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

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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 cm2 V−1 s−1 for P1, P2, and P3, respectively. Under simulated solar illumination of AM 1.5G (100 mW/cm2), a PCE of 4.48% with a Voc of 0.83 V, a Jsc of 9.30 mA/cm2, 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-butyrates (PCBM) or (6,6)-phenyl-C71-butyrates (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 (Jsc) and open-circuit voltage (Voc).2,4 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.2,4 The electron mobility of PCBM is around 2 × 10−3 cm2 V−1 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.5

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.6,7 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 rings bridged by carbon atom),7,8,9 2,7-linked carbazole (two benzene rings bridged by nitrogen atom),10,11 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...
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)-dibenzo[ghi]phenanthrene 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 dibenzo[ghi]phenanthrene 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 dibenzo[ghi]phenanthrene 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)-dibenzo[ghi]phenanthrene 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)dibenzo[ghi]phenanthrene 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 Voc of 0.83 V, a Jsc of 9.30 mA/cm², and a comparable fill factor (FF) of 0.58. The hole mobility of P3 reached 2.3 × 10⁻³ cm²V⁻¹s⁻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-Dibromodibenzo[ghi]phenanthrene 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 self-permeation chromatography (GPC) measurements were performed in 200 °C on a PL-220 (Polymer Laboratories) chromatograph connected to a differential refractometer with a 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 Kα 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 tetraethylammonium tetrafluoroborate solution in CH₂CN 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 CH₂CN) reference electrode were used. The experiments were calibrated with the standard ferrocenium/ferroenium (Fc/Fc⁺) redox system and assumption that the energy level of Fc⁺ 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/PC₇₀BM 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 μm). 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:PC₇₀BM (1:3)/LiF/Al. The conductivity of ITO was 20 Ω/□. PEDOT:PSS is Baytron AI 4083 from H.C. Starck and was filtered with a 0.45 mm 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 PC₇₀BM 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-3015, 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 25 °C.

Synthesis of 2,8-Dihydroxymethinobenzophene-5,5-dioxide (3). To a solution of 2,8-dibromodibenzo[ghi]phenanthrene (1) (200 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 methinobenzophene-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-dihydroxymethinobenzophene-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)-dibenzo[ghi]phenanthrene-5,5-dioxide (4). A mixture of compound 3, alkyl bromide, potassium carbonate, and butanol 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 CHCl₃. The combined organic layers were washed with water, dried over anhydrous MgSO₄, and reduced pressure. The residue was partitioned between chloroform (100 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 x 3). The combined organic layers were washed with water (200 mL), dried over anhydrous MgSO₄, 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.

**Synthesis of 3,7-Dibromo-2,8-bis(octyloxy)dibenzothiophene-S,S-dioxide (5b).** To an ice bath cooled solution of LiAlH₄ in dry diethyl ether (100 mL) was added a solution of 2,7-dibromo-3,6-bis(alkoxy)dibenzothiophene (6). The reaction mixture was stirred at room temperature for 6 h. The mixture was stirred under 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 x 3). The combined organic layers were washed with water (200 mL), dried over anhydrous MgSO₄, 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.
A mixture was stirred overnight and allowed to warm to rt gradually. The borate (13.97 mL, 60.16 mmol) was added rapidly, and the resulted residue was chromatographically puri ed on silica gel column eluting with acetone to a dark red solid in a yield of 47% (52 mg). Since P1 has poor solubility in CHCl3 or chlorobenzene (CB) at room temperature, 11C NMR is di cult to obtain. 11C NMR (400 MHz, CD2D2) 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. Calc for C42H46N2O2S4: C 68.25, H 6.45, N 3.27 GPC (PS standards): \( M_n = 16.3 \text{ kg/mol}, M_w = 47.9 \text{ kg/mol}, PDI = 1.4 \).
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, C6D6) 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, C6D6) 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 C58H78N2O4S4: 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-Dibromodibenzotheiophene was reacted with n-BuLi at −78 °C followed by quenching the anions with trisopropyl borate to afford the crude dibenzotheiophene-2,8-diboronic acid (2), which was used for the next step without further purification. The oxidation of 2 with H2O2 in acetic acid afforded 2,8-dihydroxydibenzotheiophene-S-dioxide (3) in a total yield of 92%. Williamson etherification with alkyl bromides and K2CO3 in butanone afforded 2,8-bis(alkoxy)dibenzotheiophene-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)dibenzotheiophene-S,S-dioxides (5a−c) in yields of 78−85%. The reduction of 5a−c with LiAlH4 in diethyl ether at 0 °C afforded 3,7-dibromo-2,8-bis(alkoxy)-dibenzotheiophene-S,S-dioxides (6a−c) in yields of 90−95%. Suzuki cross-coupling of 6a−c and 4,4,5,5-tetramethyl-2-(thiophen-2-yl)
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 diboronic ester monomer 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-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 at 150 °C with 1,2,4-trichlorobenzene as an eluent. The decomposition temperature determined by TGA in N₂ based on 5% weight loss. The calculated absorption band edge of the copolymer film, \( E_{\text{g,opt}} = 1240/\lambda_{\text{edge}} \).
(TG) 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 mobilities 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 × 104 and 5.04 × 104 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 × 104 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 (Eg,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 benzo thiadiazole 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 film 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_{HOMO} = −e(E_{ox} + 4.71) (eV) and the LUMO energy level was calculated by the equation E_{LUMO} = E_{HOMO} + E_{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 PC71BM 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, which should provide an enough driving force for efficient exciton dissociation. As shown in Figure 1a, 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-diodooctane (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

