonate (14.01 g, 101.4 mmol), and butanone (200 mL) were used. 4c was obtained in a yield of 92% (15.98 g). ^1H NMR (400 MHz, CDCl_3) δ : 7.61–7.59 (d, 2H), 7.08–7.07 (d, 2H), 6.88–6.86 (dd, 2H), 3.99–3.95 (t, 4H), 1.78–1.71 (m, 4H), 1.44–1.37 (m, 4H), 1.33–1.18 (m, 16H), 0.84–0.80 (t, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ : 163.65, 133.69, 130.43, 123.44, 115.81, 107.41, 68.78, 31.79, 29.30, 29.21, 29.03, 25.95, 22.65, 14.10. Anal. Calcd for $\text{C}_{28}\text{H}_{40}\text{O}_4\text{S}$: C, 71.15; H, 9.53. Found: C, 71.41; H, 9.67.

General Procedure for the Synthesis of 3,7-Dibromo-2,8-bis(alkoxy)dibenzothiophene-*S,S*-dioxide (5). To an ice bath cooled solution of 2,8-bis(alkoxy)dibenzothiophene-*S,S*-dioxide and a small amount of iodine in chloroform (200 mL) was added dropwise a solution of bromine in chloroform (60 mL) over 0.5 h. The mixture was stirred at room temperature for 6 h. An aqueous solution of Na_2SO_3 (10%, 100 mL) was added to quench the excess Br_2 . The organic layer was separated, and the aqueous one was extracted with CHCl_3 . The combined organic layers were washed with water, dried over with anhydrous MgSO_4 , and evaporated to dryness. The residue was recrystallized from a solvent mixture of dichloromethane and petroleum ether (2:1, v/v) to afford 5.

Synthesis of 3,7-Dibromo-2,8-bis(dodecyloxy)dibenzothiophene-*S,S*-dioxide (5a). 2,8-Bis(octyloxy)dibenzothiophene-*S,S*-dioxide (2.00 g, 3.42 mmol) and bromine (2.19 g, 13.68 mmol) were used. 5a was obtained as a colorless crystal in a yield of 81% (2.06 g). ^1H NMR (400 MHz, CDCl_3) δ : 7.85–7.84 (d, 2H), 7.01–6.99 (d, 2H), 4.15–4.12 (t, 4H), 1.95–1.88 (m, 4H), 1.60–1.52 (m, 4H), 1.41–1.27 (m, 32H), 0.90–0.87 (t, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ : 159.94, 131.89, 130.33, 126.63, 114.56, 104.49, 70.01, 31.94, 29.69, 29.66, 29.60, 29.55, 29.36, 29.33, 28.97, 26.03, 22.70, 14.11. Anal. Calcd for $\text{C}_{36}\text{H}_{54}\text{Br}_2\text{O}_4\text{S}$: C, 58.22; H, 7.33. Found: C, 58.43; H, 7.58.

Synthesis of 3,7-Dibromo-2,8-bis(2-ethylhexyloxy)dibenzothiophene-*S,S*-dioxide (5b). 2,8-Bis(2-ethylhexyloxy)dibenzothiophene-*S,S*-dioxide (6.00 g, 12.69 mmol) and bromine (8.12 g, 50.77 mmol) were used. 5b was obtained as a colorless crystal in a yield of 78% (6.24 g). ^1H NMR (400 MHz, CDCl_3) δ : 7.63 (s, 2H), 6.84 (s, 2H), 3.94–3.93 (d, 2H), 1.79–1.74 (m, 2H), 1.56–1.45 (m, 18H), 1.43–1.40 (t, 6H), 1.35–1.31 (t, 6H). ^{13}C NMR (100

MHz, CDCl_3) δ : 158.97, 130.82, 129.11, 125.43, 113.57, 103.43, 71.11, 38.45, 29.50, 28.14, 22.91, 21.97, 13.07, 10.32. Anal. Calcd for $\text{C}_{28}\text{H}_{38}\text{Br}_2\text{O}_4\text{S}$: C, 53.34; H, 6.08. Found: C, 52.97; H, 6.22.

Synthesis of 3,7-Dibromo-2,8-bis(octyloxy)dibenzothiophene-*S,S*-dioxide (5c). Bromine (20.29 g, 126.94 mmol) and 2,8-bis(octyloxy)dibenzothiophene-*S,S*-dioxide (15.00 g, 31.73 mmol) were used. 5c was obtained as a colorless crystal in a yield of 85% (17.01 g). ^1H NMR (400 MHz, CDCl_3) δ : 7.77 (s, 2H), 6.92 (s, 2H), 4.13–4.10 (t, 4H), 1.96–1.89 (m, 4H), 1.61–1.54 (m, 4H), 1.44–1.33 (m, 16H), 0.93–0.89 (t, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ : 159.82, 131.77, 129.96, 126.37, 114.43, 104.38, 69.89, 31.80, 29.29, 29.21, 28.93, 26.03, 22.68, 14.13. Anal. Calcd for $\text{C}_{28}\text{H}_{38}\text{Br}_2\text{O}_4\text{S}$: C, 53.34; H, 6.08. Found: C, 53.42; H, 5.78.

General Procedure for the Synthesis of 3,7-Dibromo-2,8-bis(alkoxy)dibenzothiophene (6). To an ice bath cooled suspension of LiAlH_4 in dry diethyl ether (100 mL) was added a solution of 2,7-dibromo-3,6-bis(alkoxy)dibenzothiophene-*S,S*-dioxide (5) in dry diethyl ether (200 mL). The mixture was stirred under a nitrogen atmosphere for 20 min at 0 °C. Ethyl acetate (50 mL) was added to quench the reaction, and the solvent was moved under reduced pressure. The residue was partitioned between chloroform 150 (mL) and dilute hydrochloric acid aqueous solution (100 mL, 0.01 M), the organic layer was separated, and the aqueous layer was extracted with chloroform (100 mL \times 3). The combined organic layers were washed with water (200 mL), dried over anhydrous MgSO_4 , and evaporated to dryness. The residue was purified by flash column chromatography on silica gel eluting with petroleum ether (60–90 °C) to afford the desired product 6.

Synthesis of 3,7-Dibromo-2,8-bis(dodecyloxy)dibenzothiophene (6a). 5a (1.8 g, 2.42 mmol) and LiAlH_4 (0.368 g, 9.69 mmol) were used, and 6a was obtained as a colorless solid (1.60 g, 93%). ^1H NMR (400 MHz, CDCl_3) δ : 7.85 (s, 2H), 7.35 (d, 2H), 4.08–4.04 (t, 4H), 1.88–1.81 (m, 4H), 1.52–1.46 (m, 4H), 1.33–1.19 (m, 32H), 0.82–0.79 (t, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ : 152.35, 134.02, 131.72, 125.77, 111.77, 103.81, 68.76, 30.91, 28.67, 28.64, 28.60, 28.58, 28.37, 28.34, 28.18, 25.07, 21.67, 13.09. Anal. Calcd for $\text{C}_{36}\text{H}_{54}\text{Br}_2\text{O}_2\text{S}$: C, 60.84; H, 7.66. Found: C, 61.02; H, 7.95.

Synthesis of 3,7-Dibromo-2,8-bis(2-ethylhexyloxy)dibenzothiophene (6b). 5b (4.00 g, 6.34 mmol) and LiAlH_4 (0.96 g, 25.38 mmol) were used, and 6b was obtained as a colorless solid (3.42 g, 90%). ^1H NMR (400 MHz, CDCl_3) δ : 7.95 (s, 2H), 7.46 (s, 2H), 4.07–4.05 (d, 4H), 1.89–1.85 (m, 2H), 1.67–1.56 (m, 18H), 1.54–1.51 (t, 6H), 1.49–1.45 (t, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ : 153.55, 135.06, 132.62, 126.79, 112.86, 104.53, 71.91, 39.57, 30.63, 29.19, 24.05, 23.06, 14.11, 11.29. Anal. Calcd for $\text{C}_{28}\text{H}_{38}\text{Br}_2\text{O}_2\text{S}$: C, 56.19; H, 6.40. Found: C, 56.42; H, 6.69.

Synthesis of 3,7-Dibromo-2,8-bis(octyloxy)dibenzothiophene (6c). 5c (10.00 g, 15.86 mmol) and LiAlH_4 (2.41 g, 63.44 mmol) were used, and 6c was obtained as a colorless solid (9.02 g, 95%). ^1H NMR (400 MHz, CDCl_3) δ : 7.87 (s, 1H), 7.38 (s, 1H), 4.10–4.06 (t, 4H), 1.88–1.81 (m, 4H), 1.53–1.46 (m, 4H), 1.36–1.18 (m, 16H), 0.84–0.81 (t, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ : 153.38, 135.05, 132.76, 126.81, 112.80, 104.87, 104.85, 69.79, 31.82, 29.69, 29.33, 29.24, 29.18, 26.08, 22.67, 14.10. Anal. Calcd for $\text{C}_{28}\text{H}_{38}\text{Br}_2\text{O}_2\text{S}$: C, 56.19; H, 6.40. Found: C, 56.33; H, 6.68.

General Procedure for the Synthesis of 3,7-Bis(thiophene-2-yl)-2,8-bis(alkoxy)dibenzothiophene (7). A mixture of 3,7-dibromo-2,8-bis(alkoxy)dibenzothiophene (6), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane, K_2CO_3 , toluene, water, and tetrabutylammonium bromide (TBAB) was carefully degassed before and after $\text{Pd}(\text{PPh}_3)_4$ was added. The reaction mixture was stirred at 120 °C under a nitrogen atmosphere for 3 days. The organic layer was separated, the aqueous one was extracted with CH_2Cl_2 , and the combined organic layers were dried over anhydrous MgSO_4 and evaporated to dryness. The residue was chromatographically purified on silica gel column eluting with CH_2Cl_2 /petroleum ether (60–90 °C) (1:10, v/v).

