Molecular Engineering of Conjugated Polymers for Solar Cells and Field-Effect Transistors: Side-Chain Versus Main-Chain Electron Acceptors

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ABSTRACT: Two model polymers, containing fluorene as an electrondonating moiety and benzothiadiazole (BT) as an electronaccepting moiety, have been synthesized by Suzuki coupling reaction. Both polymers are composed of the same chemical composition, but the BT acceptor can be either at a side-chain (i.e., S-polymer) or along the polymer main chain (i.e., M-polymer). Their optical, electrochemical, and photovoltaic properties, together with the field-effect transistor (FET) characteristics, have been investigated experimentally and theoretically. The FET carrier mobilities were estimated to be 5.20×10^{-5} and 3.12×10^{-4} cm² V⁻¹ s⁻¹ for the S-polymer and M-polymer, respectively. Furthermore, polymeric solar cells (PSCs) with the ITO/ PEDOT:PSS/S-polymer or M-polymer:PC₇₁BM(1:4)/Al structure

INTRODUCTION Solar energy is considered to be one of the most promising renewable energy to solve the growing global energy problem. Various solar cells, such as siliconbased solar cells,¹ dye-sensitized solar cells (DSSCs)^{2,3} and polymer solar cells (PSCs),⁴⁻⁶ have been developed. Among them, PSCs have generated a great deal of interest due to some competitive advantages, including their light weight, low cost, and easy fabrication on large-area flexible substrates by solution processing.⁴⁻⁶ However, PSCs are still suffered from multiple drawbacks, such as their limited solar absorption efficiency, insufficient charge transport in active layer and inadequate device stability.^{7,8} To overcome these limitations, several approaches have been developed for efficient materials and device engineering.

In particular, bulk heterojunctions (BHJs), consisting interpenetrating networks of an electron-donating conjugated polymer and a fullerene-based electron acceptor, has been developed as ideal photovoltaic materials for high-performance PSCs.⁹ The interpenetrating network in a BHJ-PSC provides the spatially distributed interfaces necessary for a were constructed and demonstrated to show a power conversion efficiency of 0.82 and 1.24% for the S-polymer and M-polymer, respectively. The observed superior device performances for the M-polymer in both FET and PSCs are attributable to its relatively low band-gap and close molecular packing for efficient solar light harvesting and charge transport. This study provides important insights into the design of ideal structure–property relationships for conjugate polymers in FETs and PSCs. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 271– 279, 2012

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high-yield photogeneration of excitons, an efficient charge separation, and a facile collection of the separated electrons and holes. Furthermore, BHJ-PSCs can be easily fabricated by simple solution processing methods to form a single active layer of the interpenetrating network.

BHJ-PSCs based on regio-regular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) have showed a significant enhancement in the power conversion efficiency (PCE; up to $\sim 5\%$).¹⁰⁻¹² However, these PSCs have a relatively low open-circuit voltage ($V_{\rm oc} \sim 0.6$ V) as P3HT can utilize only less than 25% of solar photons. Therefore, conjugated polymers with an optimized molecular geometry and a lower band-gap are needed for replacing P3HT in high-performance BHJ-PSCs, In this context, various synthetic routes have been devised to produce new low band-gap conjugated polymers.¹³ One of the promising strategies is to synthesize conjugated polymers with alternating donor (D) and acceptor (A) units along its backbone,¹⁴ leading to a reduced band-gap through the partial intramolecular charge transfer (ICT) between the donor and

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FIGURE 1 Chemical structures of the S-polymer and M-polymer.

acceptor.^{13,14} For this purpose, many electron-rich units, such as triphenylamine, fluorene, and carbazole, and electron-deficient units, including benzothiadiazole (BT) and quinoxaline, have been incorporated into the main-chain D-A polymers.¹⁵⁻¹⁷

Along with the extensively studied main-chain D-A polymers for PSC applications,^{15,16,18–20} certain specialized conjugated polymers with electron acceptors located in side chain have also been developed to show high-photovoltaic efficiencies.^{21–23} Comparing with their main chain counterparts, the side-chain D-A conjugated polymers possess some additional advantages, including a high light absorption efficiency²¹ and an enhanced isotropic charge transfer^{21–23} attractive for photovoltaic applications.

