Macromolecules

Synthesis and Photovoltaic Properties of Quinoxaline-Based Alternating Copolymers for High-Efficiency Bulk-Heterojunction Polymer Solar Cells

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S Supporting Information

ABSTRACT: A series of quinoxaline-based copolymers, namely, poly[N-9"-heptadecanyl-2,7-carbazole-*alt*-5,5-(5',8'-di-2-thienyl-quinoxaline)] (P1), poly[N-9"-heptadecanyl-2,7-carbazole-*alt*-5,5-(5',8'-di-2-thienyl-2,3-bis(4-octyloxyl)phenyl)quinoxaline] (P2), and poly[N-9"-heptadecanyl-2,7-carbazole-*alt*-5,5-(5',8'-di-2-thienyl-2,3-bis(4-(3,7-dimethyloctyloxy)phenyl)quinoxaline] (P3), were synthesized and characterized for use in polymer solar cells (PSCs). We describe the effect of modifying the alkyl group of the side chain of the quinoxaline derivatives on the electronic and optoelectronic properties of the polymers. The field-effect



hole mobility as well as the electronic energy levels and processability of the materials for PSC applications were investigated. Among the studied quinoxaline-based copolymers, P2 showed the best photovoltaic performance with an open-circuit voltage (V_{OC}) of 0.82 V, a short-circuit current density (J_{SC}) of 9.96 mA/cm², a fill factor (FF) of 0.49, and a power-conversion efficiency of 4.0% when a P2/PC₇₁BM blend film was used as the active layer under AM 1.5 G irradiation (100 mW/cm²).

INTRODUCTION

Recently, polymer solar cells (PSCs) have attracted considerable attention because of their unique advantages, which include low cost, lightweight, solution processability, and flexibility. Thus, enormous effort has been focused on improving the power conversion efficiency (PCE) of PSCs for future commercial applications.¹⁻⁸ To date, highly efficient PSCs based on poly-(3-hexylthiophene) (P3HT) as the electron-donor material and [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM) as the acceptor have been reported with a power conversion efficiency of 4-5%.^{9,10} One of the main factors limiting the performance of PSCs is the mismatch of their absorption to the terrestrial solar spectrum. Recently, several studies on low-band gap conjugated polymers have been pursued in order to match the absorption spectrum of the active layer to the solar spectrum.¹¹⁻¹³ The most successful approach to achieving low-band gap polymers is a copolymerized donor-acceptor structure. Copolymerization of the donor, with a higher HOMO (highest occupied molecular orbital) energy level, and the acceptor, with a lower LUMO (lowest unoccupied molecular orbital) energy level, results in a lower band gap polymer due to an intramolecular charge transfer (ICT) from the donor to the acceptor.^{14,15} Another approach to designing low-band gap conjugated polymers is the introduction of electron-releasing effects, such as long flexible alkyl and alkoxy

chains, to increase the conjugation length.^{16,17} However, pendant chains can give rise to affect steric interactions and the coplanarity of the polymer backbone, resulting in a change of the optical and electrochemical properties of the donor—acceptor polymers.

Among the various conjugated polymers, polyfluorene and polycarbazole derivatives have deep HOMO levels that increase the open-circuit voltage ($V_{\rm OC}$) of the PSCs.^{18,19} Recently, Leclerc et al. reported a systematic study of PSCs using various poly(2,7-carbazole) derivatives. In that work, the researchers varied the electron-withdrawing unit of the polymers.^{20,21} Poly[*N*-9"-heptadecanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole) (PCDTBT) and PC₆₁BM composites provide a promising efficiency of 3.6%. Further optimization of the device for PCDTBT led to a PCE of 6.1%.⁶ However, all these polymers, except for PCDTBT, show hole-mobility values between 10^{-5} and 10^{-4} cm²/(V s) in organic field-effect transistors (OFETs), resulting in a low power-conversion efficiency of 1–2%.

In this study, poly[*N*-9"-heptadecanyl-2,7-carbazole-*alt*-5,5-(5',8'-di-2-thienylquinoxaline)] (P1), poly[*N*-9"-heptadecanyl-2,

