9-Alkylidene-9H-Fluorene-Containing Polymer for High-Efficiency Polymer Solar Cells

Chun Du,† Cuihong Li,*‡§ Weiwei Li,† Xiong Chen,† Zhishan Bo,*‡ Wénping Hu,*‡§ and Fengling Zhang*§

†Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
college of Chemistry, Beijing Normal University, Beijing 100875, China
§Department of Physics, Chemistry and Biology, Linköping University, SE-58183 Linköping, Sweden
‡Fraunhofer Institute for Solar Energy Systems ISE, Heidenhofstrasse 2, 79110 Freiburg, Germany

ABSTRACT: A novel donor–acceptor copolymer containing 9-alkylidene-9H-fluorene unit in the main chain, poly[9-(1′-hexylheptylidene)-2,7-fluorene-alt-5,5-(4,7′-di-2-thienyl-5,6′-dialkoxy-2,1,3-benzothiadiazole)] (PAFDTBTT), has been synthesized and evaluated in bulk heterojunction polymer solar cells (BHJ PSCs). The polymer possesses a low band gap of 1.84 eV, a low-lying HOMO energy level (5.32 eV), and excellent solubility in common organic solvents. PSCs based on PAFDTBTT and (6,6)-phenyl-C71-butyric acid methyl ester (PC71BM) demonstrate a power conversion efficiency (PCE) of 6.2% with a high fill factor (FF) of 0.70, which indicates that 9-alkylidene-9H-fluorene can be a very useful building block for constructing narrow band gap conjugated polymers for high-efficiency BHJ PSCs.

INTRODUCTION

Polymer solar cells (PSCs) are the most promising alternatives to inorganic-based solar cells because of their light weight, flexibility, and large-scale manufacturing with low cost roll-to-roll process.1,2 The introduction of the bulk heterojunction (BHJ) concept has led to intensive research worldwide and rapid development in the field of PSCs.3,4 The BHJ is formed by blending an electron-rich polymer as a donor and an electron-deficient fullerene derivative as an acceptor.5,6 Such BHJ not only provides abundant donor–acceptor interfaces for exciton dissociation but also forms an interpenetrating network for free charges transport to collecting electrodes.3,4 Very recently, power conversion efficiency (PCE) higher than 7% has been achieved by several groups,5–10 which is significant progress in the field.

Until now, fullerene derivatives have been proved to be the best and most commonly used electron acceptors.11,12 Therefore, great efforts have been focused on developing new polymers with narrow band gap and beneficial nanoscale morphology.5–10,13–19 Open-circuit voltage ($V_{oc}$) and short-circuit current ($J_{sc}$) are two most important parameters determining PCEs of PSCs. $V_{oc}$ is proportional to the difference between the highest occupied molecular orbital (HOMO) energy level of a donor and the lowest unoccupied molecular orbital (LUMO) energy level of an acceptor, and $J_{sc}$ depends mainly on the LUMO energy level difference between the donor and the acceptor. Empirically, the minimum energy difference of 0.3 eV is required for efficient exciton dissociation.20 Thus, the ideal LUMO energy level of the polymer would be ~3.9 eV, since PCBM possesses a LUMO of 4.2 eV. After years of intensive study, some design criteria for efficient donor materials can be summarized as follows:21 (1) with relatively narrow band gap (the optimal value is about 1.5 eV)22,23 to efficiently absorb sunlight for converting into $J_{sc}$; (2) with balanced HOMO and LUMO energy levels for a maximum $V_{oc}$ and minimum LUMO offset to avoid unnecessary energy loss; (3) good solubility and appropriate miscibility with fullerene derivatives for solution processing and an optimal nanoscale morphology. On the basis of above rules, various low band gap polymers have been synthesized and utilized in PSCs.5–10,13–19 9,9-Dialkylfluorene has been used as a building block for constructing donor–acceptor conjugated polymers in PSCs. In 2003, a low band gap polyfluorene derivative (PFDTBTT) was first reported as a donor in BHJ solar cells with a PCE of 2.2%.24 Although PFDTBTT-based PSCs demonstrated a considerable $V_{oc}$ of 1 V, the low photocurrent, which maybe result from the low carrier mobility of the polymer, limited the efficiency. Later, PFDTBTT polymers carrying different flexible alkyl chains have been studied by several groups, and the PCE was improved to 4.5%.25 Yang et al. found that the bulky side chains at the 9-position sp2-hybridized carbon in fluorene unit of PFDTBTT hindered π–π stacking of polymer chains in solid film, which impedes carrier transport.26