In this article, two model conjugated polymers composed of a well-known fluorene donor, thiophene bridge and BT acceptor were designed and synthesized. These polymers have the same chemical composition, but the location of the BT acceptor varies (i.e., S-polymer vs. M-polymer) (Fig. 1). We further studied their optical, electrochemical and photovoltaic properties, together with the field-effect transistor (FET) characteristics, by experimental measurements and theoretical calculations. To our best knowledge, there is no report on direct comparison of polymers, which have the same chemical compositions except the location of electron acceptor. It is anticipated that the different location of acceptor in conjugated polymers (i.e., side-chain vs. mainchain) can have significant influences on their basic properties such as optical and electrochemical properties, as well as device performances. The positional effects of an electron acceptor in conjugate polymers on various properties have been clearly demonstrated by the distinctive results obtained from this study, which provides important insights into the design of future conjugated polymers with not only main or side chain acceptor but also ideal structure-property relationships for conjugated polymers for FET and PSC applications.

EXPERIMENTAL

Materials and Instruments

4-Bromo-2,1,3-benzothiadiazole was purchased from ACROS Chemical, Inc. 4,7-Dibromo-2,1,3-benzothiadazole was prepared according to the reported procedure.²⁴ 3-Thienylboronic acid and 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3propandiol) ester were purchased from Aldrich Chemical, Inc. All other chemicals and solvents were obtained from Aldrich Chemical, Inc. ¹H and ¹³C NMR spectra were recorded on a Varian VNMRS 600 spectrometer. UV–vis spectra were measured on a Perkin-Elmer LS 35. Cyclic voltametry (CV) measurement was performed using a VersaSTAT3 potentiostat from Princeton Applied Research. For CV measurements, a glassy carbon electrode coated with a thin layer of the polymer sample and platinum wire were used as the working and counter electrode, respectively. Ag wire was used as a pseudo-reference electrode with ferrocene/ferrocenium external standard. Gel permeation chromatography (GPC) was recorded on an Agilent 1200 series using THF as an eluent. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a Q600 and Q200 from TA instruments, respectively.

Fabrication and Analysis of Polymer Solar Cells (PSCs)

The poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) (Baytron PH) were purchased from H.C. Starck (Germany). [6,6]-Phenyl-C71-butyric acid methyl ester (PC₇₁BM) was purchased from Electronic Materials (EM) Index, Co., Ltd. The solar cell device has a typical structure of glass/indium-tin-oxide (ITO)/PEDOT:PSS/Active Layer/Al. These devices were fabricated according to the following procedures. First, the ITO-coated glass substrate was consecutively cleaned with detergent, then sonicated in acetone and isopropyl alcohol, and subsequently dried in an oven overnight at 100 °C. PEDOT:PSS layer was spin-coated (after passing through a $0.45-\mu m$ syringe filter) at 5000 rpm for 40 s on top of the ITO-coated glass, followed by baking at 140 °C for 10 min in air before being transferred into a glove box. Thereafter, each of the S-polymer or M-polymer solutions with different polymer to PC71BM ratios in chlorobenzene (CB) was spin-coated on top of the PEDOT:PSS layer at 1500-2000 rpm for 60 s. A 100-nm thick Al electrode was then deposited on top of the active layer under vacuum (<10⁻⁶ torr; 1 torr \sim 133 Pa) on a thermal evaporator inside a glove box. The size of the deposited Al electrode defined the active area of these devices as 13.5 mm². Each of the devices was then annealed at 90–130 $^\circ$ C for 10 min in the glove box filled with N2 prior to the performance measurements inside the glove box using a high quality optical fiber to guide the light from the solar simulator equipped with a Keithley 2635A source measurement unit. The J-V curves for devices were measured under AM 1.5G illumination at 100 mW cm⁻². Internal power conversion efficiency (IPCE) measurements were also conducted using an EQE



SCHEME 1 Synthetic scheme for S-polymer and M-polymer: (a) Pd(PPh₃)₄, K₂CO₃, toluene/water, 80 °C, 12 h, (b) *N*-bromosuccinimide, THF, RT, 8 h, (c) Pd(PPh₃)₄, K₂CO₃, toluene/water, 90 °C, 2 days, and (d) Pd(PPh)₂Cl₂, THF, 12 h.

system (Model QEX7) by PV Measurements, Inc. (Boulder, Colorado).

Fabrication and Analysis of FETs

Highly *n*-doped silicon (Si) wafers covered with a layer of 200 nm of thermally grown silicon dioxide (SiO₂) were used as substrates. Prior to use, the substrates were cleaned by acetone, isopropanol and dried in an oven at 100 °C for 20 min, followed by the treatment with octadecyltrichlorosilane (OTS) at RT for over 12 h. The doped Si and SiO₂ were used as a gate electrode and a gate dielectric layer, respectively. The active polymer layer (60 nm) was then deposited by spin-coating at 2000 rpm. Thereafter, Au (60 nm) was evaporated onto the polymer layer through a shadow mask to obtain source and drain electrodes. The channel length and width are 2950 and 50 μ m, respectively. All TFTs were made in a top-contact geometry, and all fabrication processes were carried out in a glove box filled with N2. Electrical measurements were performed using a Keithley semiconductor parametric analyzer (Keithley 4200-SCS) under N₂ atmosphere. The field-effect mobility (μ) was determined by using the following equation in the saturation regime; I_{ds} = (WC_i/2L) \times $\mu \times (V_{as} - V_T)^2$, where C_i is the specific capacitance of the SiO_2 dielectric ($C_i = 15 \text{ nF/cm}^2$), V_T is the threshold voltage.