3,7-Bis(thiophene-2-yl)-2,8-bis(dodecyloxy)dibenzothiophene (7a). 3,7-Dibromo-2,8-bis(dodecyloxy)dibenzothiophene (6a) (5.00 g, 8.35 mmol), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane

(7.02 g, 33.42 mmol), K_2CO_3 (11.53 g, 83.55 mmol), toluene (150 mL), water (50 mL), TBAB (1.0 g, 3.1 mmol), and $Pd(PPh_3)_4$ (193.2 mg, 0.17 mmol) were used. **7a** was obtained as a yellow solid (5.80 g, 91%). 1H NMR (400 MHz, $CDCl_3$) δ : 7.98 (s, 2H), 7.59–7.53 (d, 2H), 7.46 (s, 2H), 7.31–7.29 (d, 2H), 7.06–7.04 (t, 2H), 4.17–1.14 (t, 4H), 1.93–1.90 (m, 4H), 1.54–1.48 (m, 4H), 1.46–1.20 (m, 32H), 0.83–0.79 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 152.48, 138.38, 134.13, 131.82, 125.73, 124.91, 124.68, 123.01, 120.97, 103.35, 68.47, 30.92, 28.68, 28.65, 28.61, 28.57, 28.43, 28.34, 25.33, 21.67, 13.08. Anal. Calcd for $C_{44}H_{60}O_2S_3$: C 73.69, H 8.43. Found: C 73.94, H 8.72.

3,7-Bis(thiophene-2-yl)-2,8-bis(2-ethylhexyloxy)-dibenzothiophene (7b). 3,7-Dibromo-2,8-bis(2-ethylhexyloxy)-dibenzothiophene (**6b**) (3.50 g, 5.85 mmol), 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-1,3,2-dioxaborolane (4.91 g, 23.40 mmol), K_2CO_3 (8.00 g, 57.97 mmol), toluene (50 mL), water (15 mL), TBAB (1.00 g, 3.10 mmol), and $Pd(PPh_3)_4$ (135 mg, 0.117 mmol) were used. **7b** was obtained as a yellow solid (3.15 g, 89%). 1H NMR (400 MHz, acetone- d_6) δ : 8.24 (s, 2H), 8.04 (s, 2H), 7.72–7.71 (d, 2H), 7.54–7.52 (d, 2H), 7.15–7.14 (t, 2H), 4.18–4.17 (d, 4H), 1.91–1.88 (m, 2H), 1.71–1.27 (m, 16H), 1.00–0.96 (t, 6H), 0.92–0.89 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 154.61, 139.93, 136.38, 133.44, 127.55, 127.03, 126.70, 124.74, 122.61, 105.84, 72.18, 40.52, 31.54, 24.88, 23.71, 14.36, 11.54. Anal. Calcd for $C_{36}H_{44}O_2S_3$: C 71.48, H 7.33. Found: C 71.17, H 7.63.

General Procedure for the Synthesis of 3,7-Bis(5-bromothiophene-2-yl)-2,8-bis(alkoxy)dibenzothiophene (8). A mixture of 3,7-bis(thiophene-2-yl)-2,8-bis(alkoxy)dibenzothiophene (**7**), *N*-bromosuccinimide (NBS), chloroform, and acetic acid was stirred at room temperature in dark for 24 h. The reaction mixture was partitioned between aqueous $NaHCO_3$ solution (0.5 M) and chloroform, the organic layer was separated, and the aqueous layer was extracted with chloroform for several times. The combined organic layers were washed with aqueous $NaHCO_3$ solution for several times, dried over anhydrous $MgSO_4$, and evaporated to dryness. The residue was chromatographically purified on silica gel column eluting with CH_2Cl_2 /petroleum ether (1:10, v/v) to afford compound **8**.

3,7-Bis(5-bromothiophene-2-yl)-2,8-bis(dodecyloxy)-dibenzothiophene (8a). 3,7-Bis(thiophene-2-yl)-2,8-bis(dodecyloxy)-dibenzothiophene (**7a**) (5.00 g, 6.56 mmol), NBS (4.82 g, 16.94 mmol), chloroform (150 mL), and acetic acid (30 mL) were used. **8a** was obtained as a yellow solid (5.36 g, 85%). 1H NMR (400 MHz, $CDCl_3$) δ : 7.91 (s, 2H), 7.42 (s, 2H), 7.26–7.25 (d, 2H), 7.00–6.99 (d, 2H), 4.17–4.14 (t, 4H), 1.96–1.89 (m, 4H), 1.56–1.50 (m, 4H), 1.48–1.20 (m, 32H), 0.83–0.81 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 152.93, 140.41, 135.14, 132.75, 129.26, 124.85, 123.08, 120.63, 113.33, 103.93, 69.51, 31.95, 29.73, 29.69, 29.67, 29.62, 29.49, 29.39, 29.24, 26.36, 22.71, 14.14. Anal. Calcd for $C_{44}H_{58}Br_2O_2S_3$: C 60.40, H 6.68. Found: C 60.64, H 6.93.

3,7-Bis(5-bromothiophene-2-yl)-2,8-bis(2-ethylhexyloxy)-dibenzothiophene (8b). 3,7-Bis(thiophene-2-yl)-2,8-bis(2-ethylhexyloxy)dibenzothiophene (**7b**) (517 mg, 0.85 mmol), NBS (312 mg, 1.75 mmol), chloroform (50 mL), and acetic acid (5 mL) were used. **8c** was obtained as a yellow solid (554 mg, 85%). 1H NMR (400 MHz, $CDCl_3$) δ : 7.89 (s, 2H), 7.43 (s, 2H), 7.23–7.22 (d, 2H), 6.99–6.98 (d, 2H), 4.06–4.04 (d, 4H), 1.91–1.85 (m, 2H), 1.61–1.45 (m, 16H), 1.36–1.34 (t, 6H), 1.33–1.31 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 153.42, 139. Anal. Calcd for $C_{36}H_{42}Br_2O_2S_3$: C 56.69, H 5.55. Found: C 56.93, H 5.87.

Synthesis of 2,8-Bis(octyloxy)dibenzothiophene-3,7-diboronic Acid (9). To a solution of **6c** (12.0 g, 20.1 mmol) in dry diethyl ether (150 mL) was added dropwise *n*-BuLi (20.05 mL, 2.5 M in hexane, 50.13 mmol) at $-78^\circ C$ under a nitrogen atmosphere. The mixture was stirred at $-78^\circ C$ for 30 min, allowed to warm to room temperature (rt) gradually, and then stirred at rt for a further 50 min. The solution was then cooled down to $-78^\circ C$ again, triisopropyl borate (13.97 mL, 60.16 mmol) was added rapidly, and the resulted mixture was stirred overnight and allowed to warm to rt gradually. The mixture was partitioned between aqueous dilute hydrochloric acid and diethyl ether, the organic layer was separated, and the aqueous layer was extracted with diethyl ether (200 mL \times 3). The organic layer was

washed with brine, dried over anhydrous $MgSO_4$, and evaporated to dryness under reduced pressure. The residue was recrystallized from acetone to afford **9** as a colorless solid (7.63 g, 72%). 1H NMR (400 MHz, DMSO) δ : 8.06 (s, 2H), 8.00 (s, 2H), 7.87 (m, 4H), 4.22–4.19 (t, 4H), 1.88–1.81 (m, 4H), 1.52–1.45 (m, 4H), 1.37–1.28 (m, 16H), 0.88–0.87 (t, 6H). ^{13}C NMR (100 MHz, DMSO) δ : 160.67, 137.82, 131.75, 129.44, 104.59, 68.30, 31.18, 28.72, 28.66, 28.63, 25.58, 22.05, 13.89. Anal. Calcd for $C_{28}H_{42}B_2O_6S$: C 63.65, H 8.01. Found: C 63.95, H 8.92.