Supporting Information

Received: June 29, 2011
Revised: August 19, 2011
Published: September 08, 2011
In order to have high mobility in solid films, the polymer chains are required to closely pack in solid state. On the other hand, lateral flexible side chains are necessary to guarantee the conjugated polymers with desired solubility and processability in common organic solvents. We must make a balance between close packing and good solubility in designing high-efficiency polymer photovoltaic materials. 9-Alkylidene-9H-fluorene has a sp²-hybridized carbon at the 9-position as shown in Scheme 1a. Compared with 9,9-dialkyl-substituted fluorene, the 9-alkylidene-9H-fluorene unit is inclined to take on a planar conformation, which facilitates the polymer backbones forming close packing in solid state to enhance charge carrier transportation. Here, we demonstrated for the first time that 9-alkylidene-9H-fluorene can be a very useful building block for constructing main chain donor—acceptor alternating narrow band gap conjugated polymers for high-efficiency PSCs. Poly[9-(1'-hexylheptylidene)-2,7-fluorene-alt-5,5-(4',7'-di-2-thienyl-5',6'-dialkoxy-2',1',3'-benzo [c][c] diazole)] (PAFDTBT) (Scheme 1b) has been synthesized and used as a donor in BHJ PSCs. The two hexyl chains on the 9-alkylidene-9H-fluorene unit and the two octyloxy chains on the 2',1',3'-benzo[c][c] diazole unit can provide PAFDTBT good solubility in common organic solvents and will not interfere with the polymer chain packing in solid state. Under simulated solar illumination of AM 1.5G (100 mW/cm²), PCE of 6.2% is achieved in the PSCs composed of PAFDTBT and (6,6)-phenyl-C71-butyric acid methyl ester (PC71BM). The devices illustrate a VOC of 0.89 V, a JSC of 9.9 mA/cm², and a considerably high fill factor (FF) of 0.70. Such high FF at JSC = 9.9 mA/cm² indicates that PAFDTBT with good electric property is a promising donor material for solar cell application. Noticeably, PAFDTBT exhibited much improved PSCs performance when compared with the analogous 9,9-dialkylfluorene-based polymer P1 (Scheme 1b) which showed general PSCs performance with PCE of only 3.1% in our previous report.

RESULTS AND DISCUSSION

Material Synthesis. The synthesis of PAFDTBT is outlined in Scheme 1b. Starting from commercially available 2,7-dibromo-9H-fluorene, 2,7-dibromo-9-(1'-hexylheptylidene)-9H-fluorene (1) was synthesized according to the literature procedure. 2,7-Bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(1'-hexylheptylidene) fluorene (M2) was accomplished in a yield of 60% by Miyaura reaction of 1 and bis(pinacolato)diboron at 80 °C with PdCl₂(dppf) as the catalyst precursor, potassium acetate as the base, and N,N-dimethylformamide (DMF) as the solvent. The synthesis of monomer M1 has been reported in our previous paper. Suzuki—Miyaura—Schütter polymerization of M1 and M2 was carried out in a biphasic mixture of tetrahydrofuran (THF) and toluene (1:1)/aqueous NaHCO₃ with Pd(PPh₃)₄ as the catalyst precursor. After polymerization for 72 h, phenylboronic acid and then bromobenzene were consecutively added at a time interval of 4 h to end-cap the polymer. In order to have stable and high photovoltaic performance conjugated polymers, capping of the end-groups is necessary. PAFDTBT was obtained as a dark red solid in a yield of 92%. The molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC) at 150 °C using 1,2,4-trichlorobenzene as an eluent calibrated with polystyrene standards. PAFDTBT showed a number-average molecular weight (Mn) of 15.9 kg/mol, a weight-average molecular weight (Mw) of 60.5 kg/mol, and a polydispersity index (PDI) of 3.8. High-molecular-weight polymer PAFDTBT...
could be readily dissolved in chloroform, chlorobenzene, 1,2-dichlorobenzene (1,2-DCB), 1,2,4-trichlorobenzene, etc., at elevated temperature. Thermogravimetric analysis (TGA) indicated that PAFDTBT is of good stability up to 340 °C under a nitrogen atmosphere, and differential scanning calorimetry (DSC) revealed no obvious glass transition for PAFDTBT. The X-ray diffraction (XRD) pattern of the powdery sample of PAFDTBT exhibits two peaks as shown in Figure S1 (see Supporting Information); the first peak with small angle of 4.9° indicated the distance of 17.9 Å between polymer backbones separated by alkyl side chains, and the second peak at 21.4° showed the formation a π–π distance of 4.1 Å between the polymer backbones. Such a short distance indicates the planar conformation and the close stacking of the polymer backbones in the solid state.32