Syntheses

Scheme 1 outlines the reaction route to S-polymer and M-polymer while the synthetic details for some compounds involved are given below:

4-(Thiophen-3-yl)benzo[c][1,2,5]thiadiazole (1)

A mixture of 4-bromo-2,1,3-benzothiadiazole (0.50 g, 2.32 mmol), 3-thienylboronic acid (0.3 g, 2.34 mmol) and tetrakis (triphenylphosphine)palladium(0) (0.13 g, 0.11 mmol) was dissolved in 7 mL toluene, and then 2 M aqueous solution of potassium carbonate (3 mL) was added. After stirring at 80 °C for 12 h under argon, the mixture was poured into water and extracted with chloroform. The organic layers were dried over magnesium sulfate and filtered. Upon solvent evaporation, the residues were subjected to column chromatography using ethyl acetate/*n*-hexane (1/7, v/v) to give **1** as yellowish viscous oil (0.30 g, 60% yield). MS (GC) = m/z 218.

¹H NMR (600 MHz, CDCl₃): δ (ppm) = 8.37 (d, 1H), 7.94 (d, 1H), 7.80 (d, 1H), 7.77 (d, 1H), 7.64 (dd, 1H), 7.47 (dd, 1H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) = 155.6, 153.0, 137.5, 129.6, 128.7, 127.1, 126.1, 125.7, 125.4, 120.0.

5-Dibromothiophen-3-yl)benzo[c][1,2,5]thiadiazole (2)

A mixture of 1 (0.18 g, 0.84 mmol) and *N*-bromosuccinimide (NBS; 0.36 g, 2.02 mmol) in 10 mL THF was stirred at room



temperature for 8 h. The reaction mixture was poured into water and extracted with chloroform. The organic layers were separated, dried over magnesium sulfate and filtered. Solvents were removed and the crude residue was further purified by recrystallization from chloroform/methanol (1/4, v/v) to give **2** as yellow powder (0.16 g, 51% yield). MS (GC): m/z = 376. Melting point: 169–171 °C.

¹H NMR (600 MHz, CDCl₃): δ (ppm) = 8.01 (d, 1H), 7.78 (d, 1H), 7.69 (dd, 1H), 7.40 (s, 1H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) = 155.2, 153.2, 137.8, 132.5, 129.2, 127.0, 125.9, 121.7, 111.4, 110.4.

4-Bromo-7-(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (3)

A mixture of 4,7-bromo-2,1,3-benzothiadiazole (0.50 g, 1.70 mmol), 2-(tributylstannyl)thiophene (0.64 g, 1.72 mmol) and bis(triphenylphosphine)palladium(II) dichloride (0.013 g, 0.017 mmol) was dissolved in 10 mL THF. After refluxing for 12 h under argon, the mixture was poured into water and extracted with chloroform. The organic layers were separated, dried over magnesium sulfate and filtered. Upon solvent evaporation, the residues were subjected to column chromatography using chloroform/*n*-hexane (1/4, v/v) to give **3** as orange solid (0.35 g, 63% yield). MS (GC): m/z = 295. Melting point: 88–89 °C.

¹H NMR (600 MHz, CDCl₃): δ (ppm) = 8.10 (d, 1H), 7.86 (d, 1H), 7.73 (d, 1H), 7.49 (d, 1H), 7.21 (dd, 1H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) = 153.7, 152.9, 151.8, 138.4, 132.3, 128.1, 127.3, 125.8, 113.9, 112.3.

4-Bromo-7-(5-bromothiophen-2-yl)benzo[c][1,2,5] thiadiazole (4)

A mixture of **3** (0.43 g, 1.45 mmol) and NBS (0.28 g, 1.59 mmol) in THF was stirred at room temperature for 8 h. The reaction mixture was poured into water and extracted with chloroform. The organic layers were separated, dried over magnesium sulfate and filtered. Upon solvent evaporation, the crude residue was further purified by recrystallization from chloroform/methanol (1/3, v/v) to give **4** as red powder (0.29 g, 53% yield). MS (GC): m/z = 376. Melting point: 174–175 °C.