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7-carbazole-alt-5,5-(5',8'-di-2-thienyl-2,3-bis(4-octyloxyl)phenyl)quinoxaline] (P2), and poly N-9''-heptadecanyl-2,7-carbazole-*alt*-5,5-(5',8'-di-2-thienyl-2,3-bis(4-(3,7-dimethyloctyloxy)phenyl)quinoxaline] (P3), which have the same polymer backbone but different side chains, were studied in order to achieve a higher efficiency value and investigate the side-chain effect. Actually, the synthesis and solar cell devices of the polymer called P1 has actually been published earlier,²¹ and P1 was synthesized for the purpose of direct comparison. Although the backbone of the copolymers with similar structure have been described in the literature except differences in the solubilizing side chains, 2^{2-25} the effect of the alkoxy side chains on the electronic, optoelectronic, and photovoltaic properties has not been reported for PSCs based on polymers with quinoxaline units. Compared to P1, the alkoxy side chains on the quinoxaline units, which have been used earlier in other polymers for solar cells,²⁶ can enhance the solubility and the charge transfer to electron acceptors such as PCBM. In general, bulky side chains have a negative effect on the carrier mobility, since interchain hopping of carriers requires a favorable overlapping of the electron wave function of adjacent conjugated units on the polymer main chains.²⁷ Therefore, from the viewpoint of $\pi - \pi^*$ stacking, the quinoxaline- (Qx-) based copolymers with different side chains were designed and synthesized. We systematically investigated the synthesis, thermal stability, optical and electrochemical properties, field-effect carrier mobilities, and photovoltaic characteristics of the resulting polymers. Our results provide valuable information on the relationship between polymer design at the molecular level and its electrical performance in field-effect transistors (FETs) and polymer solar cells.

RESULTS AND DISCUSSION

Synthesis and Characterization of the Polymers. The synthetic routes for preparing the Qx-based polymers are shown in Scheme 1. Three types of Qx-based copolymers, namely, poly[*N*-9"-heptadecanyl-2,7-carbazole-*alt*-5,5-(5',8'-di-2-thienylquinoxaline)] (P1), poly[N-9''-heptadecanyl-2,7-carbazole-*alt*-5,5-(5',8'-di-2-thienyl-2,3-bis(4-octyloxyl)phenyl)quinoxaline (P2), and poly[N-9"-heptadecanyl-2,7-carbazole-alt-5,5-(5',8'di-2-thienyl-2,3-bis(4-(3,7-dimethyloctyloxy)phenyl)quinoxaline] (P3), were synthesized by polycondensation of 2,7-bis(4',4',5',5'tetramethyl-1',3',2'-dioxaborolane-2'-yl)-N-9"-heptadecanylcarbazole and the corresponding dibrominated quinoxaline derivatives through the palladium-catalyzed Suzuki reaction. The crude polymers were extracted with chloroform, recollected by precipitating them in methanol, and extracted again with methanol and acetone successively using a Soxhlet apparatus to remove byproducts and oligomers. The chemical structure of the polymers was verified with ¹H NMR spectroscopy and elemental analysis. P2 and P3 were readily soluble in common organic solvents, such as toluene, chloroform, and tetrahydrofuran (THF), whereas P1 dissolved only in warm chloroform or warm chlorinated benzene. The molecular weights were determined by using gel permeation chromatography (GPC) against polystyrene standards in a chloroform eluent and were found to be in the range of 6-37 kDa with a polydispersity index of 2.0-2.9 (Table 1). With additional solubilizing chains on the Qx unit, P2 and P3 displayed a higher molecular weight, which is ascribable to the increased solubility of these polymers.

The thermal properties of the copolymers were evaluated in a nitrogen atmosphere by thermogravimetric analysis (TGA) and

differential scanning calorimetry (DSC) at a heating rate of 10 °C/min. All the polymers exhibited a good thermal stability, showing less than 5% weight loss at temperatures up to 400 °C. Compared to P1, P2 and P3 have a lower glass transition temperature (T_g), which is attributed to the alkoxy side chains on the quinoxaline units. The physical properties of the polymers are summarized in Table 1.

Optical Properties. The UV-vis absorption spectra of the polymers in chloroform and in the spin-cast film are shown in Figures 1 and 2, respectively, and the corresponding absorption properties are summarized in Table 2. Both in solution and in the films, the polymers exhibited two distinct absorption bands: one at about 375–400 nm and the other one in the range: 495–545 nm. The nature of these bands, observed for the low-band gap polymer with push-pull units, still remains to be elucidated. Jesperson et al. attributed the highest energy band to a $\pi - \pi^*$ transition whereas the lowest energy band was assigned to an intramolecular charge transfer (ICT) between the donor and the acceptor.^{28,2} To obtain further information about the ICT electronic structure of the polymers, we carried out density functional theory (DFT) calculations for the model compound using the DMol 3 software. Figure S1 (Supporting Information) shows the calculated molecular orbitals of the model compounds. As shown in Figure S1, the HOMO was delocalized over the polymer backbone, whereas the LUMO was highly localized on the Qx unit (Supporting Information).

