Macromolecules

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

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S Supporting Information

ABSTRACT: A novel donor—acceptor copolymer containing 9-alkylidene-9*H*-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)] (PAFDTBT), 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 PAFD-TBT 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.^{3,4} 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} Opencircuit 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 exicton dissociation.^{2,20} Thus, the ideal LUMO energy level of the polymer would be \sim 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_{sci} (2) with balanced HOMO and LUMO energy levels for a maximum Voc 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 (PFDTBT) was first reported as a donor in BHJ solar cells with a PCE of 2.2%.²⁴ Although PFDTBT-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, PFDTBT 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 sp³-hybridized carbon in fluorene unit of PFDTBT hinders $\pi - \pi$ stacking of polymer chains in solid film, which impedes carrier transport.²

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Scheme 1. (a) Chemical Structures of 9,9-Dialkyl-Substituted 9H-Fluorene and 9-Alkylidene-9H-fluorene; (b) Synthetic Route to Polymer PAFDTBT and Chemical Structure of the 9,9-Dialkyl-9H-fluorene-Based Polymer P1^a



^{*a*} Conditions and reagents: (i) *t*-BuOK, CS₂, MeI, DMSO, rt; (ii) C₆H₁₃MgBr, Li₂CuCl₄, THF, -5 °C; (iii) PdCl₂(dppf), potassium acetate, bis(pinacolato)diboron, DMF, 80 °C; (iv) Pd(PPh₃)₄, NaHCO₃, THF-toluene (v/v, 1:1)/H₂O, reflux; (v) phenylboronic acid, then bromobenzene.

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,²⁶ which facilitates the polymer backbones forming close packing in solid state to enhance charge carrier transportation.²⁶ Here, we demonstrated for the first time that 9-alkylidene-9Hfluorene 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'-benzothiadiazole)] (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'-benzothiadiazole 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/cm^2), 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 $V_{\rm oc}$ of 0.89 V, a $J_{\rm sc}$ of 9.9 mA/cm², and a considerably high fill factor (FF) of 0.70. Such high FF at $J_{sc} = 9.9 \text{ mA/cm}^2$ 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.²⁷

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.²⁶ 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.²⁸ Suzuki-Miyaura-Schlüter 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.^{29–31} 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 numberaverage molecular weight (M_n) of 15.9 kg/mol, a weight-average molecular weight (M_w) of 60.5 kg/mol, and a polydispersity index (PDI) of 3.8. High-molecular-weight polymer PAFDTBT



Figure 1. UV-vis absorption spectra of PAFDTBT (a) and P1 (b) in CHCl₃ (solid line) and in film (dashed line) at 20 °C.



Figure 2. J-V curves for the BHJ solar cells derived from the blend of PAFDTBT:PC₇₁BM (a) and P1:PC₇₁BM (b) in 1,2-DCB with (dashed line) and without (solid line) 0.5 vol % DIO.

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

active layer	solvent	$V_{\rm oc} \left[{\rm V} ight]$	$J_{\rm sc} [{\rm mA/cm}^2]$	FF	PCE [%]	thickness [nm]
PAFDTBT:PC71BM	1,2-DCB	0.89	10.5	0.51	4.8	87
PAFDTBT:PC71BM	1,2-DCB + 0.5% DIO	0.89	9.9	0.7	6.2	85
$P1:PC_{71}BM^{a}$	1,2-DCB	0.97	6.7	0.47	3.1	80
P1:PC ₇₁ BM	1,2-DCB + 0.5% DIO	0.97	4.1	0.56	2.3	80
^{<i>a</i>} Data from ref 27.						

could be readily dissolved in chloroform, chlorobenzene, 1,2dichlorobenzene (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 angel 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 $\pi - \pi$ 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

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-9*H*-fluorenebased 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 show in Figure 1b. PAFDTBT shows a larger red-shift (about 50 nm from the solution to the film state) than 9,9-dialkyl-9*H*-fluorene-based **P1**, which is attributed to that 9-alkylidene-9*H*-fluorene-based PAFDTBT has a more planar structure and aggregation (an orderly $\pi - \pi$ stacking) is formed



Figure 3. EQE curves of the solar cells based on the PAFDTBT: $PC_{71}BM$ (1:3, w/w) blends in 1,2-DCB with (dashed line) and without (solid line) 0.5 vol % DIO.

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 $PC_{71}BM$ in 1,2-DCB at different weight ratios, different concentration, 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 $PC_{71}BM$ 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 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.



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 6. AFM images (5 × 5 μ m²) of PAFDTBT/PC₇₁BM film prepared by spin-coating from 1,2-DCB solution without (a) and with (b) DIO (0.5 vol %).