¹H NMR (600 MHz, CDCl₃): δ (ppm) = 7.85 (d, 1H), 7.79 (d, 1H), 7.65 (d, 1H), 7.16 (d, 1H). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) = 153.7, 151.4, 139.8, 132.3, 130.8, 127.7, 126.1, 125.2, 115.1, 112.8.

S-Polymer

2 (0.21 g, 0.57 mmol) and 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propandiol) ester (0.285 g, 0.57 mmol) were dissolved in 6 mL dry toluene under argon. The mixture was purged with argon to remove oxygen. Tetrakis(triphenylphosphine) palladium(0) (0.026 g, 0.022 mmol) and degassed 2 M potassium carbonate aqueous solution (4 mL) were added. The mixture was stirred at 90 °C for 48 h under argon. Upon completion of the reaction, the mixture was poured into methanol and the precipitate was collected by suction filtration. Then the resultant solid was dissolved in THF and filtered. The filtrate was poured into methanol again. The precipitate was collected and further purified

with Soxhlet extraction using methanol, hexane, acetone, and chloroform. Finally, the polymer in chloroform fraction was recovered by evaporation of the solvent to give S-polymer as dark yellowish powder (0.23 g, 74% yield). $M_{\rm w} = 67900$ g/ mol and PDI = 3.18 GPC (THF).

¹H NMR (CDCl₃, 600 MHz): δ (ppm) = 8.01–7.91 (broad), 7.77–7.27 (broad), 7.18–7.05 (broad), 2.18–2.01 (broad), 1.90–1.81 (broad), 1.70–1.42 (broad), 1.30–0.62 (broad), 0.59–0.37 (broad). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) = 154.2, 152.9, 150.8, 150.0, 140.4, 139.4, 133.1, 132.4, 129.5, 129.3, 128.8, 128.3, 127.7, 126.7, 125.7, 133.7, 122.4, 121.6, 119.6, 119.4, 118.9, 54.1, 39.3, 30.5, 28.7, 22.7, 21.6, 13.1. Anal. Calcd. For $C_{35}H_{38}N_2S_2$: C, 76.32%; H, 6.95%; N, 5.09%. Found: C, 75.14%; H, 7.05%; N, 4.72%.

M-Polymer

4 (0.12 g, 0.32 mmol) and 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propandiol) ester (0.28 g, 0.32 mmol) were dissolved in 6 mL dry toluene under argon. The mixture was purged with argon to remove oxygen. Tetrakis(triphenylphosphine)palladium(0) (0.015 g, 0.013 mmol) and degassed 2 M potassium carbonate aqueous solution (4 mL) were added. The mixture was stirred at 90 °C for 48 h under argon. Upon completion of the reaction, the mixture was poured into methanol and the precipitate was collected by suction filtration. Then, the resultant solid was dissolved in THF and filtered. The filtrate was poured into methanol again. The precipitate was further purified with Soxhlet extraction using methanol, hexane, acetone, and chloroform. Finally, the polymer in chloroform fraction was recovered by evaporation of the solvent to give M-polymer as reddish powder (0.13 g, 62% yield). $M_{\rm w} = 25800$ g/mol and PDI = 2.58 GPC (THF).

¹H NMR (CDCl₃, 600MHz): δ (ppm) = 8.13-8.22 (broad), 7.68-8.10 (broad), 7.51-7.59 (broad), 2.05-2.25 (broad), 1.03-1.17 (broad), 0.71-0.99 (broad). ¹³C NMR (CDCl₃, 125 MHz): δ (ppm) = 154.3, 152.9, 152.3, 151.8, 146.3, 140.6, 138.6, 136.7, 133.3, 130.1, 128.7, 128.3, 127.9, 126.3, 125.5, 125.0, 124.0, 120.1, 55.8, 40.4, 31.5, 29.8, 24.0, 22.6, 14.1. Anal. Calcd. For C₃₅H₃₈N₂S₂: C, 76.32%; H, 6.95%; N, 5.09%. Found: C, 74.61%; H, 6.61%; N, 4.67%.

RESULTS AND DISCUSSION

Synthesis and Characterization

The detailed synthetic route to monomers and polymers is given in Scheme 1. The monomer (2) for S-Polymer was prepared by two-step reaction sequence starting from 4-bromo-2,1,3-benzothiadiazole. First, Suzuki coupling reaction between 4-bromo-2,1,3-benzothiadiazole and 3-thienylboronic acid was conducted to afford **1** as viscous liquid. Bromination with NBS was then carried out to obtain monomer (2) as yellowish solid. Similar two-step synthetic procedure was used for the synthesis monomer (4) for M-polymer. By Stille coupling reaction between 4,7-dibromo-2,1,3-benzothiadiazole and 2-(tributylstannyl)thiophene, **3** was prepared as orange solid. Bromination with NBS was then executed to yield monomer (4) as red solid. Each dibromo-monomer (2)