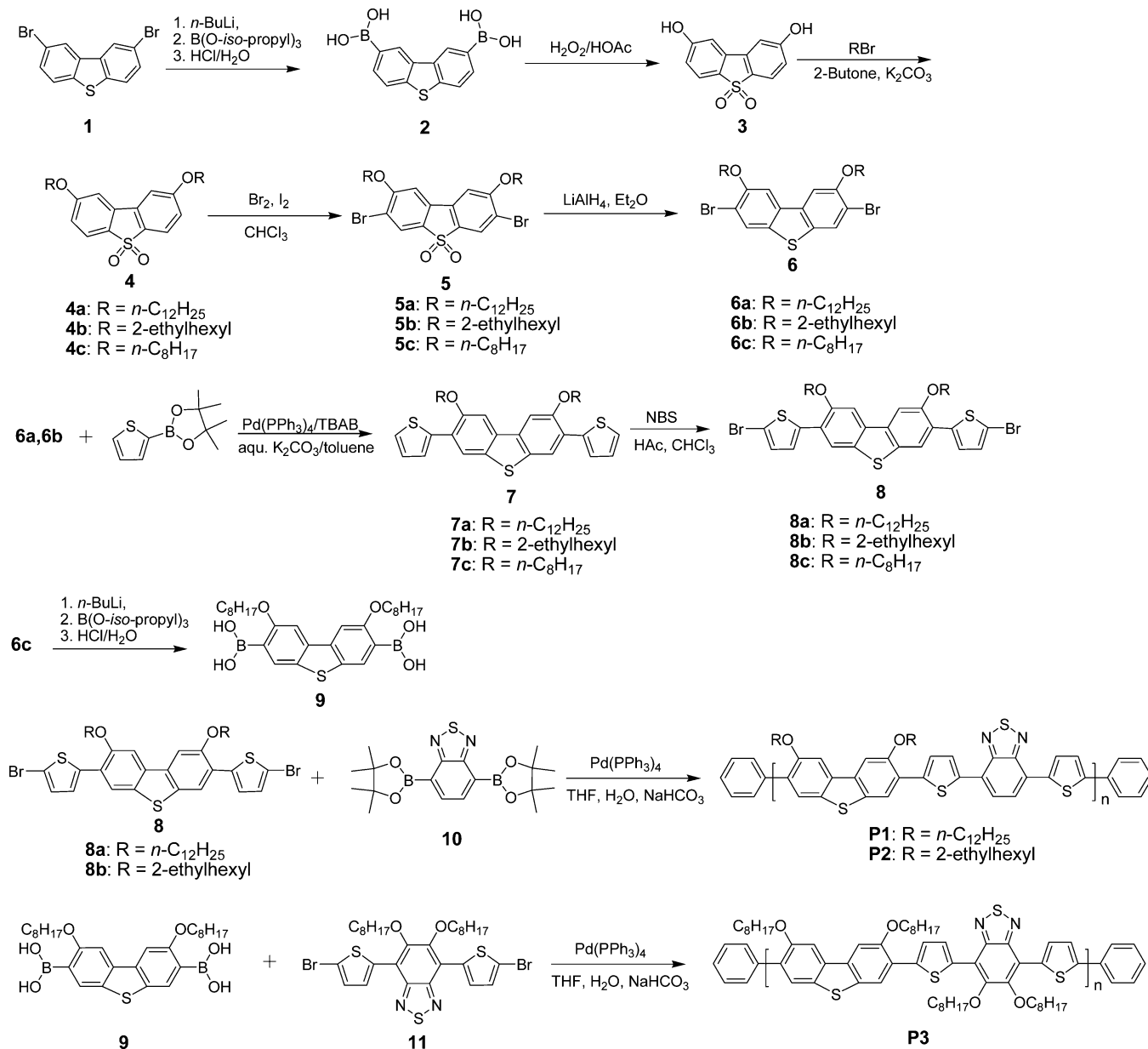
General Procedure for the Synthesis of 3,7-Linked 2,8-Bis(alkoxy)dibenzothiophene-Containing Conjugated Polymers (P1, P2, and P3). A mixture of dibromide monomer **8**, 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*c*][1,2,5]-thiadiazole (**10**), THF, toluene, H_2O , and $NaHCO_3$ was carefully degassed before and after $Pd(PPh_3)_4$ was added. The mixture was stirred and refluxed under nitrogen for 3 days. Phenylboronic acid and $Pd(PPh_3)_4$ were added and refluxed for 4 h; after that bromobenzene was added, and the mixture was refluxed overnight to complete the end-capping reaction. After being cooled to room temperature, water and chlorobenzene were added, and the organic layer was separated and washed three times with water. And then, the solution was heated to $100^\circ C$ to dissolve the polymers and filtered. After the removal of most solvent, the residue was poured into a large amount of acetone, and the resulting precipitates were collected by filtration and washed with acetone. The crude product was redissolved in a minimum amount of chlorobenzene and precipitated into a large amount of acetone. The formed precipitates were collected by filtration and dried under high vacuum.

Poly[3,7-(2,8-bis(dodecyloxy)dibenzothiophene-*alt*-5',5"-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole] (P1). **8a** (114 mg, 0.13 mmol), **10** (51 mg, 0.13 mmol), THF (10 mL), toluene (10 mL), H_2O (2 mL), $NaHCO_3$ (0.2 g, 2.4 mmol), and $Pd(PPh_3)_4$ (3 mg, 2.6 μ mol) were used for Suzuki polycondensation. Phenylboronic acid (20 mg, 0.16 mmol), $Pd(PPh_3)_4$ (3.03 mg, 2.6 μ mol), and bromobenzene (20 μ L, 1.91 mmol) were used for the end-capping reaction. **P1** was obtained as a dark red solid in a yield of 47% (52 mg). Since **P1** has poor solubility in $CHCl_3$ or chlorobenzene (CB) at room temperature, ^{13}C NMR is difficult to obtain. 1H NMR (400 MHz, C_6D_6) δ : 8.42 (br, 2H), 8.30 (br, 2H), 7.80 (br, 2H), 7.75 (br, 2H), 7.74 (br, 2H), 4.08 (br, 4H), 2.04 (br, 4H), 1.70 (br, 4H), 1.38 (br, 32H), 1.03–1.00 (br, 6H). Anal. Calcd for $C_{50}H_{62}N_2O_2S_4$: C 70.54, H 7.34, N 3.29. Found: C 71.27, H 7.53, N 2.82. GPC (PS standards): $M_w = 6.4$ kg/mol, $M_n = 4.7$ kg/mol, PDI = 1.4.

Poly[3,7-(2,8-bis(2-ethylhexyloxy)dibenzothiophene-*alt*-5',5"-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole] (P2). **8b** (200 mg, 0.26 mmol), **10** (102 mg, 0.26 mmol), THF (10 mL), toluene (10 mL), H_2O (2 mL), $NaHCO_3$ (0.3 g, 3.57 mmol), and $Pd(PPh_3)_4$ (6 mg, 5.2 μ mol) were used for Suzuki polycondensation. Phenylboronic acid (20 mg, 0.16 mmol), $Pd(PPh_3)_4$ (6 mg, 5.2 μ mol), and bromobenzene (20 μ L, 1.91 mmol) were used for the end-capping reaction. **P2** was obtained as a dark red solid in a yield of 63% (122 mg). 1H NMR (400 MHz, C_6D_6) δ : 8.51 (br, 2H), 8.17 (br, 2H), 8.08 (br, 2H), 7.92 (br, 2H), 7.60 (br, 2H), 4.53 (br, 4H), 2.25–1.82 (br, 2H), 1.66–1.55 (br, 16H), 1.31–1.29 (br, 6H), 1.23–1.13 (br, 6H). ^{13}C NMR (100 MHz, C_6D_6) δ : 154.14, 153.02, 139.81, 134.84, 134.15, 126.17, 125.96, 104.38, 71.87, 40.08, 31.07, 29.59, 29.39, 24.51, 24.35, 23.43, 23.29, 14.33, 11.54, 11.38, 1.24. Anal. Calcd for $C_{42}H_{46}N_2O_2S_4$: C 68.25, H 6.27, N 3.79. Found: C 68.83, H 6.45, N 3.27. GPC (PS standards): $M_w = 16.3$ kg/mol, $M_n = 14.6$ kg/mol, PDI = 1.2.

Poly[3,7-(2,8-bis(octyloxy)dibenzothiophene-*alt*-5',5"-di(thiophen-2-yl)-5,6-bis(octyloxy)benzo[*c*][1,2,5]thiadiazole] (P3). A mixture of **9** (471 mg, 0.89 mmol) and 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(octyloxy)benzo[*c*][1,2,5]thiadiazole (**11**) (637 mg, 0.89 mmol), THF (30 mL), H_2O (6 mL), and $NaHCO_3$ (1.50 g, 17.83 mmol) was carefully degassed before and after $Pd(PPh_3)_4$ (20.6 mg, 17.83 μ mol) was added. The mixture was stirred and refluxed under nitrogen for 3 days. Phenylboronic acid (50 mg, 0.41 mmol) and $Pd(PPh_3)_4$ (20.6 mg, 17.83 μ mol) were added and refluxed for 4 h; after that bromobenzene (500 μ L, 47.76 mmol) was added, and the mixture was refluxed overnight to complete the end-capping reaction.

Scheme 1. Synthesis of Monomers and Copolymers



After being cooled to room temperature, water and chlorobenzene were added, and the organic layer was separated and washed three times with water. And then, the solution was heated to 100 °C to dissolve the polymers and filtered. After the removal of most solvent, the residue was poured into a large amount of acetone, and the resulting precipitates were collected by filtration and washed with acetone. The crude product was redissolved in a minimum amount of chlorobenzene and precipitated into a large amount of acetone. The formed precipitates were collected by filtration and dried in high vacuum. **P3** was obtained as a dark red solid in a yield of 86% (762 mg). ^1H NMR (400 MHz, C_6D_6) δ : 8.96 (br, 2H), 8.45 (br, 2H), 8.09 (br, 2H), 7.94 (br, 2H), 4.46 (br, 8H), 2.29–2.20 (br, 8H), 1.76–1.69 (br, 8H), 1.54–1.41 (br, 32H), 1.04–1.02 (br, 12H). ^{13}C NMR (100 MHz, C_6D_6) δ : 154.10, 152.09, 151.33, 141.58, 135.66, 135.03, 134.80, 126.16, 124.40, 121.87, 117.93, 104.64, 69.54, 32.20, 32.16, 31.00, 30.07, 29.84, 29.79, 29.67, 26.65, 26.53, 23.02, 14.33, 1.24, 1.19. Anal. Calcd for $\text{C}_{58}\text{H}_{78}\text{N}_2\text{O}_4\text{S}_4$: C 69.98, H 7.90, N 2.81. Found: C 69.10, H 7.97, N 2.08. GPC (PS standards): M_w = 86.6 kg/mol, M_n = 27.7 kg/mol, PDI = 3.1.

RESULTS AND DISCUSSION

Material Synthesis and Characterization. The syntheses of the monomers and polymers are outlined in Scheme 1. 2,8-Dibromodibenzothiophene was reacted with $n\text{-BuLi}$ at -78 °C followed by quenching the anions with triisopropyl borate to afford the crude dibenzothiophene-2,8-diboronic acid (**2**), which was used for the next step without further purification. The oxidation of **2** with H_2O_2 in acetic acid afforded 2,8-dihydroxydibenzothiophene-S-dioxide (**3**) in a total yield of 92%. Williamson etherification with alkyl bromides and K_2CO_3 in butanone afforded 2,8-bis(alkoxy)dibenzothiophene-S,S-dioxides (**4a–c**) in yields of 76–92%. Bromination of **4a–c** with bromine in chloroform at room temperature furnished 3,7-dibromo-2,8-bis(alkoxy)dibenzothiophene-S,S-dioxides (**5a–c**) in yields of 78–85%. The reduction of **5a–c** with LiAlH_4 in diethyl ether at 0 °C afforded 3,7-dibromo-2,8-bis(alkoxy)-dibenzothiophene (**6a–c**) in yields of 90–95%. Suzuki cross-coupling of **6a–c** and 4,4,5,5-tetramethyl-2-(thiophen-2-yl)-

Table 1. Physical, Electronic, and Optical Properties of P1, P2, and P3

polymer	M_n^a (kg/mol)	M_w (kg/mol) ^a	PDI	T_g^b (°C)	λ_{\max} [nm] solution	λ_{\max} [nm] film	$E_{g,opt}^c$ (eV)	HOMO (eV)	LUMO (eV)
P1	4.7	6.4	1.4	383	401, 530	408, 566	1.80	−5.23	−3.43
P2	14.6	16.3	1.2	391	400, 529	414, 567	1.79	−5.29	−3.50
P3	27.7	86.6	3.1	324	401, 532	402, 560	1.98	−5.34	−3.37

^a M_n and PDI of the polymers were determined by GPC using polystyrene standards at 150 °C with 1,2,4-trichlorobenzene as an eluent.