The red shift observed for P2 and P3, compared to P1, is due to the introduction of the benzene groups on the quinoxaline unit and not electron-donating effect of the alkoxy chains on the para position of the benzene rings. The dihedral angle between the benzene rings and the quinoxlaine rings are significant, as can be seen from the calculated structures (Figure S1, Supporting Information). However, this result currently lacks a theoretical explanation. The absorption maxima of the polymer films are red-shifted by 25-33 nm compared to those of the polymer solutions. This red-shift indicates higher coplanarity of the polymer and/or enhanced intermolecular electronic interactions in the solid state. The optical band gap obtained from the extrapolation of the absorption edges of the film are in the order of P3(1.91 eV) < P2(1.97 eV) < P1(2.01 eV). The smaller band gap should help improve the absorption efficiency in the solar spectrum.

Electrochemical Properties. To determine the energy levels of the HOMO and the LUMO, we investigated the electrochemical properties of the polymers by using cyclic voltammetry (CV). A platinum (Pt) electrode, modified with a polymer film by means of dip-coating, was used as the working electrode while a Pt wire was used as the counter electrode and $Ag/AgNO_3$ (0.10 M) served as the reference electrode. The CV measurements were carried out in tetrabutylammonium tetrafluoroborate (TBABF₄, 0.1 M)/acetonitrile electrolyte at room temperature under nitrogen atmosphere at a scan rate of 50 mV/s.³⁰ The HOMO level of the polymers can be deduced from the oxidation onsets assuming that the energy level of ferrocene (Fc) is 4.8 eV below the vacuum level.³¹ In the anodic scan, the onset of oxidation for P1, P2, and P3 occurred at 0.54, 0.52, and 0.50 V, which corresponds to ionization-potential values of -5.34, -5.32, and -5.30 eV, respectively (Figure 3). The electrondonating alkoxy groups in P2 and P3 slightly raise the HOMO level and consequently reduce the band gap of the copolymer.

Unfortunately, it was difficult to obtain the LUMO energies for the copolymers using this technique, so these values were Scheme 1. Synthetic Scheme for the Monomer and Copolymers



estimated from the optical band gaps (taken as the absorption onsets of the UV–vis spectra for the polymer films) and the HOMO energies.³² The energies of the LUMO levels of P1, P2, and P3 are listed in Table 2.

Field-Effect Transistor Characteristics. The effects of the side-chain substitutions on the electrical transport properties of the resulting materials were examined by measuring the field-effect properties of each of the three copolymers. The field-effect

 Table 1. Physical Properties of the Polymers

polymer	$M_{\rm n} [{\rm kg/mol}]^a$	PDI	yield (%)	$T_{g} (^{\circ}C)^{b}$	$T_d (^\circ C)^c$
P1	6	2.0	68	125	420
P2	37	2.8	60	112	400
P3	24	2.9	65	109	410

^{*a*} The molecular weights were determined by using gel permeation chromatography (GPC) against polystyrene standards in chloroform eluent. ^{*b*} Glass transition temperature determined by differential scanning calorimetry (DSC) curve. ^{*c*} Temperature resulting in 5% weight loss based on initial weight.

carrier mobilities of the polymers were investigated by fabricating thin-film transistors (TFTs) with a bottom-contact geometry using Au electrodes. The detailed device-fabrication process is described in the Experimental Section. To reduce the photocurrent loss and obtain high-performance PSC devices, a high charge-carrier mobility (higher than or close to 10^{-3} cm² V⁻¹ s⁻¹) is necessary.^{33,34} Figure S2 (Supporting Information) shows plots of drain-source current (I_{ds}) as a function of drain-source voltage (V_{ds}) at different gate voltages, as well as typical output and transfer curves for the polymers (Supporting Information). TFTs of the polymers were found to exhibit typical p-channel TFT characteristics with good drain-current modulation and well-defined linear and saturation regions. The TFT mobilities were calculated in the saturation region using the following equation:⁴

$$I_{\rm ds} = (WC_{\rm i}/2L)\mu(V_{\rm G}-V_{\rm T})^2$$

where $I_{\rm ds}$ is the drain-source current in the saturated region, W and L are the channel width (120 μ m) and length (6 μ m), respectively, μ is the field-effect mobility, $C_{\rm i}$ is the capacitance per unit area of the insulation layer (SiO₂, 300 nm), and $V_{\rm G}$ and $V_{\rm T}$ are the gate and threshold voltages, respectively.

The mobilities and on/off ratios of TFTs fabricated using the resulting polymers are listed in Table 3. The field-effect mobilities for P1, P2, and P3 were determined to be 4.2×10^{-6} , 1.4×10^{-3} , and 2.1×10^{-4} cm² V⁻¹ s⁻¹, respectively. The higher mobility measured for P2 can be understood in terms of the better solubility and $\pi - \pi^*$ stacking.²⁷ The hole mobility determined for P2 is 1 order of magnitude higher than that for P3. We guess that the high mobility of P2 is due to the improved packing of P2 compared to that of polymers containing dimethyloctyloxy chains. The hole mobility of P2 was within the desired range for PSC materials (i.e., higher than or close to 10^{-3} cm² V⁻¹ s⁻¹), allowing for an efficient charge extraction and a good fill factor (FF).