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TABLE 1 Molecular Weight and Thermal Properties ofPolymers

Polymer	<i>M</i> _n (g/mol)	M _w (g/mol)	PDI	<i>T</i> _g (°C)	<i>T</i> d5% (°C)
S-polymer	21400	67900	3.18	156.4	425.0
M-polymer	10000	25800	2.57	140.5	359.0

or (4) was reacted with commercially available fluorene monomer, 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propandiol) ester, in Suzuki coupling condition to yield target S-polymer or M-polymer, respectively, which were purified by sequential Soxhlet extraction using methanol, hexane and acetone. These polymers showed a good solubility in common organic solvents, such as chloroform, toluene, and THF. GPC using polystyrene standard and THF eluent showed a relatively high-molecular weight ($M_w = 67.9$ kg/mol and PDI = 3.18) for S-polymer and a moderate molecular weight ($M_w = 25.8$ kg/mol, PDI = 2.58) for M-polymer (Table 1).

The thermograms of DSC and TGA profiles of the S-polymer and M-polymer are shown in Figure 2 with the numerical data listed in Table 1. As can be seen in Figure 2(b), the onset points of the 5% weight loss ($T_{d5\%}$) under inert atmosphere for the S-polymer and M-polymer are 425 and 359 °C, respectively. The glass transition temperatures (T_g) of the Spolymer and M-polymer are approximately 156 and 141 °C, respectively. The observed high-thermal stabilities for both polymers could minimize not only possible morphological deformation but also degradation of the polymeric active layer in either a PSC or a FET device under an applied electric field.

Optical and Electrochemical Properties

The optical properties of the polymers were investigated by UV-vis absorption measurements on dilute solutions of the polymers in chloroform and spin-cast films on quartz plates. As shown in Figure 3(a), the M-polymer exhibited absorption maximums at much longer wavelengths than those for the Spolymer both in the solution and film states, reflecting a longer effective conjugation length for the main-chain D-A polymer (M-polymer) with a more efficient ICT through 2,5-positions of the thiophene bridge (Fig. 1). The absorption peak near 405 nm in S-polymer can be attributed to the π - π * transition of fluorine-thiophene units in the polymer backbone.²⁵ However, the two absorption peaks in M-polymer were observed at 370 and 510 nm originated from the π - π * transition of fluorene units and the ICT state absorption of the conjugated polymer main chain, respectively. The film absorption spectra of both polymers showed a slight redshifted compared with the corresponding absorption spectra in solution due to the presence of stronger intermolecular interactions in the polymer films. As expected, the S-polymer showed a less significant red-shift (~ 9 nm) relative to the M-polymer (\sim 21 nm) due, probably, to the presence of bulky BT side groups in the S-polymer to prevent the polymer chains from efficient packing. The optical band-gaps (E_{σ}^{opt}) estimated from the band edges of the UV-vis absorption spectra for the S-polymer and M-polymer films are 2.42 eV and 2.01 eV, respectively.

The electrochemical properties of the S-polymer and M-polymer were investigated by CV measurements to understand the charge injection processes of these polymers in their PSCs. The cyclic voltamograms of these polymer films on a glassy carbon electrode with a 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) electrolyte in acetonitrile are shown in Figure 3(b) (see, Experimental), and the relative numerical values are summarized in Table 2. The Ag wire was served as a reference electrode and it was calibrated by ferrocene ($E_{1/2(FC/FC+)} = 0.41$ V). The onset oxidation ($E_{\text{onset}}^{\text{ox}}$) and reduction ($E_{\text{onset}}^{\text{re}}$) potentials occur at 1.04 and -1.42 V for S-polymer and 0.93 and -1.11 V for M-polymer, respectively. According to the empirical equation, $E_{\text{HOMO/LUMO}} = [-(E_{\text{onset}} - E_{1/2(\text{FC/FC}+)}) - 4.8] \text{ eV},^{20,23} \text{ the}$ HOMO and LUMO levels were estimated at -5.43 and -2.97eV for S-polymer and -5.32 and -3.28 eV for M-polymer, respectively. These HOMO and LUMO levels matched well with those of PC71BM required for high-performance BHJ PSCs (Table 2).²⁶ However, the HOMO for S-polymer is



FIGURE 2 (a) DSC thermograms of polymers with a heating rate of 10 °C min⁻¹, and (b) TGA thermograms of polymers with a heating rate of 10 °C min⁻¹ under nitrogen.