^bDecomposition temperature determined by TGA in N₂ based on 5% weight loss. ^cCalculated from the absorption band edge of the copolymer film, $E_{g,opt} = 1240/\lambda_{edge}$.

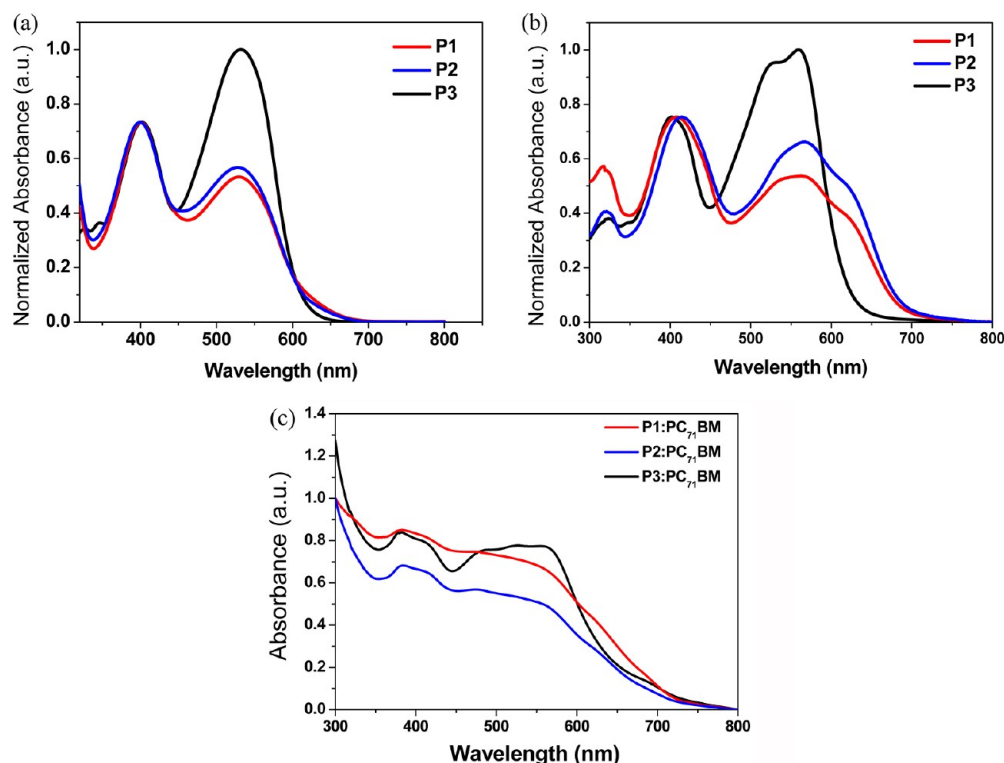


Figure 1. UV-vis absorption spectra of P1–3 in CB solution (a) and in film (b) and P1–3/PC₇₁BM blending film (1:3 by weight) (c).

1,3,2-dioxaborolane was carried out in a biphasic mixture of aqueous K₂CO₃ and toluene with Pd(PPh₃)₄ as the catalyst precursor and tetrabutylammonium bromide as the phase transfer catalyst to afford 3,7-bis(thiophene-2-yl)-2,8-bis-(alkoxy)dibenzothiophene (7a–c) in yields of 89–91%. Bromination of 7a–c with NBS in a solvent mixture of chloroform and acetic acid at room temperature afforded the desired dibromide monomers (8a–c) in yields 85–89%. 2,8-Bis(alkoxy)dibenzothiophene containing conjugated polymers P1 and P2 were synthesized as dark red solids in yields of 47 and 63%, respectively, by Suzuki polymerization of dibromide monomers 8a and 8b with diboronate ester monomer 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[c]-[1,2,5]thiadiazole (10) in a biphasic mixture of toluene/aqueous NaHCO₃ with freshly prepared Pd(PPh₃)₄ as the catalyst precursor. After the polymerization, phenylboronic acid and bromobenzene were added successively in an interval of 4 h to cap the end groups. Low yields for the polymerization are probably due to the formation of dark red precipitates during the polymerization, which cannot be fully dissolved even in chlorobenzene. It is worth noting that the obtained P1–2 are soluble in chlorobenzene (CB), 1,2-dichlorobenzene (DCB), and 1,2,4-trichlorobenzene at elevated temperature. The molecular weight and molecular weight distribution of P1–2 were determined by gel permeation chromatography (GPC) at

150 °C using 1,2,4-trichlorobenzene as an eluent calibrated with polystyrene standards and are summarized in Table 1. It should be noted that polymers P1–2 only carry two flexible alkyl chains on the dibenzothiophene at each repeating unit. To increase the molecular weight and solubility, conjugated polymer P3 carrying four alkyl chains at each repeating unit was designed and synthesized. Miyaura reaction of 4,7-dibromo-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole with bis-(pinacolato)diboron is failed to afford the desired 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole. Therefore an alternative synthetic route was adopted to synthesize polymer P3 as shown in Scheme 1. 3,7-Dibromo-2,8-bis(octyloxy)dibenzothiophene (6d) was converted to the corresponding 2,8-bis(octyloxy)-dibenzothiophene-3,7-diboronic acid (9) by treatment with *n*-Buli at −78 °C and followed by quenching the formed anions with triisopropyl borate. P3 was synthesized as a dark red solid in a yield of 86% by Suzuki polycondensation of diboronic acid 9 and 4,7-bis(5-bromothiophen-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]thiadiazole (11). As expected, polymer P3 had higher molecular weight, and it was soluble in organic solvents such as chloroform, CB, and DCB. As shown in Table 1, P3 showed a number-average molecular weight (M_n) of 27.7 kg/mol, a weight-average molecular weight (M_w) of 86.6 kg/mol, and a polydispersity index (PDI) of 3.1. Thermogravimetric analysis

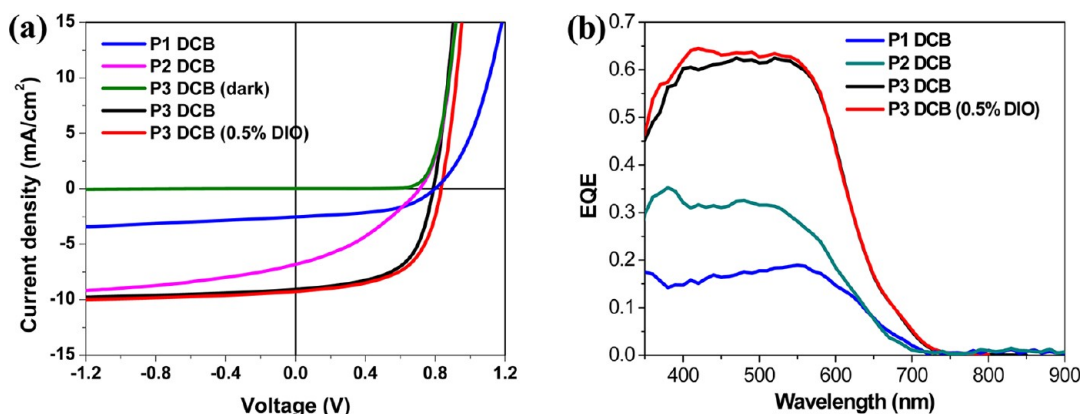


Figure 2. (a) J - V curves for the BHJ solar cells derived from the blend of polymer:PC₇₁BM (1:3, by weight) and (b) EQE curves for the BHJ solar cells derived from the blend of polymer:PC₇₁BM (1:3, by weight).¹⁹

(TGA) indicated that **P1**–**3** have good thermal stability with the decomposition temperature up to 300 °C under a nitrogen atmosphere. Differential scanning calorimetry (DSC) revealed that there is no obvious glass transition for **P1**–**3**. Hole mobility of narrow band gap conjugated polymers is closely related to their packing in the solid state. Therefore, X-ray diffractions (XRD) of powdery samples of **P1**–**3** were measured. As shown in Figure S1 (see Supporting Information), all polymers exhibit two diffraction peaks: the first peak at small-angle region reflecting the distance between polymer backbones separated by alkyl side chains and the peak at wide-angle region reflecting the π - π distance between the polymer backbones. The distances between polymer backbones separated by alkyl chains are 22.09 Å for **P1**, 18.82 Å for **P2**, and 18.58 Å for **P3**. The π - π distances between the polymer backbones are 4.29 Å for **P1**, 4.62 Å for **P2**, and 4.20 Å for **P3**. Such short distances indicate that the polymer backbones are of a relatively planar conformation and can be closely stacking in the solid state.¹⁵

Optical and Electrochemical Properties. The UV–vis absorption spectra of polymers **P1**–**3** in dilute CB solutions and as thin films at 25 °C are shown in Figure 1, and the data are also summarized in Table 1. In dilute CB solutions, **P1** and **P2** displayed a broad absorption with two peaks located at about 401 and 530 nm, respectively. As shown in Table S1 (see Supporting Information), molar extinction coefficient values of **P1** and **P2** in solutions at 530 nm are 6.02×10^4 and 5.04×10^4 M⁻¹ cm⁻¹, respectively. The molar absorption coefficient of the high-energy peak is larger than the low-energy one. Different from **P1** and **P2**, **P3** in dilute CB solution exhibited a weak absorption peak at 401 nm and an intense absorption peak at 532 nm. The molar extinction coefficient of **P3** in solution at 530 nm is 9.94×10^4 M⁻¹ cm⁻¹, and the data are also summarized in Table S1. It is worthy noting that the molar absorption coefficient of the high-energy peak is smaller than the low-energy one. On going from solution to film, the absorption spectra of all polymers became broader and red-shifted as shown in Figure 1b. Especially, the absorption of **P1** and **P2** in films is much broader than that of **P3**. The absorption onsets of **P1**, **P2**, and **P3** in films are 690, 694, and 627 nm, respectively. The optical band gaps ($E_{g, \text{opt}}$) of **P1**, **P2**, and **P3** in films were therefore calculated to be 1.80, 1.79, and 1.98 eV, respectively. The band gap of **P3** is larger than that of **P1** and **P2** mainly because of the electronic effect. Unsubstituted benzothiadiazole is a strong acceptor unit; the