Optical and Electrochemical Properties. The absorption spectra of PAFDTBT in chloroform solution and in a film at 20 °C are shown in Figure 1a. In chloroform solution, PAFDTBT displays two absorption bands centered at 380 and 522 nm. In comparison with solution absorption, the absorption peaks in the film are red-shifted to 392 and 571 nm, respectively, and became broader. The red shift that occurs in going from the solution to the film is attributed to the aggregation of the polymer chains in the solid state. The onset of the optical absorption of the PAFDTBT film is at 671 nm, corresponding to an optical band gap of 1.84 eV. The HOMO energy level is determined by cyclic voltammogram to be at −5.32 eV, and the LUMO energy level of PAFDTBT is calculated to be −3.48 eV according to the HOMO energy level and the optical band gap. Such high LUMO energy level is expected to provide an enough driving force for efficient exciton dissociation.21 Meanwhile, the low-lying HOMO energy level of PAFDTBT can offer a high V_{oc} when blended with a fullerene derivative as an acceptor. As PAFDTBT has low absorption around 450 nm, PC71BM was chosen as an electron acceptor for the BHJ solar cells to increase light absorption in

Table 1. Photovoltaic Parameters of PAFDTBT:PC71BM and P1:PC71BM Fabricated from 1,2-DCB with or without 0.5 vol % DIO

<table>
<thead>
<tr>
<th>active layer</th>
<th>solvent</th>
<th>V_{oc} [V]</th>
<th>J_{sc} [mA/cm²]</th>
<th>FF</th>
<th>PCE [%]</th>
<th>thickness [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAFDTBT:PC71BM</td>
<td>1,2-DCB</td>
<td>0.89</td>
<td>10.5</td>
<td>0.51</td>
<td>4.8</td>
<td>87</td>
</tr>
<tr>
<td>PAFDTBT:PC71BM</td>
<td>1,2-DCB + 0.5% DIO</td>
<td>0.89</td>
<td>9.9</td>
<td>0.7</td>
<td>6.2</td>
<td>85</td>
</tr>
<tr>
<td>P1:PC71BM</td>
<td>1,2-DCB</td>
<td>0.97</td>
<td>6.7</td>
<td>0.47</td>
<td>3.1</td>
<td>80</td>
</tr>
<tr>
<td>P1:PC71BM</td>
<td>1,2-DCB + 0.5% DIO</td>
<td>0.97</td>
<td>4.1</td>
<td>0.56</td>
<td>2.3</td>
<td>80</td>
</tr>
</tbody>
</table>

Data from ref 27.
visible region.33 As can be observed in Figure 1a, the PAFDTBT/PC71BM BHJ film (1:3 by weight) has broad absorption covering the UV−vis range. For the analogous 9,9-dialkyl-9H-fluorene-based polymer P1, the absorption spectrum in solution shows the maximum absorption bands are 389 and 528 nm, which are almost similar as the absorption peaks of PAFDTBT in solution. However, there is a red shift of only 20 nm when it goes from the solution to the solid state as shown in Figure 1b. PAFDTBT shows a larger red-shift (about 50 nm from the solution to the film state) than 9,9-dialkyl-9H-fluorene-based P1, which is attributed to that 9-alkylidene-9H-fluorene-based PAFDTBT has a more planar structure and aggregation (an orderly π−π stacking) is formed in the solid state. Meanwhile, PAFDTBT possesses a lower optical band gap of 1.84 eV than that of P1 (2.04 eV) deduced from the onset of the optical absorption at 608 nm.27 The optical properties indicate PAFDTBT is a promising material for solar cell applications.