FIGURE 3 (a) Normalized absorption spectra of the S-polymer and M-polymer in solutions and films, and (b) cyclic voltammograms of the S-polymer and M-polymer at a scan rate of 50 mV s⁻¹.

slightly lower (~0.1 eV) than that of M-polymer, due to more twisted structure and limited conjugation of the polymer chain.²⁷ The lower HOMO level is favorable in PSCs because it is responsible for the open circuit voltage (V_{oc}) of devices.²⁸ In addition, the electrochemical band-gaps (E_g^{CV}) of S-polymer and M-polymers are 2.46 and 2.04 eV, respectively, which agree well with their optical band-gap (E_g^{opt}) obtained from their UV-vis absorption spectra.

Theoretical Calculations

The frontier molecular orbital of the repeat units and optimized geometry for both the S-polymer and M-polymer were calculated by density functional theory (DFT) on the B3LYP/ 6-31G(d) level with Gaussian 09 program (Fig. 4).²⁹ In the case of M-polymer, the HOMO was found to delocalize on the whole repeating unit, whereas it was partially localized on the benzothiadiazole side chain acceptor in the S-polymer. This result agreed well with UV-vis spectra shown in Figure 3(a), in which M-polymer revealed more red-shifted absorption due to the longer effective conjugation length through efficient 2,5-positions of the thiophene linker and the efficient formation of a ICT state. However, the LUMO of both polymers is mainly localized on acceptor unit and these electron redistributions between the HOMO and LUMO showed a pronounced intramolecular charge separation for the transition state.

Furthermore, the tilted angles of benzothiadiazole unit related to the adjacent thiophene linker in the S-polymer and M-polymer were estimated to be 10.9° and 8.3° , respectively [Fig. 4(b)]. Thus, the more planar geometry with an

favorable conjugation through 2,5-positions of the thiophene in M-polymer should lead to a longer effective conjugation length.

Field-Effect Transistor

Carrier mobilities play an important role in bulk-heterojuction PSCs. To investigate carrier mobility, FETs were fabricated with S-polymer and M-polymer in the top contact geometry, as described in Experimental section. Figure 5(a,b) shows the transport characteristics of FET devices fabricated with the S-polymer and M-polymer in the form of I_{ds} versus $V_{\rm gs}$ and $|I_{\rm ds}|^{1/2}$ versus $V_{\rm gs}$ (both at $V_{\rm gs}=-60$ V). Both $I_{\rm ds}$ versus V_{gs} curves of S-polymer and M-polymer represent typical p-type semiconductor behavior arising from the electron-donating 9,9'-dihexylfluorene group in polymer chain. The saturation-regime mobility was estimated from the slope of drain-to-source current $|I_{ds}|^{1/2}$ as a function of the gate voltage ($V_{\rm g}$).³⁰ The hole mobilities estimated from the FET measurements are 5.20 \times 10⁻⁵ cm² V⁻¹ s⁻¹ and 3.12 \times 10^{-4} cm² V⁻¹ s⁻¹ for S-polymer and M-polymer, respectively. The observed higher hole mobility of M-polymer than that of S-polymer can be attributed to the well-dispersed molecular frontier orbital in HOMO through planar geometry over the whole molecule of the M-polymer, which is beneficial for a high hole mobility.³¹ In addition to the relatively high fieldeffect mobilities, both S-polymer and M-polymer displayed excellent p-type output characteristics with clear saturation. Figure 5(c,d) shows the drain current (I_{ds}) of the devices reached saturation along with the drain voltage ($V_{\rm ds}$) at different gate voltages (V_{gs}).

TABLE 2 Optical and Electrochemical Properties of the S-Polymer and M-Polymers

	λ_{max}^{obs} (nr	n)						
Sample	Solution	Film	$E_{\rm g}^{ m opt}$ (eV)	$E_{\rm onset}^{\rm ox}$ (V) ^a	$E_{\rm onset}^{\rm red}$ (V) ^a	HOMO (eV) ^b	LUMO (eV) ^b	E_{g}^{CV} (eV)
S-polymer	406	415	2.42	1.04	-1.42	-5.43	-2.97	2.46
M-polymer	500	525	2.01	0.93	-1.11	-5.32	-3.28	2.04

^a Onset oxidation and reduction potentials were measured by CV.

^b HOMO/LUMO = $\left[-(E_{\text{onset}} - E_{1/2(\text{FC/FC}+)}) + 4.8\right]$ eV, where $E_{1/2(\text{FC/FC}+)} = 0.41$ V and 4.8 eV is the energy level of ferrocene below the vaccum.



FIGURE 4 (a) The frontier molecular orbitals and the optimized geometries of the repeating unit of S-polymer and M-polymer calculated with DFT at the B3LYP/6-31G level, and (b) energy minimized structures of S-polymer and M-polymer, showing tilted angles.