**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
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

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

<table>
<thead>
<tr>
<th>active layer solvent</th>
<th>thickness (nm)</th>
<th>V_{oc} (V)</th>
<th>J_{sc} (mA/cm²)</th>
<th>FF</th>
<th>PCE (%) (max)</th>
<th>PCE (%) (av)</th>
<th>( \mu_{hole} ) (cm² V⁻¹ s⁻¹)</th>
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<tr>
<td>P1:PC71BM DCB</td>
<td>92</td>
<td>0.79</td>
<td>2.60</td>
<td>0.51</td>
<td>1.02</td>
<td>0.99</td>
<td>1.3 \times 10^{-4}</td>
</tr>
<tr>
<td>P2:PC71BM DCB</td>
<td>95</td>
<td>0.72</td>
<td>6.80</td>
<td>0.35</td>
<td>1.71</td>
<td>1.69</td>
<td>2.7 \times 10^{-4}</td>
</tr>
<tr>
<td>P3:PC71BM DCB</td>
<td>84</td>
<td>0.79</td>
<td>9.07</td>
<td>0.59</td>
<td>4.19</td>
<td>4.48</td>
<td>2.3 \times 10^{-3}</td>
</tr>
<tr>
<td>P3:PC71BM DCB⁴</td>
<td>80</td>
<td>0.83</td>
<td>9.30</td>
<td>0.58</td>
<td>4.48</td>
<td>4.32</td>
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</tbody>
</table>

⁴0.5% DIO additive (v/v). ⁵Measured by using the organic field-effect transistor (OFET) method.
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 $V_{oc} = (|E_{donor} - E_{HOMO}| - |E_{PCBM} - E_{LUMO}|)/e - 0.3 \text{ V}$ 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.

Figure 4. AFM images ($5 \times 5 \mu m^2$) of the blends of polymer:PC$_{71}$BM (1:3, by weight) spin-cast from DCB solutions: (a) P1, (b) P2, (c) P3, and (d) P3 (containing 0.5% DIO in volume).
capacitance per unit area of the gate dielectric layer (SiO₂, 500 nm, C₀ = 7.5 nF/cm²), and Vₚ is the threshold voltage. The output and transfer characteristic curves of the spin-coated film of P1, P2, and P3 on OTS-treated Si/SiO₂ 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 × 10⁻⁴ cm² V⁻¹ 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 × 10⁻³ cm² V⁻¹ 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 benzo thiadiazole ring will not generate steric hindrance, since the electrostatic attraction between ether oxygens and thienyl sulfur atoms of P3 will enhance planarization. Closer distance between the polymer chains can facilitate charge hopping in the polymer. 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/PC₇₁BM 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:PC₇₁BM (1:3, by weight) are shown in Figure 4. The P1:PC₇₁BM (1:3, by weight) and P2:PC₇₁BM (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. 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:PC₇₁BM (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. The root-mean-square (rms) roughness for the P3:PC₇₁BM (1:3, by weight) blend films are 0.326 nm, which is lower than P1 or P2:PC₇₁BM (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)dibenzo thiophene as the donor unit and benzo thiadiazole (P1 and P2) or 3,4-bis(octyloxy)-benzo thiadiazole (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/PC₇₁BM (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.

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Notes

The authors declare no competing financial interest.

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