Photovoltaic Properties. The photovoltaic properties of PAFDTBT were investigated by blending PAFDTBT and PC71BM in 1,2-DCB at different weight ratios, different concentrations, different spin-coating speeds, and containing different volumes of 1,8-diiodooctane (DIO) as a processing additive. The characterization showed that the optimized stoichiometry of PAFDTBT to PC71BM is 1:3 by weight, the blend concentration is 28 mg/mL, DIO content is 0.5 vol % in 1,2-DCB, and the spin-

![Figure 3](image1.png)

**Figure 3.** EQE curves of the solar cells based on the PAFDTBT:PC71BM (1:3, w/w) blends in 1,2-DCB with (dashed line) and without (solid line) 0.5 vol % DIO.

![Figure 4](image2.png)

**Figure 4.** Output (a) and transfer characteristics (b) of the spin-coated film of PAFDTBT transistors based on OTS-modified Si/SiO2 substrate. Output (c) and transfer characteristics (d) of the spin-coated film of the blend of PAFDTBT:PC71BM transistors based on OTS-modified Si/SiO2 substrate.

![Figure 5](image3.png)

**Figure 5.** Transfer characteristics of the device of the film from the blend of PAFDTBT:PC71BM in 1,2-DCB with (dashed line) and without (solid line) 0.5 vol % DIO.
coating speed is 600 rpm. The photovoltaic device structure employed in this study was ITO/PEDOT:PSS (40 nm)/PAFDTBT:PC71BM (85 nm)/LiF (0.4 nm)/Al (95 nm). Figure 2a shows the typical current density–voltage (J–V) characteristics of solar cells under 1 sun of simulated AM 1.5G solar radiation (100 mW/cm²). PSCs were first fabricated from the blend of PAFDTBT:PC71BM = 1:3 in 1,2-DCB. In this condition, the best performance was obtained at a weight ratio of 1:3, with \( V_{oc} = 0.89 \text{V}, J_{sc} = 10.5 \text{mA/cm}^2, \) FF = 0.51, and an overall PCE of 4.8%. The noticeably feature of PAFDTBT-based solar cells is high \( V_{oc} \) which has been expected from the deep lying HOMO energy levels of PAFDTBT. In addition, almost all devices present comparable parameters with \( J_{sc} \) above 10 mA/cm² as shown in Figure S2 (see Supporting Information). Furthermore, the device performance can be pronouncedly improved with the addition of a small amount (0.5 vol %) of the processing additive DIO. In this condition, PCE of 6.2% was achieved in the champion solar cell with \( V_{oc} = 0.89 \text{V}, J_{sc} = 9.9 \text{mA/cm}^2, \) and FF = 0.70. It is especially striking that FF was improved 37% with the addition of the additive DIO although \( V_{oc} \) is the same as and \( J_{sc} \) is almost even up with the PSCs without DIO according to the statistical data in Figure S2. Just as expected, PAFDTBT-based PSCs exhibited higher \( J_{sc} \) especially higher FF than P1-based PSCs as shown in Figure 2b, which showed PCE of 3.1% with \( V_{oc} = 0.97 \text{V}, J_{sc} = 6.7 \text{mA/cm}^2, \) and FF = 0.47. The addition of the processing additive DIO cannot enhance the photovoltaic performance of P1-based solar cells. The photovoltaic parameters are summarized in Table 1. Therefore, it can be concluded that 9-alkylidene-9H-fluorene as a donor unit presents some advantages over 9,9-dialkyl-substituted 9H-fluorene units. First of all, the alkyl chains on 9-alkylidene-9H-fluorene could decrease the steric hindrance compared with 9,9-dialkyl-substituted 9H-fluorene units and also form a planar structure to improve the intermolecular stacking of the polymers, resulting in the improved charge mobility. Further, the extended π-conjugation in the 9-alkylidene-9H-fluorene unit will act as a stronger electron-rich donor, resulting in a lower band gap. Third, due to the better crystallinity of PAFDTBT, favorable morphology of the blend film for good photovoltaic performance can be achieved with the help of the additive. The external quantum efficiencies (EQEs) were measured under illumination of monochromatic light. As shown in Figure 3, a significant photo-to-current response can be observed in nearly the entire visible range of 370–570 nm with EQE value of 50–60% for both the PAFDTBT-based devices with and without DIO. This high EQE response and high FF of 0.70 also indicate balanced charge transport and improved active-layer morphology due to the addition of DIO.34