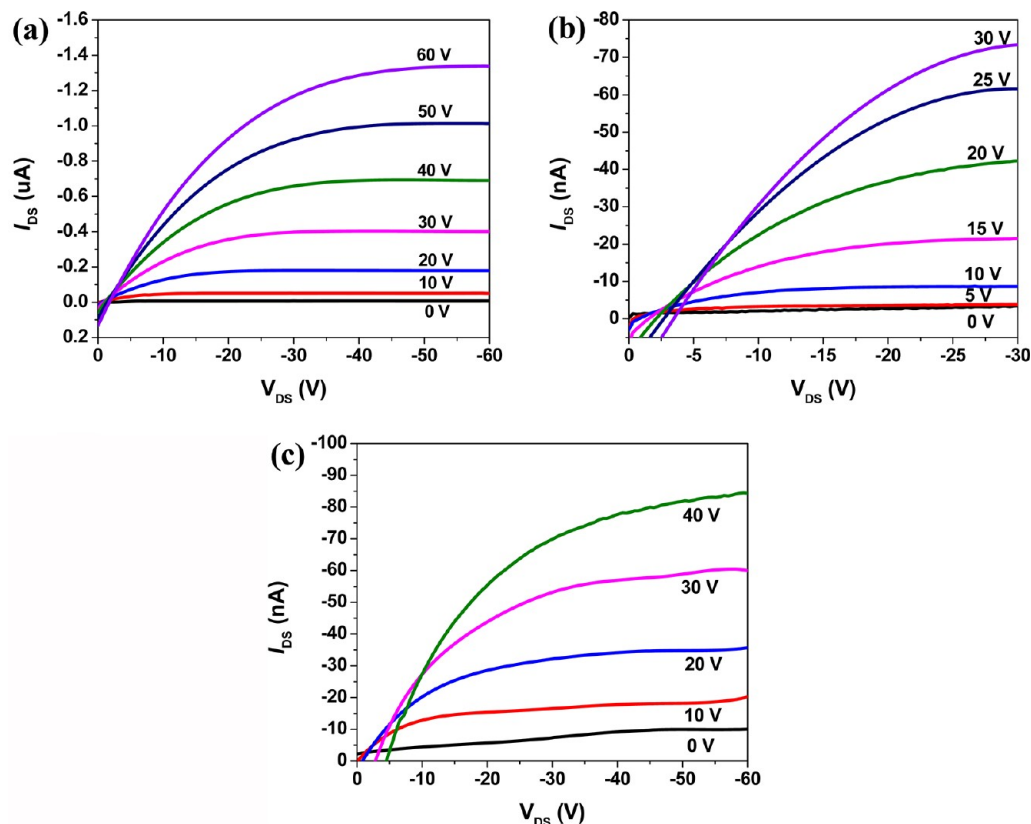
attaching two electron-donating alkoxy chains on the benzothiadiazole ring will weaken its electron withdrawing ability, and as a result the low-energy absorption peak of **P3** in solution should be blue-shifted in comparison with that of **P1** and **P2**, namely, in solution the optical band gaps of **P1** and **P2** should be narrower than that of **P3**. However, the S–O electronic interaction of **P3** will lead to a planarization of the polymer backbone,¹⁶ and as a result, the absorption spectrum of **P3** will red-shift and the optical band gap of **P3** in solution will decrease. Considering these two effects, the optical band gaps of **P1**, **P2**, and **P3** in solutions happen to be almost the same as shown Figure 1a. On going from solution to film, the polymer backbone of **P1** and **P2** could become more planar due to the π - π stacking, resulting in a drastic decreasing of their optical band gap. For **P3**, due to the S–O interaction, the polymer backbone is probably already of a more planar structure in solution. On going from solution to film, the packing of polymer chains cannot cause a significant decreasing of the optical band gap. Therefore, in films the band gap of **P3** should be higher than that of **P1** and **P2**. The HOMO energy level was determined by cyclic voltammogram according to the equation $E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.71)$ (eV) and the LUMO energy level was calculated by the equation $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{g, \text{opt}}$.¹⁷ HOMO and LUMO energy levels were therefore determined to be -5.23 and -3.43 eV for **P1**, -5.29 and -3.50 eV for **P2**, and -5.34 and -3.37 eV for **P3**. The data are summarized in Table 1. Considering the LUMO level of PCBM is -4.2 eV, the offsets between donor polymers **P1**–**3** and the acceptor PCBM are in the range of 0.7–0.9 eV,^{2f,4a,18} which should provide an enough driving force for efficient exciton dissociation. As shown in Figure 1c, the **P1**–**3**/PC₇₁BM (1:3 by weight) blend films demonstrate a broad absorption in the range of 300–700 nm.

Photovoltaic Properties. Devices used for the evaluation the photovoltaic performances of polymers were fabricated with a device configuration of ITO/PEDOT:PSS/Polymer:PC₇₁BM/LiF/Al. The thickness of PEDOT:PSS layer, LiF layer, and Al electrode is about 40, 0.6, and 100 nm, respectively. The photovoltaic properties of **P1**–**3** were screened by blending **P1**–**3** and PC₇₁BM in DCB in different weight ratios, different concentration, and different spin-coating speeds with or without 1,8-diiodooctane (DIO) as a processing additive. After the optimization, solar cells fabricated with the blends of polymer and PC₇₁BM in a weight ratio of 1:3 and with DCB as the processing solvent gave the best performance. The typical

Table 2. Photovoltaic Parameters of PSCs Based on P1–3 as Donor and PC₇₁BM as Acceptor with a Weight Ratio of 1:3 under the Illumination of AM1.5G, 100 mW/cm²

active layer	solvent	thickness (nm)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE (%) (max)	PCE (%) (av)	μ _{hole} ^b (cm ² V ⁻¹ s ⁻¹)
P1:PC ₇₁ BM	DCB	92	0.79	2.60	0.51	1.02	0.99	1.3 × 10 ⁻⁴
P2:PC ₇₁ BM	DCB	95	0.72	6.80	0.35	1.71	1.69	2.7 × 10 ⁻⁴
P3:PC ₇₁ BM	DCB	84	0.79	9.07	0.59	4.19		2.3 × 10 ⁻³
P3:PC ₇₁ BM	DCB ^a	80	0.83	9.30	0.58	4.48	4.32	

^a0.5% DIO additive (v/v). ^bMeasured by using the organic field-effect transistor (OFET) method.

**Figure 3.** Output curves at different gate voltages (V_G) for OFETs using spin-coated P1 (a), P2 (b), and P3 (c) on OTS-treated Si/SiO₂ substrate.

current density–voltage (J – V) curves of photovoltaic cells with the blends of P1–3/PC₇₁BM (1:3, by weight) as the active layer under 1 sun of simulated AM 1.5G solar radiation (100 mW/cm²) are shown in Figure 2. The device results of each polymer-based solar cells are summarized in Table 2. The film spin-coated from P1:PC₇₁BM (1:3, by weight) in DCB solution show extremely rough surface with visible particles, which might be due to the poor solubility of P1 in DCB solution. Therefore, the device fabricated from P1:PC₇₁BM (1:3, by weight) in DCB solution provided unsatisfactory result. PCE of 1.02% with a V_{oc} of 0.79 V, a J_{sc} of 2.60 mA/cm², and an FF of 0.51 was achieved for P1-based solar cells. For P2, the incorporation of branched side chains endowed the polymer with better solubility in solutions than P1, the photovoltaic performance was enhanced a little with PCE of 1.71% with a V_{oc} of 0.72 V, a J_{sc} of 6.80 mA/cm², and an FF of 0.35 by the device fabricated from P2:PC₇₁BM (1:3, by weight) in DCB solution. It is worth mentioning that P3-based devices exhibited higher PCE of 4.19% with a V_{oc} of 0.79 V, a J_{sc} of 9.07 mA/cm², and an FF of 0.59. Significantly, with the addition of DIO as the additive into the processing solvent, the PCE of P3 based on solar cells could be further increased to 4.48% with a V_{oc} of 0.83

V, a J_{sc} of 9.30 mA/cm², and an FF of 0.58. The best photovoltaic performance for P3:PC₇₁BM (1:3, by weight) was achieved with DCB as the processing solvent, the concentration of the blend 30 mg/mL, and DIO (0.5 vol%) as the additive. However, for P1 and P2, the use of additive (DIO or 1-chloronaphthalene) did not show any positive effect on their photovoltaic performances. Obviously, higher J_{sc} for P3-based solar cells accounts for the better photovoltaic performance than P1 and P2. J_{sc} can be improved mainly from the increased light absorption, the good hole mobility of polymer for charge transfer, and optimal film nanoscale morphology for charge separation and transport. Since the molecular weight of donor polymers can significantly influence the performance of polymer solar cells, usually the high molecular weight sample gives better photovoltaic performance than the low molecular weight sample. To elucidate the influence of molecular weight on polymer solar cell device performance, we use low molecular weight sample of P2 to fabricate devices. The low molecular weight P3 has an M_n of 6060 g/mol, an M_w of 8300 g/mol, and a PDI of 1.4. Using the same device fabrication conditions like high molecular weight P3, the low molecular weight P3-based devices give a worse performance with a PCE of 3.1%, which is