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/cm^2). PSCs were first fabricated from the blend of PAFDTBT:PC₇₁BM in 1,2-DCB. In this condition, the best performance was obtained at a weight ratio of 1:3, with $V_{\rm oc} = 0.89$ V, $J_{\rm sc} = 10.5$ mA/cm², FF = 0.51, and an overall PCE of 4.8%. The noticeably feature of PAFDTBT-based solar cells is high V_{oct} 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 $V_{\rm oc}$ = 0.89 V, $J_{\rm sc}$ = 9.9 mA/cm², and FF = 0.70. It is especially striking that FF was improved 37% with the addition of the additive DIO although $V_{\rm oc}$ 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, 27 which showed PCE of 3.1% with $V_{\rm oc} = 0.97$ V, $J_{\rm sc} = 6.7$ mA/cm², 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-9*H*-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 PAFDTBTbased 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 1.67×10^{-3} cm² V⁻¹ 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,³⁵ 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 imes 10^{-3} cm² V⁻¹ 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 3.93×10^{-3} cm² V⁻¹ 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.^{36,37} 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.³⁶ 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.³⁸ 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 incompleted 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.⁴ 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-9*H*-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 V, 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-9*H*-fluorene-containing low band gap conjugated polymers used for BHJ PSCs. Our research results suggest that 9-alkylidene-9*H*-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 literature³⁹ 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 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 DM 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 FLR025. 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 by using cyclic voltammetry (CHI 630A electrochemical analyzer) with a standard three-electrode electrochemical cell in a 0.1 M tetrabutylammonium tetrafluoroborate solution in CH₃CN at room temperature at atmosphere with 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/ferrocenium (Fc) redox system and assumption that the energy level of Fc is 4.8 eV below vacuum.⁴⁰

Synthesis of 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9-(1'-hexylheptylidene)fluorene (M2). A mixture of 2,7-dibromo-9-(1'-hexylheptylidene)fluorene (1) (0.20 g, 0.4 mmol), bis-pinacoldiboron (0.26 g, 1.0 mmol), PdCl₂(dppf) (9.76 mg, 0.012 mmol), and potassium acetate (0.24 g, 2.4 mmol) in DMF (20 mL) 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 recrystallization 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, 6H). 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. Calcd for C₃₈H₅₆B₂O₄: C 76.26, H 9.43. Found: C 76.48, H 9.41.

Synthesis of Poly[9-(1'-hexylheptylidene)-2,7-fluorenealt-5,5-(4',7'-di-2-thienyl-5',6'-dialkoxy-2',1',3'-benzothiadiazole)] (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 $Pd(PPh_3)_4$ (1.8 mg, 1.6 μ mol) was added. The mixture was stirred and refluxed under nitrogen. After 3 days phenylboronic acid (10 mg) and $Pd(PPh_3)_4$ (1.8 mg, 1.6 μ mol) were added to the reaction, and then 4 h later, bromobenzene (100 μ L) 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. And 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, a 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). 13 C 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. Calcd for C56H70N2O2S3: C 74.79, H 7.85, N 3.11. Found: C 72.97, H 7.61, N 2.67. GPC (PS standards): $M_w = 60500 \text{ g/mol}, M_n = 15900 \text{ g/mol}, \text{ and}$ PDI = 3.8.

Polymer Solar Cell Fabrication and Characterization. Polymer solar cells (PSCs) were fabricated with the device configuration of ITO/PEDOT:PSS/polymer:PC71BM (1:3)/LiF/Al. The conductivity of ITO was 15 Ω/\Box , and PEDOT:PSS is Baytron Al 4083 from H.C. Starck. Prior to use, the substrates were subjected to cleaning with ultrasonication in acetone, 2-propanol, and deionized water successively for 10 min each. The substrates were dried under a steam of nitrogen and subjected to the treatment of UV-ozone for 20 min. PEDOT:PSS in water was filtered with a 0.45 μ m 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 PC71BM was dissolved in 1,2-DCB or 1,2-DCB with different volumes of DIO and heated at 90 °C for overnight to ensure the sufficient dissolution and then spun-cast onto the PEDOT:PSS layer. The prepared films were kept in a vacuum chamber overnight before evaporated 0.4 nm LiF followed by 95 nm Al at a pressure of 1×10^{-6} mbar. Six cells were fabricated on one substrate with an effective area of 0.092 cm². The measurement of devices was conducted in the glovebox. The temperature while measuring the I-V curves was ~25 °C. Detailed information on the setup for device characterization can be found in ref 41.

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 wate = 2:1), 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.⁴² Polymer or polymer/PC₇₁BM films were casted or spin-coated on the OTS-modified Si/SiO2 substrate from 1,2-DCB or 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 width/length = 50 (channel width = 2.5 mm, channel length = 50 μ m). *J*-*V* characteristics were obtained using a Keithley 4200 SCS with a Micromanipulator 6150 probe station in a clean and shielded box at room temperature in air. In order to confirm the reproducibility, about 10-20 transistors were examined at each condition.

ASSOCIATED CONTENT

Supporting Information. XRD, the performance parameters distribution characterization, AFM images, PL spectra, detailed mobility performance. This material is available free of charge via the Internet at http://pubs.acs.org.

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