Bottom-gate, top-contact organic field effect transistors (OFETs) were fabricated from PAFDTBT and the blend of PAFDTBT:PC71BM (1:3, w/w) to investigate the charge transport property. The hole mobility of the pristine PAFDTBT film spin-cast from 1,2-DCB solution was 1.67 \times 10^{-3} \text{cm}^2 \text{V}^{-1} \text{s}^{-1} with on/off ratios in the order of 10^5. When PAFDTBT film was treated by solvent-assistant annealing at 120 °C for 15 min, the hole mobility was further improved 1 order of magnitude to 1.0 \times 10^{-2} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}. Moreover, the hole mobility of the film spin-cast from the blend of PAFDTBT:PC71BM (1:3, w/w) in 1,2-DCB solution was also investigated, which is 1.40 \times 10^{-3} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}. The output and transfer characteristic curves of the related OFETs are shown in Figure 4. Significantly, the hole mobility of the film spin-cast from the blend of PAFDTBT:PC71BM (1:3, w/w) in 1,2-DCB solution was further improved for almost 3 times to 3.93 \times 10^{-3} \text{cm}^2 \text{V}^{-1} \text{s}^{-1} with the addition of DIO (0.5 vol %) without further device optimization as shown in Figure 5. The data are summarized in Table S1 (see Supporting Information). Hence, the large increase in FF with the addition of DIO was attributed, at least partially, to the increased hole mobility induced by DIO.

Atomic force microscopy (AFM) was used to investigate the surface morphology of the blend of PAFDTBT:PC71BM = 1:3 in 1,2-DCB with or without the additive DIO, since the morphology of the blend film can largely affect charge separation and transport. As shown in Figure 6, AFM images show the blend film of PAFDTBT:PC71BM = 1:3 in 1,2-DCB with or without the additive DIO both possess uniform and finer structures. However, without the additive the surface of the active layers of PAFDTBT:PC71BM is quite smooth, with a root-mean-square (rms) of 0.486 nm. Meanwhile, with the addition of DIO (0.5 vol %), the surface of the active layers become rough, with a rms of...
0.735 nm, which suggested larger phase separation is more favorable for charge transport. The increase of surface roughness and the occurring of the phase separation are responsible for the enhancement of FF with the addition of DIO. Without addition of DIO, despite high charge separation efficiency observed by efficient photoluminescence (PL) quenching for PAFDTBT (see Figure S4 in Supporting Information), a small fraction of carriers might recombine at donor/acceptor interfaces before reaching the electrodes, since the charge transfer state (CT) emission occurred at 850 nm in PL spectra. With addition of DIO, the phase separation of the active layers of PAFDTBT:PC71BM increases, and charge separation efficiency decrease a little as shown by incomplete PAFDTBT PL quenching, but the charge carrier mobility increased and recombination decreased, which resulted in improved FF. The appropriated domain sizes and phase separation can produce the best photovoltaic performance. With the addition of a larger amount of DIO (1% and 2%), the blend morphology showed strikingly different. The roughness increased a lot and too big phase separation deteriorated photovoltaic performance (Figure S3 and Table S2 in Supporting Information). Only 0.5% DIO provided the best performance. This finding highlights that controlling the morphology of the donor/acceptor network is critical to optimize efficiency.

**CONCLUSIONS**

A novel 9-alkylidene-9H-fluorene containing main chain donor–acceptor type polymer (PAFDTBT) has been designed, synthesized, and applied in BHJ PSCs. PCE of 6.2% with $V_{oc} = 0.89$, $J_{sc} = 9.9$ mA/cm², and FF = 0.70 was achieved in PSCs based on PAFDTBT:PC71BM, which indicates that PAFDTBT is a promising candidate for high-efficiency solar cells. To the best of our knowledge, PAFDTBT is the first 9-alkylidene-9H-fluorene-containing low band gap conjugated polymers used for BHJ PSCs. Our research results suggest that 9-alkylidene-9H-fluorene can be a very useful building block for the construction of narrow band gap conjugated polymers for high-efficiency BHJ polymer photovoltaic cells.