Photovoltaic Properties

To investigate the photovoltaic properties of the S-polymer and M-polymer, multilayered devices of ITO/PEDOT:PSS/polymer:PC₇₁BM/Al were fabricated and their performances were tested under 100 mW cm² AM 1.5 illumination. To optimize the device performance, various ratios of the polymer:PC₇₁BM in active layer, ranging from 1:2 to 1:4, were investigated and the results are summarized in Table 3. The highest PCE was obtained at the ratio of 1:4 for both polymers. The current-voltage (J-V) curves of the photovoltaic



FIGURE 5 (a,b) Transport characteristics of TFTs of S-polymer and M-polymer. The p-type output curves at different gate voltages for (c) S-polymer and (d) M-polymer.

	Polymer:				
Sample	PC ₇₁ BM (w:w)	$V_{\rm oc}$ (V)	$J_{\rm sc}~({\rm mA/cm^2})$	Fill Factor (FF)	PCE (%)
S-polymer	1:2	0.92	2.67	0.30	0.73
	1:3	0.93	2.89	0.28	0.77
	1:4	0.91	3.38	0.27	0.82
M-polymer	1:2	0.86	3.08	0.30	0.81
	1:3	0.86	3.33	0.34	0.99
	1:4	0.84	4.41	0.33	1.24

TABLE 3 Photovoltaic Performances of Polymer/PC₇₁BM-Based Solar Cells

devices for both polymers at optimized condition are shown in Figure 6(a). The open-circuit voltage (V_{oc}), short-circuit current (J_{sc}) , fill factor (FF) and power conversion efficiency (PCE) for the photovoltaic device based on the S-polymer are 0.91 V, 3.38 mA, 0.27 and 0.82%, respectively. Those of M-polymer are 0.84 V, 4.41 mA, 0.33 and 1.24%, respectively. IPCE spectra of photovoltaic devices for both polymers were given in Figure 6(b), which shows the typical IPCE curves from 350 to 600 nm with the maximum values of 30%. Mpolymer has higher IPCE values at longer wavelengths from 450 to 600 nm. The increased photocurrent in PSCs with Mpolymer is originated from not only the efficient solar light absorption in longer wavelength confirmed by IPCE spectra but also the higher hole mobility of M-polymer proven by FETs measurements. The whole mobility of M-polymer is approximately one order of magnitude higher than that of Spolymer. An interesting feature of S-polymer based PSCs is the high $V_{\rm oc}$ of 0.91 V, which is related to the deep-lying HOMO level (Table 2) and is highly desirable for photovoltaic cells.²⁸

So far, we have investigated the basic properties and device performances of two model D-A polymers with the same composition but different locations for the electron acceptor. M-polymer with main chain acceptor showed superior FET and PSCs performances to those of S-polymer with side chain acceptor due to the better molecular packing of Mpolymers in the solid state associated with its more coplanar structures and a lower band-gap related to the more effective ICT through the 2,5-positions of thiophene bridge.

CONCLUSIONS

Two model D-A conjugated polymers with the same chemical composition, but the BT acceptor can be either at a sidechain (i.e., S-polymer) or along the polymer main chain (i.e., M-polymer), have been synthesized. These polymers consist of fluorene, thiophene, and BT as an electron-donor, conjugated linker and electron acceptor, respectively. Combined experimental and calculation tools have been used to investigate their optical, electrochemical, FET and photovoltaic properties of both polymers. M-polymer with main chain acceptor showed superior FET and PSC performances to those of S-polymer with side chain acceptor. The better performances of M-polymer could be explained by better molecular packing of M-polymers in the solid state associated with its more coplanar structures and a lower band-gap related to the more effective ICT through the 2,5-positions of thiophene bridge. This study provides important insights into the design of ideal structure-property relationships for conjugate polymers in FETs and PSCs.

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FIGURE 6 (a) J–V curves and (b) IPCE spectra of the polymer solar cells based on S-polymer and M-polymer. The weight ratio of polymer and PC₇₁BM is 1:4.

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REFERENCES AND NOTES

1 Poortmans, J.; Arkhipov, V. Thin Film Solar Cells: Fabrication, Characterization And Applications. Wiley, **2006**.

2 Mishra, A.; Fischer, M. K. R.; Bauerle, P. *Angew. Chem. Int. Ed.* **2009**, *48*, 2474–2499.

3 O'regan, B.; Gratzel, M. Nature 1991, 353, 737-740.

4 Brabec, C. J.; Winder, C.; Sariciftci, N. S.; Hummelen, J. C.; Dhanabalan, A.; van Hal, P. A.; Janssen, R. A. J. *Adv. Funct. Mater.* **2002**, *12*, 709–712.