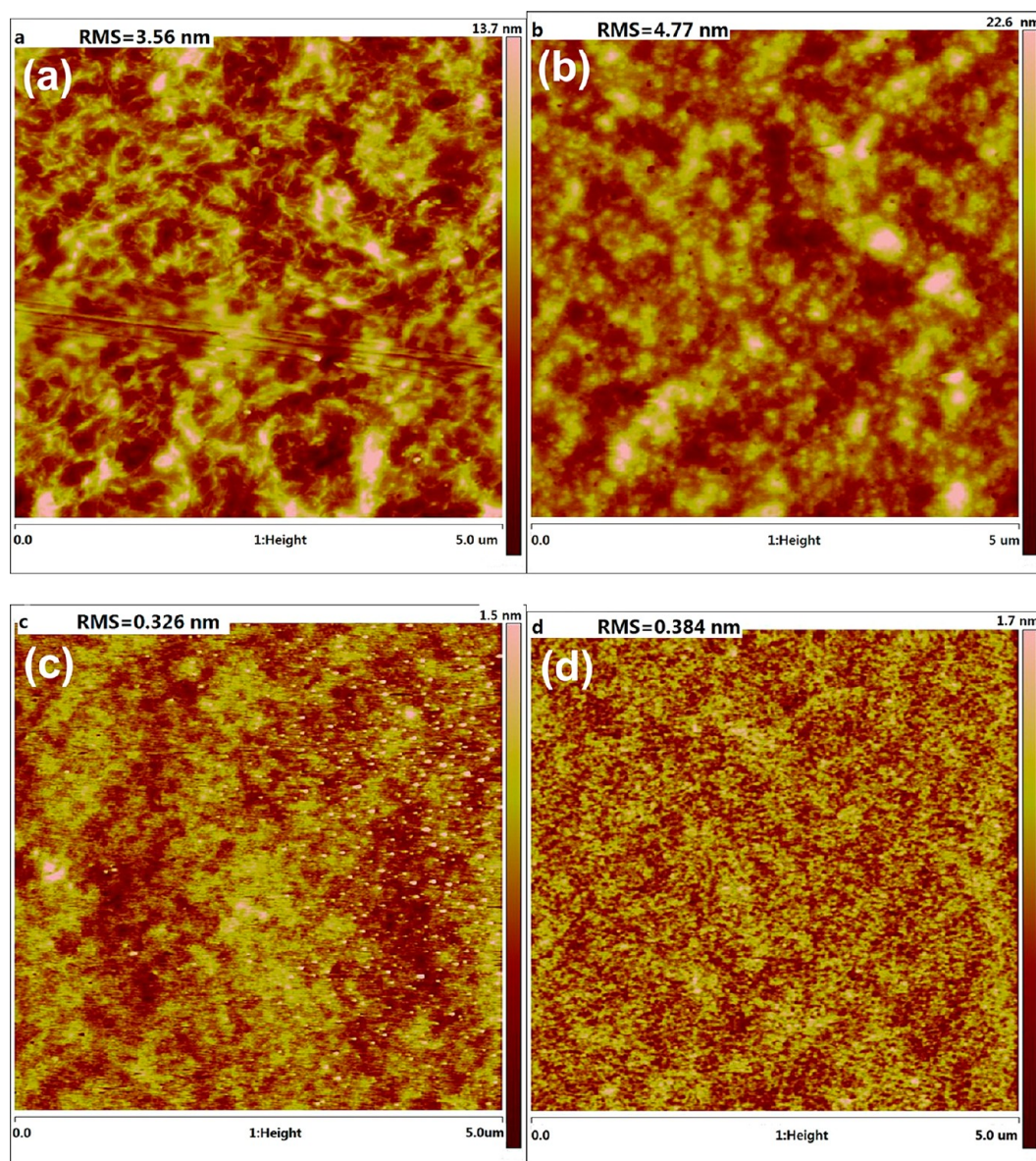


Figure 4. AFM images ($5 \times 5 \mu\text{m}^2$) of the blends of polymer:PC₇₁BM (1:3, by weight) spin-cast from DCB solutions: (a) **P1**, (b) **P2**, (c) **P3**, and (d) **P3** (containing 0.5% DIO in volume).

still markedly higher than that of **P2**. This result demonstrates that both the chemical structure and the molecular weight can influence on the performance of the polymers. Obviously, higher J_{sc} for **P3** was attributed, at least partially, to the intenser absorption in the visible region, the higher hole mobility, and the better nanoscale film morphology of its active layer. The above results demonstrate that the photovoltaic performance can be improved by fine-tuning the conjugated polymer structure. Additionally, the theoretical V_{oc} was estimated according to the formula $V_{\text{oc}} = (|E_{\text{donor}}^{\text{HOMO}}| - |E_{\text{PCBM}}^{\text{LUMO}}|)/e - 0.3 \text{ V}^{2f}$ to be 0.73, 0.79, and 0.84 V for **P1**, **P2**, and **P3**-based polymer solar cells, respectively, which are roughly consistent with measured values as shown in Table 2.

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 under illumination of monochromatic light. As shown in Figure 3, a significant and broader photo-to-current response from 300 to 700 nm than the

corresponding absorption spectra (Figure 2b) can be observed for each polymer-based solar cell, which indicates PC₇₁BM compensates for the absorption valley of the polymers and the contribution from PC₇₁BM to the photocurrent is very pronounced. The EQE value of the devices for **P3**-based PSCs reached above 50% from nearly the entire visible range of 350–600 nm. Especially, the device for **P3**-based PSCs with the addition of DIO (0.5 vol %) exhibited the maximum EQE of 65% at 418 nm. Significantly, 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.

Transport Properties. The transport properties of the 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 $I_{\text{SD}} = (W/2L)C_i\mu(V_{\text{G}} - V_{\text{T}})^2$ where W is the channel width, L is the channel length, C_i is the

capacitance per unit area of the gate dielectric layer (SiO_2 , 500 nm, $C_i = 7.5 \text{ nF/cm}^2$), and V_T is the threshold voltage. The output and transfer characteristic curves of the spin-coated film of **P1**, **P2**, and **P3** on OTS-treated Si/SiO_2 substrates are shown in Figure 3. The hole mobilities of **P1** and **P2** film spin-cast from DCB solution by annealing at 110°C for 3 min are 1.3×10^{-4} and $2.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. Significantly, the hole mobility of the film spin-cast from the blend of **P3** showed better charge transfer ability with the hole mobility of $2.3 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ without further device optimization. The higher hole mobility is attributed to the stronger intermolecular interactions between the planar polymer chains that can bring the polymer chain into close proximity as evidenced by the XRD results. The side chains on the benzothiadiazole ring will not generate steric hindrance, since the electrostatic attraction between ether oxygens and thienyl sulfur atoms of **P3** will enhance planarization.¹⁶ Closer distance between the polymer chains can facilitate charge hopping in the polymer.²⁰ Obviously, the hole mobility of the film spin-cast from the blend of **P3** exhibited 1 order of magnitude higher than **P1** and **P2**. Such high mobility is beneficial for charge transfer in the resulting PSCs. The mobility data are summarized in Table 2. The transport properties indicate **P3** is a promising material for solar cell applications.

Film Morphologies. The morphology of the blend film is crucial for the photovoltaic performance, which largely affects the charge separation and transport. Therefore, the morphologies of polymer/ PC_{71}BM blend films spin-coated from DCB solutions were investigated by atomic force microscopy (AFM) using tapping mode. AFM height images of the blend films of **P1–3**: PC_{71}BM (1:3, by weight) are shown in Figure 4. The **P1**: PC_{71}BM (1:3, by weight) and **P2**: PC_{71}BM (1:3, by weight) blend films spin-coated from DCB solutions showed rough surfaces with larger domain size of several hundred nanometers and the root-mean-square (rms) of 3.56 nm for **P1** and 4.77 nm for **P2**. An interpenetrating bicontinuous network between polymer and PCBM with an ideal domain size of 10–20 nm is desirable for high-performance PSCs.²¹ Such large phase separation for **P1**- and **P2**-based blend films increases the distance to the nearest interface, leading to a lower photocurrent. The blend films of **P3**: PC_{71}BM (1:3, by weight) from DCB show very smooth surfaces which are strikingly different from that of **P1** and **P2**. No large domain was observed, indicating no obvious phase separation occurs.²² The root-mean-square (rms) roughness for the **P3**: PC_{71}BM (1:3, by weight) blend films are 0.326 nm, which is lower than **P1** or **P2**: PC_{71}BM (1:3, by weight) blend films. With the addition of DIO (0.5 vol %), AFM images still exhibited uniform and finer nanostructures and rms has been increased a little to 0.384 nm as shown in Figure 3d. Neither larger nor smaller phase separation is favorable for efficient charge separation and transportation. Only appropriate phase separation and domain size can produce the best photovoltaic performance.

CONCLUSIONS

In summary, narrow band gap conjugated polymers with 3,7-linked 2,8-bis(alkoxy)dibenzothiophene as the donor unit and benzothiadiazole (**P1** and **P2**) or 3,4-bis(octyloxy)-benzothiadiazole (**P3**) as the acceptor unit have been synthesized, characterized, and used as polymer donors for BHJ polymer solar cells. All the three polymers show broad absorption in the visible region with two peaks located at 400

and 530 nm, respectively, and **P3** exhibits much stronger ICT absorption than **P1** and **P2**. The photovoltaic performance of **P3**-based polymer solar cell devices is much better than that of **P1**- and **P2**-based devices. Polymer solar cells with the **P3**/ PC_{71}BM (1:3, by weight) blend as active layer show the best photovoltaic performance with a PCE of 4.48%. Our results demonstrate that the photovoltaic performance can be improved by fine-tuning the structure of conjugated polymers.

ASSOCIATED CONTENT

Supporting Information

Molar extinction coefficient data, XRD patterns, DSC and TGA curves, cyclic voltammograms, PL spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

*E-mail: licuihong@bnu.edu.cn (C.L.); zsbo@bnu.edu.cn (Z.B.).