**EXPERIMENTAL SECTION**

**Materials and Instruments.** Unless otherwise noted, all chemicals were purchased from Aldrich or Acros and used without further purification. Solvents were dried using standard procedures. The catalyst precursor Pd(PPh₃)₄ was prepared according to the literature and stored in a Schlenk tube under nitrogen. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium with benzophenone as an indicator under nitrogen atmosphere. Hexane and dichloromethane (CH₂Cl₂) were distilled from CaH₂. Chloroform was distilled before using. 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 300 or AV 400 spectrometer in CDCl₃. UV–vis absorption spectra were obtained on a Shimadzu UV–vis spectrometer model UV–1601PC. Fluorescence spectra were recorded on a Varian FLS920. Elemental analyses were performed on a Flash EA 1112 analyzer. Thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on TA2100 and Perkin-Elmer Diamond DSC instrument, respectively, under a nitrogen atmosphere at a heating rate of 10 °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) chromatography 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 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 KR radiation. The electrochemical behavior of PAFDTBT was investigated using cyclic voltammetry (CHI 630A electrochemical analyzer) with a standard three-electrode electrochemical cell in a 0.1 M tetrabutylammonium tetrfluoroborate solution in CH₃CN at room temperature at a scanning rate of 0.1 V s⁻¹. A glassy carbon 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/ferrocnium (Fc) redox system and assumption that the energy level of Fc is 4.8 eV below vacuum.

**Synthesis of 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolo-5-yl)-9-(1’-hexylthiophenyl)fluorene (M2).** A mixture of 2,7-dibromo-9-(1’-hexylthiophene)fluorene (1) (0.20 g, 0.4 mmol), bis-pinacol diboron (0.26 g, 1.0 mmol), PdCl₂(dppf) (9.76 mg, 0.012 mmol), and potassium acetate (0.24 g, 2.4 mmol) was stirred for 3 days at 80 °C. After cooling the reaction mixture, water was added to the above solution for extraction with diethyl ether. The obtained organic layer was washed with brine and dried over Na₂SO₄. After the solvent was removed under pressure, the crude product was purified by flash column chromatography (SiO₂, petroleum ether 60 – 90 °C/ethyl acetate = 4/1 by volume) to give a pale yellow oil; after crystallization from petroleum ether M2 was obtained in 60% yield as a white crystal (141 mg). ¹H NMR (400 MHz, CDCl₃) δ: 8.24 (s, 2H), 7.82 – 7.80 (d, 2H), 7.75 – 7.67 (d, 2H), 2.84 – 2.80 (m, 4H), 1.76 – 1.72 (m, 4H), 1.63 – 1.60 (m, 4H), 1.42 – 1.41 (m, 8H), 1.36 (s, 24H), 0.96 – 0.93 (m, 16H). ¹³C NMR (100 MHz, CDCl₃) δ: 152.3, 142.0, 138.3, 132.7, 131.4, 130.9, 119.1, 83.6, 37.9, 31.7, 29.8, 28.2, 24.9, 22.8, 14.1. Anal. Calc'd for C₃₆H₃₄B₂O₂: C = 76.26, H = 9.43. Found: C = 76.48, H = 9.41.