5 Gunes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, 107, 1324–1338.

6 Yu, G.; Gao, J.; Hummelen, J.; Wudl, F.; Heeger, A. *Science* 1995, *270*, 1789–1791.

7 Huo, L.; Tan, Z.; Zhou, Y.; Zhou, E.; Han, M.; Li, Y. *Macromol. Chem. Phys.* **2007**, *208*, 1294–1300.

8 Wang, E.; Wang, M.; Wang, L.; Duan, C.; Zhang, J.; Cai, W.; He, C.; Wu, H.; Cao, Y. *Macromolecules* **2009**, *42*, 4410–4415.

9 Mayer, A. C.; Scully, S. R.; Hardin, B. E.; Rowell, M. W.; McGehee, M. D. *Mater. Today* **2007**, *10*, 28–33.

10 Kim, Y.; Cook, S.; Tuladhar, S. M.; Choulis, S. A.; Nelson, J.; Durrant, J. R.; Bradley, D. D. C.; Giles, M.; McCulloch, I.; Ha, C. S. *Nature Mater.* **2006**, *5*, 197–203.

11 Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nature Mater.* **2005**, *4*, 864–868.

12 Ma, W.; Yang, C.; Gong, X.; Lee, K.; Heeger, A. J. *Adv. Funct. Mater.* **2005**, *15*, 1617–1622.

13 Grabowski, Z. R.; Rotkiewicz, K.; Rettig, W. *Chem. Rev.* **2003**, *103*, 3899–4032.

14 Amir, E.; Sivanandan, K.; Cochran, J. E.; Cowart, J. J.; Ku, S. Y.; Seo, J. H.; Chabinyc, M. L.; Hawker, C. J. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 1933–1941.

15 Beaujuge, P. M.; Amb, C. M.; Reynolds, J. R. *Acc. Chem. Res.* **2010**, *43*, 1396–1407.

16 Cheng, Y. J.; Yang, S. H.; Hsu, C. S. *Chem. Rev.* 2009, 109, 5868–5923.

17 Huo, L.; Tan, Z.; Wang, X.; Zhou, Y.; Han, M.; Li, Y. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 4038–4049.

18 Kroon, R.; Lenes, M.; Hummelen, J. C.; Blom, P. W. M.; de Boer, B. *Polym. Rev.* 2008, *48*, 531–582.

19 Roncali, J.; Leriche, P.; Cravino, A. *Adv. Mater.* **2007**, *19*, 2045–2060.

20 Padhy, H.; Huang, J. H.; Sahu, D.; Patra, D.; Kekuda, D.; Chu, C. W.; Lin, H. C. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 4823–4834.

21 Chang, Y. T.; Hsu, S. L.; Chen, G. Y.; Su, M. H.; Singh, T. A.; Diau, E. W. G.; Wei, K. H. *Adv. Funct. Mater.* **2008**, *18*, 2356–2365.

22 Huang, F.; Chen, K. S.; Yip, H. L.; Hau, S. K.; Acton, O.; Zhang, Y.; Luo, J.; Jen, A. K. Y. *J. Am. Chem. Soc.* **2009**, *131*, 13886–13887.

23 Sahu, D.; Padhy, H.; Patra, D.; Huang, J.; Chu, C.; Lin, H. C. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 5812–5823.

24 Pilgram, K.; Zupan, M.; Skiles, R. *J. Heterocyclic Chem.* 1970, 7, 629–633.

25 Belletete, M.; Morin, J. F.; Beaupre, S.; Ranger, M.; Leclerc, M.; Durocher, G. *Macromolecules* **2001**, *34*, 2288–2297.

26 Chen, J. J. A.; Chen, T. L.; Kim, B.; Poulsen, D. A.; Mynar, J. L.; Frechet, J. M. J.; Ma, B. *ACS Appl. Mater. Inter.* **2010**, *2*, 2679–2686.

27 Zhang, S.; Guo, Y.; Fan, H.; Liu, Y.; Chen, H. Y.; Yang, G.; Zhan, X.; Li, Y.; Yang, Y. *J. Polym. Sci. Part A: Polym. Chem.* **2009**, *47*, 5498–5508.

28 Coakley, K. M.; McGehee, M. D. Chem. Mater. 2004, 16, 4533–4542.

29 Frisch, M.; Trucks, G.; Schlegel, H.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. Gaussian 09, revision A. 02; Gaussian, Inc.: Wallingford, CT, **2009**.

30 Bao, Z.; Locklin, J. J. Organic Field-Effect Transistors, Vol. 128. CRC, **2007**.

31 Cho, S.; Seo, J. H.; Kim, S. H.; Song, S.; Jin, Y.; Lee, K.; Suh, H.; Heeger, A. J. *Appl. Phys. Lett.* **2008**, *93*, 263301-1–263301-3.