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) (a) Brabec, C. J.; Cravino, A.; Meissner, D.; Sariciftci, N. S.; Fromherz, T.; Rispens, M. T.; Sanchez, L.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 374. (b) Brabec, C. J.; Padinger, F.; Dyakonov, V.; Hummelen, J. C.; Janssen, R. A. J.; Sariciftci, N. S. *AIP Conf. Proc.* **1998**, *442*, 519. (c) Brabec, C. J.; Padinger, F.; Hummelen, J. C.; Janssen, R. A. J.; Sariciftci, N. S. *Synth. Met.* **1999**, *102*, 861. (d) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Funct. Mater.* **2001**, *11*, 15. (e) Brabec, C. J.; Sariciftci, N. S. *Monatsh. Chem.* **2001**, *132*, 421. (f) Chen, H. Y.; Hou, J. H.; Zhang, S. Q.; Liang, Y. Y.; Yang, G. W.; Yang, Y.; Yu, L. P.; Wu, Y.; Li, G. *Nat. Photonics* **2009**, *3*, 649. (g) Cheng, Y. J.; Yang, S. H.; Hsu, C. S. *Chem. Rev.* **2009**, *109*, 5868. (h) Coakley, K. M.; McGehee, M. D. *Chem. Mater.* **2004**, *16*, 4533. (i) Freebody, M. *Photonics. Spectra* **2009**, *43*, 45. (j) Gendron, D.; Leclerc, M. *Energy Environ. Sci.* **2011**, *4*, 1225. (k) Gunes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324. (l) Hadipour, A.; de Boer, B.; Wildeman, J.; Kooistra, F. B.; Hummelen, J. C.; Turbiez, M. G. R.; Wienk, M. M.; Janssen, R. A. J.; Blom, P. W. M. *Adv. Funct. Mater.* **2006**, *16*, 1897. (m) Hoppe, H.; Sariciftci, N. S. *J. Mater. Res.* **2004**, *19*, 1924. (n) Kim, J. Y.; Lee, K.; Coates, N. E.; Moses, D.; Nguyen, T. Q.; Dante, M.; Heeger, A. J. *Science* **2007**, *317*, 222. (o) Li, C.; Liu, M. Y.; Pschirer, N. G.; Baumgarten, M.; Mullen, K. *Chem. Rev.* **2010**, *110*, 6817. (p) Li, G.; Shrotriya, V.; Huang, J. S.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat. Mater.* **2005**, *4*, 864. (q) Liang, Y. Y.; Yu, L. P. *Acc. Chem. Res.* **2010**, *43*, 1227. (r) Ma, W. L.; Yang, C. Y.; Gong, X.; Lee, K.; Heeger, A. J. *Adv. Funct. Mater.* **2005**, *15*, 1617. (s) Peet, J.; Kim, J. Y.; Coates, N. E.; Ma, W. L.; Moses, D.; Heeger, A. J.; Bazan, G. C. *Nat. Mater.* **2007**, *6*, 497. (t) Sariciftci, N. S. *Abstr. Am. Chem. Soc.* **2001**, *222*, U281. (u) Thompson, B. C.; Frechet, J. M. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 58. (2) (a) Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789. (b) Bundgaard, E.; Krebs, F. C. *Sol. Energy Mater. Sol. Cells* **2007**, *91*, 1019. (c) Dhanabalan, A.; van Hal, P. A.; van Duren, J. K. J.; van Dongen, J. L. J.; Janssen, R. A. J. *Synth. Met.* **2001**, *119*, 169. (d) Moon, J. S.; Jo, J.; Heeger, A. J. *Adv. Energy Mater.* **2012**, *2*, 304. (e) Park, S. H.; Roy, A.; Beaupre, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat.*