**Synthesis of Poly[(9’-1-hexylthiophenyl)-2,7-fluorene-alt-5,5-(4’,7’-di-2-thienyl-5’-6’-dialkoxy-2’,1’,3’-benzo thiadiazole)] (PAFDTBT).** A mixture of M1 (100.0 mg, 0.14 mmol) and M2 (83.74 mg, 0.14 mmol), THF (10 mL), toluene (10 mL), H₂O (2 mL), and NaHCO₃ (0.2 g, 2.4 mmol) was carefully degassed before and after Pd(PPh₃)₄ (1.8 mg, 1.6 μmol) was added. The mixture was stirred and refluxed under nitrogen. After 3 days phenylboronic acid (10 mg) and Pd(PPh₃)₄ (1.8 mg, 1.6 μmol) was added to the reaction, and then 4 h later, bromobenzene (100 mL) was added and the reaction refluxed overnight to complete the end-capping reaction. After being cooled to room temperature, water and chlorobenzene were then added; the organic layer was separated and washed three times with water. Then the solutions were 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 again dissolved 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. A dark red polymer PAFDTBT (115 mg; yield of 92%) was obtained. ¹H NMR (400 MHz, CDCl₃) δ: 8.50 (br, 2H), 8.14 (br, 2H), 7.77 – 7.67 (br, 4H), 7.46 (br, 2H), 4.20 (br, 4H), 2.90 (br, 4H), 2.01 (br, 4H), 1.84 (br, 4H), 1.70 (br, 4H), 1.30 – 1.64 (br, 28H), 0.91 – 0.90 (br, 12H). ¹³C NMR (100 MHz, CDCl₃) δ: 151.70, 150.89, 146.77, 146.67, 139.50, 138.83, 133.37, 133.10, 131.88, 124.44, 122.59, 122.28, 119.68, 117.42, 74.40, 37.90, 32.00, 31.93, 30.68, 30.18, 29.74, 29.43, 28.20, 26.19, 22.80, 22.72, 14.35, 14.27. Anal. Calc'd for C₃₆H₃₄N₂O₂S₄: C = 74.79, H = 7.85, N = 3.11. Found: C = 72.97, H = 7.61, N = 2.67. GPC (PS standards): $M_m = 60 500$ g/mol, $M_w = 15 900$ g/mol, and PDI = 3.8.
Polymer Solar Cell Fabrication and Characterization. Polymer solar cells (PSCs) were fabricated with the device configuration of ITO/PEDOT:PSS/polymer:PC_{71}BM (1:3)/LiF/Al. The conductivity of ITO was 15 Ω·cm, and PEDOT:PSS is Baytron Al 4083 from H.C. Starck. Prior to use, the substrates were subject to cleaning with ultrasonication in acetone, 2-propanol, and deionized water successively for 10 min each. The substrates were dried under a stream of nitrogen and subjected to the treatment of UV-ozone for 20 min. PEDOT:PSS in water was filtered with a 0.45 μm PVDF film, spun-cast onto the clean substrates, and then transferred into the glovebox and baked at 130 °C for 10 min. The blend of PAFDTBT and PC_{71}BM was dissolved in 1,2-DCB or 1,2-DCB with 0.5 vol % DIO with the polymer concentration of 7 wt %. The mixture was stirred for 12 h and then kept in a vacuum chamber for 2 days. 30 μL of the mixture was casted on the ITO/PEDOT:PSS substrate. The spin-coated or casted films were then baked at 110 °C for 2 min and 130 °C for 10 min. The blend of F6TBT and PC_{71}BM was dissolved in 1,2-DCB or 1,2-DCB with 0.5 vol % DIO with the polymer concentration of 5 wt % and then kept in a vacuum chamber for 2 days. 30 μL of the mixture was casted on the ITO/PEDOT:PSS substrate. The spin-coated or casted films were then baked at 110 °C for 2 min and 130 °C for 10 min.

Fabrication and Characterization of Organic Field-Effect Transistors (OFETs). Top-contact devices were fabricated based on Si/SiO_{2} substrates (the back low resistance Si as gate, SiO_{2} (500 nm) as gate insulator) with a capacitance of 7.5 nF cm^{-1}, 1,2-DCB and 0.5 vol % DIO with the polymer concentration of 7 mg mL^{-1}. Electrodes of Au (25 nm) were vacuum-deposited on films with a width/length = 50 (channel width = 2.5 mm, channel length = 50 μm). J–V characteristics were obtained using a Keithley 4200 SCS with a Micromanipulator 6150 probe station in a clean and shielded box at 20 °C. The voltage was increased from -4 to +4 V with 0.1 V increments, and the current was measured at each voltage. 20 transistors were examined at each condition.

Acknowledgment
We thank the financial support by the NSF of China (20834006 and 50821062) and 973 Program (2011CB935703 and 2009CB623603) F.Z. thanks the financial support for the collaboration with IC, CAS from Swedish Research Council (VR), and for visiting Fraunhofer ISE from VINNOVA (VINNMER).

References