- Photonics* **2009**, *3*, 297. (f) Scharber, M. C.; Wuhlbacher, D.; Koppe, M.; Denk, P.; Waldauf, C.; Heeger, A. J.; Brabec, C. L. *Adv. Mater.* **2006**, *18*, 789. (g) Sun, Y. M.; Takacs, C. J.; Cowan, S. R.; Seo, J. H.; Gong, X.; Roy, A.; Heeger, A. J. *Adv. Mater.* **2011**, *23*, 2226. (h) Sun, Y. M.; Welch, G. C.; Leong, W. L.; Takacs, C. J.; Bazan, G. C.; Heeger, A. J. *Nat. Mater.* **2012**, *11*, 44. (i) van Duren, J. K. J.; Dhanabalan, A.; van Hal, P. A.; Janssen, R. A. J. *Synth. Met.* **2001**, *121*, 1587.
- (3) (a) Son, H. J.; Wang, W.; Xu, T.; Liang, Y. Y.; Wu, Y. E.; Li, G.; Yu, L. P. *J. Am. Chem. Soc.* **2011**, *133*, 1885. (b) Price, S. C.; Stuart, A. C.; Yang, L. Q.; Zhou, H. X.; You, W. *J. Am. Chem. Soc.* **2011**, *133*, 4625. (c) Chu, T. Y.; Lu, J. P.; Beaupre, S.; Zhang, Y. G.; Pouliot, J. R.; Wakim, S.; Zhou, J. Y.; Leclerc, M.; Li, Z.; Ding, J. F.; Tao, Y. *J. Am. Chem. Soc.* **2011**, *133*, 4250. (d) Amb, C. M.; Chen, S.; Graham, K. R.; Subbiah, J.; Small, C. E.; So, F.; Reynolds, J. R. *J. Am. Chem. Soc.* **2011**, *133*, 10062. (e) Zhou, H. X.; Yang, L. Q.; Stuart, A. C.; Price, S. C.; Liu, S. B.; You, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 2995. (f) Huo, L. J.; Zhang, S. Q.; Guo, X.; Xu, F.; Li, Y. F.; Hou, J. H. *Angew. Chem., Int. Ed.* **2011**, *50*, 9697. (g) Huo, L. J.; Hou, J. H.; Zhang, S. Q.; Chen, H. Y.; Yang, Y. *Angew. Chem., Int. Ed.* **2010**, *49*, 1500. (h) Tan, Z. A.; Zhang, W. Q.; Zhang, Z. G.; Qian, D. P.; Huang, Y.; Hou, J. H.; Li, Y. F. *Adv. Mater.* **2012**, *24*, 1476. (i) Su, M. S.; Kuo, C. Y.; Yuan, M. C.; Jeng, U. S.; Su, C. J.; Wei, K. H. *Adv. Mater.* **2011**, *23*, 3315. (j) Liang, Y. Y.; Xu, Z.; Xia, J. B.; Tsai, S. T.; Wu, Y.; Li, G.; Ray, C.; Yu, L. P. *Adv. Mater.* **2010**, *22*, E135. (k) He, Z. C.; Zhong, C. M.; Huang, X.; Wong, W. Y.; Wu, H. B.; Chen, L. W.; Su, S. J.; Cao, Y. *Adv. Mater.* **2011**, *23*, 4636.
- (4) (a) Dennler, G.; Scharber, M. C.; Ameri, T.; Denk, P.; Forberich, K.; Waldauf, C.; Brabec, C. J. *Adv. Mater.* **2008**, *20*, 579. (b) He, F.; Yu, L. P. *J. Phys. Chem. Lett.* **2011**, *2*, 3102. (c) Li, Y. F. *Acc. Chem. Res.* **2012**, *45*, 723.
- (5) Mihailetschi, V. D.; Blom, P. W. M.; Hummelen, J. C.; Rispens, M. T. *J. Appl. Phys.* **2003**, *94*, 6849.
- (6) (a) Qin, R. P.; Li, W. W.; Li, C. H.; Du, C.; Veit, C.; Schleiermacher, H. F.; Andersson, M.; Bo, Z. S.; Liu, Z. P.; Inganas, O.; Wuerfel, U.; Zhang, F. L. *J. Am. Chem. Soc.* **2009**, *131*, 14612. (b) Du, C.; Li, C. H.; Li, W. W.; Chen, X.; Bo, Z. S.; Veit, C.; Ma, Z. F.; Wuerfel, U.; Zhu, H. F.; Hu, W. P.; Zhang, F. L. *Macromolecules* **2011**, *44*, 7617. (c) Song, J. S.; Du, C.; Li, C. H.; Bo, Z. S. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 4267. (d) Ko, S. W.; Hoke, E. T.; Pandey, L.; Hong, S. H.; Mondal, R.; Risko, C.; Yi, Y. P.; Noriega, R.; McGehee, M. D.; Bredas, J. L.; Salleo, A.; Bao, Z. A. *J. Am. Chem. Soc.* **2012**, *134*, 5222.
- (7) (a) Chen, H. Y.; Hou, J. H.; Hayden, A. E.; Yang, H.; Houk, K. N.; Yang, Y. *Adv. Mater.* **2010**, *22*, 371. (b) He, Z. C.; Zhang, C.; Xu, X. F.; Zhang, L. J.; Huang, L.; Chen, J. W.; Wu, H. B.; Cao, Y. *Adv. Mater.* **2011**, *23*, 3086. (c) Huang, Y.; Guo, X.; Liu, F.; Huo, L. J.; Chen, Y. N.; Russell, T. P.; Han, C. C.; Li, Y. F.; Hou, J. H. *Adv. Mater.* **2012**, *24*, 3383. (d) Wang, E. G.; Hou, L. T.; Wang, Z. Q.; Hellstrom, S.; Zhang, F. L.; Inganas, O.; Andersson, M. R. *Adv. Mater.* **2010**, *22*, 5240. (e) Inganäs, O.; Svensson, M.; Zhang, F.; Gadisa, A.; Persson, N. K.; Wang, X.; Andersson, M. R. *Appl. Phys. A: Mater. Sci. Process.* **2004**, *79*, 31. (f) Wang, J. Y.; Hsu, S. K.; Yip, H. L.; Davies, J. A.; Chen, K. S.; Zhang, Y.; Sun, Y.; Jen, A. K. Y. *Chem. Mater.* **2011**, *23*, 765. (g) Duan, C. H.; Huang, F.; Cao, Y. *J. Mater. Chem.* **2012**, *22*, 10416. (h) Duan, C. H.; Cai, W. Z.; Zhong, C. M.; Li, Y. H.; Wang, X. H.; Huang, F.; Cao, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 4406. (i) Hou, J. H.; Chen, H. Y.; Zhang, S. Q.; Chen, R. I.; Yang, Y.; Wu, Y.; Li, G. J. *Am. Chem. Soc.* **2009**, *131*, 15586. (j) Seo, J. H.; Gutacker, A.; Sun, Y. M.; Wu, H. B.; Huang, F.; Cao, Y.; Scherf, U.; Heeger, A. J.; Bazan, G. C. *J. Am. Chem. Soc.* **2011**, *133*, 8416. (k) Wang, E. G.; Ma, Z. F.; Zhang, Z.; Vandewal, K.; Henriksson, P.; Inganäs, O.; Zhang, F. L.; Andersson, M. R. *J. Am. Chem. Soc.* **2011**, *133*, 14244. (l) Min, J.; Zhang, Z. G.; Zhang, S. Y.; Zhang, M. J.; Zhang, J.; Li, Y. F. *Macromolecules* **2011**, *44*, 7632. (m) Wang, X. C.; Sun, Y. P.; Chen, S.; Guo, X.; Zhang, M. J.; Li, X. Y.; Li, Y. F.; Wang, H. Q. *Macromolecules* **2012**, *45*, 1208. (n) Zou, Y. P.; Gendron, D.; Neagu-Plesu, R.; Leclerc, M. *Macromolecules* **2009**, *42*, 6361. (o) Coffin, R. C.; Peet, J.; Rogers, J.; Bazan, G. C. *Nat. Chem.* **2009**, *1*, 657. (p) Huo, L. J.; Hou, J. H. *Polym. Chem.* **2011**, *2*, 2453.
- (8) (a) Chen, J. W.; Cao, Y. *Acc. Chem. Res.* **2009**, *42*, 1709. (b) Peng, Q.; Liu, X. J.; Su, D.; Fu, G. W.; Xu, J.; Dai, L. M. *Adv. Mater.* **2011**, *23*, 4554. (c) Beaujuge, P. M.; Tsao, H. N.; Hansen, M. R.; Amb, C. M.; Risko, C.; Subbiah, J.; Choudhury, K. R.; Mavrinskiy, A.; Pisula, W.; Bredas, J. L.; So, F.; Mullen, K.; Reynolds, J. R. *J. Am. Chem. Soc.* **2012**, *134*, 8944. (d) Hou, J. H.; Chen, H. Y.; Zhang, S. Q.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2008**, *130*, 16144. (e) Balan, B.; Vijayakumar, C.; Saeki, A.; Koizumi, Y.; Seki, S. *Macromolecules* **2012**, *45*, 2709. (f) Bundgaard, E.; Krebs, F. C. *Macromolecules* **2006**, *39*, 2823. (g) Price, S. C.; Stuart, A. C.; You, W. *Macromolecules* **2010**, *43*, 4609. (h) Zhou, E. J.; Cong, J. Z.; Yamakawa, S.; Wei, Q. S.; Nakamura, M.; Tajima, K.; Yang, C. H.; Hashimoto, K. *Macromolecules* **2010**, *43*, 2873.
- (9) (a) Inganäs, O.; Zhang, F. L.; Andersson, M. R. *Acc. Chem. Res.* **2009**, *42*, 1731. (b) Gadisa, A.; Mammo, W.; Andersson, M.; Admassie, S.; Zhang, F.; Andersson, M. R.; Inganäs, O. *Adv. Funct. Mater.* **2007**, *17*, 3836. (c) Svanstrom, C. M. B.; Rysz, J.; Bernasik, A.; Budkowski, A.; Zhang, F.; Inganas, O.; Andersson, M. R.; Magnusson, K. O.; Benson-Smith, J. J.; Nelson, J.; Moons, E. *Adv. Mater.* **2009**, *21*, 4398. (d) Svensson, M.; Zhang, F. L.; Veenstra, S. C.; Verhees, W. J. H.; Hummelen, J. C.; Kroon, J. M.; Inganas, O.; Andersson, M. R. *Adv. Mater.* **2003**, *15*, 988. (e) Zhang, F. L.; Mammo, W.; Andersson, L. M.; Admassie, S.; Andersson, M. R.; Inganäs, L.; Admassie, S.; Andersson, M. R.; Inganäs, O. *Adv. Mater.* **2006**, *18*, 2169. (f) Tian, R. Y.; Yang, R. Q.; Peng, J. B.; Cao, Y. *Chin. Phys.* **2005**, *14*, 1032. (g) Lee, J. F.; Hsu, S. L. C.; Lee, P. I.; Chuang, H. Y.; Chen, J. S.; Chou, W. Y. *J. Polym. Sci., Part A: Polym. Chem.* **2011**, *49*, 4618. (h) Li, W. W.; Qin, R. P.; Zhou, Y.; Andersson, M.; Li, F. H.; Zhang, C.; Li, B. S.; Liu, Z. P.; Bo, Z. S.; Zhang, F. L. *Polymer* **2010**, *51*, 3031.
- (10) (a) Blouin, N.; Michaud, A.; Leclerc, M. *Adv. Mater.* **2007**, *19*, 2295. (b) Kim, J.; Yun, M. H.; Anant, P.; Cho, S.; Jacob, J.; Kim, J. Y.; Yang, C. *Chem.—Eur. J.* **2011**, *17*, 14681. (c) Wakim, S.; Beaupre, S.; Blouin, N.; Aich, B. R.; Rodman, S.; Gaudiana, R.; Tao, Y.; Leclerc, M. *J. Mater. Chem.* **2009**, *19*, 5351. (d) Fu, Y.; Cha, H.; Lee, G. Y.; Moon, B. J.; Park, C. E.; Park, T. *Macromolecules* **2012**, *45*, 3004. (e) Wang, E. G.; Hou, L. T.; Wang, Z. Q.; Ma, Z. F.; Hellstrom, S.; Zhuang, W. L.; Zhang, F. L.; Inganas, O.; Andersson, M. R. *Macromolecules* **2011**, *44*, 2067. (f) Boudreault, P. L. T.; Beaupre, S.; Leclerc, M. *Polym. Chem.* **2010**, *1*, 127. (g) Wakim, S.; Aich, B. R.; Tao, Y.; Leclerc, M. *Polym. Rev.* **2008**, *48*, 432.
- (11) (a) Beaupre, S.; Boudreault, P. L. T.; Leclerc, M. *Adv. Mater.* **2010**, *22*, E6. (b) Chen, M. H.; Hou, J.; Hong, Z.; Yang, G.; Sista, S.; Chen, L. M.; Yang, Y. *Adv. Mater.* **2009**, *21*, 4238. (c) Boudreault, P. L. T.; Michaud, A.; Leclerc, M. *Macromol. Rapid Commun.* **2007**, *28*, 2176.
- (12) (a) Jiang, W.; Zhou, Y.; Geng, H.; Jiang, S. D.; Yan, S. K.; Hu, W. P.; Wang, Z. H.; Shuai, Z. G.; Pei, J. A. *J. Am. Chem. Soc.* **2011**, *133*, 1. (b) Jiang, W.; Qian, H. L.; Li, Y.; Wang, Z. *J. Org. Chem.* **2008**, *73*, 7369.
- (13) Tolman, C. A.; Seidel, W. C.; Gerlach, D. H. *J. Am. Chem. Soc.* **1972**, *94*, 2669.
- (14) Zhang, S. L.; Chen, R. F.; Yin, J.; Liu, F.; Jiang, H. J.; Shi, N. E.; An, Z. F.; Ma, C.; Liu, B.; Huang, W. *Org. Lett.* **2010**, *12*, 3438.
- (15) Yamamoto, T.; Komarudin, D.; Arai, M.; Lee, B. L.; Suganuma, H.; Asakawa, N.; Inoue, Y.; Kubota, K.; Sasaki, S.; Fukuda, T.; Matsuda, H. *J. Am. Chem. Soc.* **1998**, *120*, 2047.
- (16) Irvin, J. A.; Schwendeman, I.; Lee, Y.; Abboud, K. A.; Reynolds, J. R. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2164.
- (17) Sun, Q. J.; Wang, H. Q.; Yang, C. H.; Li, Y. F. *J. Mater. Chem.* **2003**, *13*, 800.
- (18) (a) Ameri, T.; Dennler, G.; Waldauf, C.; Denk, P.; Forberich, K.; Scharber, M. C.; Brabec, C. J.; Hingerl, K. *J. Appl. Phys.* **2008**, *103*, 084506. (b) Waldauf, C.; Scharber, M. C.; Schilinsky, P.; Hauch, J. A.; Brabec, C. J. *J. Appl. Phys.* **2006**, *99*, 104503.
- (19) Fu, G. C. *Acc. Chem. Res.* **2008**, *41*, 1555.
- (20) (a) Barche, J.; Janietz, S.; Ahles, M.; Schmechel, R.; von Seggern, H. *Chem. Mater.* **2004**, *16*, 4286. (b) Osaka, I.; Akita, M.; Koganezawa, T.; Takimiya, K. *Chem. Mater.* **2012**, *24*, 1235.

(21) (a) Chu, C. W.; Yang, H. C.; Hou, W. J.; Huang, J. S.; Li, G.; Yang, Y. *Appl. Phys. Lett.* **2008**, *92*, 103306. (b) Ruderer, M. A.; Muller-Buschbaum, P. *Soft Mater.* **2011**, *7*, 5482.

(22) (a) Maturova, K.; van Bavel, S. S.; Wienk, M. M.; Janssen, R. A. J.; Kemerink, M. *Adv. Funct. Mater.* **2011**, *21*, 261. (b) Yao, Y.; Hou, J. H.; Xu, Z.; Li, G.; Yang, Y. *Adv. Funct. Mater.* **2008**, *18*, 1783. (c) Blom, P. W. M.; Mihailetchi, V. D.; Koster, L. J. A.; Markov, D. E. *Adv. Mater.* **2007**, *19*, 1551.