Photovoltaic Characteristics. Bulk-heterojunction polymer solar cells were fabricated with the structure of ITO/PEDOT: PSS/polymer:PC₇₁BM/LiF/Al. The detailed device-fabrication process is described in the Experimental Section. Optimal performance of the polymers was obtained from a 14 mg/mL dichlorobenzene solution, at a 400 rpm spin-coating rate and a polymer/PC₇₁BM ratio of 1:3 (w/w). The thicknesses of the layers were PEDOT:PSS (60 nm), active layer (80 nm), LiF (0.7 nm), and Al (100 nm). According to the optoelectronic and TFT properties described earlier, P2 is a suitable material for PSC applications.

Figure 4 shows the current—voltage characteristics of a PSC device based on blends of the polymer and fullerene. The output characteristics of the resulting polymer-based devices are summarized in Table 3. The best PSC performance was observed for P2/PC₇₁BM devices, which reached a PCE of 4.0%, with a short-circuit current density (J_{SC}) of 9.96 mA/cm², an open-circuit



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Figure 1. UV-vis absorption of the copolymers in chloroform solutions.



Figure 2. UV-vis absorption of thin film of the copolymers.

voltage (V_{OC}) of 0.82 V, and a fill factor (FF) of 0.49 under AM 1.5 G irradiation (100 mW/cm²).

The $V_{\rm OC}$ value is closely related to the energy difference between the HOMO of the polymer and the LUMO of the electron acceptor, PC71BM.35 As expected from the HOMO energy levels of the polymers, those polymers with the same backbone units have a similar $V_{\rm OC}$ value because of their almost identical electronic structures. However, the trend of V_{OC} for P1 does not seem to fit the electrochemical potentials, which can be explained in terms of the morphology of the blended film. A low solubility has an impact on the mechanical properties of the film, the interface resistance, and the nanoscale morphology, resulting in a low open-circuit voltage and a low fill factor.²¹ Figure 5 shows atomic force microscopy (AFM) images (1 μ m × 1 μ m scan area) of the blend film (polymer: $PC_{71}BM = 1:3$) for a better understanding of the device characteristics. P2 shows homogeneously well-distributed small-sized domains whereas P1 exhibits larger polymer–PC₇₁BM domains and phase separations. These results indicate that P2 may form a well-distributed bicontinuous interpenetrating network of polymer–PC71BM domains, showing good agreement with the improved current-voltage characteristics observed for this system in comparison to the other polymers. The measured short-circuit current (I_{SC}) for P1, P2, and P3 was 2.70, 9.96, and 6.24 mA/cm², respectively. These results are also in good agreement with the OFET measurements. The hole mobility determined in pure P2 is about 1 order of

Table 2. C	Optical and	Electrochemical	Properties	of the Polymers
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polymer	$\lambda_{\max}^{abs,sol} (nm)^a$	$\lambda_{ m max}^{ m abs, film} \ ({ m nm})^a$	HOMO $(eV)^b$	LUMO (eV) ^c	$E_{\rm g}^{\rm opt} ({\rm eV})^d$
P1	379, 496	390, 529	-5.34	-3.33	2.01
P2	389, 510	395, 535	-5.32	-3.35	1.97
P3	391, 521	396, 543	-5.30	-3.39	1.91

^{*a*} The UV—vis absorption spectra of the polymers were measured in chloroform solution and thin film. ^{*b*} HOMO levels of the polymer were determined from onset voltage of the first oxidation potential with reference to ferrocene at -4.8 eV. ^{*c*} LUMO levels of the polymer were estimated from the optical band gaps and the HOMO energies. ^{*d*} Optical bandgap calculated from the UV—vis absorption onset in film.



Figure 3. Cyclic voltammograms of the copolymers.

Table 3. FET and PSC Performances of the Polymers

polymer	$\mu ({ m cm}^2{ m V}^{-1}{ m s}^{-1})^a$	$I_{\rm on}/I_{\rm off}{}^a$	$V_{\rm OC}$ $(V)^b$	$J_{\rm SC}$ $({\rm mA/cm}^2)^b$	FF^b	РСЕ (%) ^b
P1	4.2×10^{-6}	10^{2}	0.61	2.70	0.29	0.48
P2	1.4×10^{-4}	10	0.82	9.96	0.49	4.0
P3	2.1×10^{-1}	$6 \times 10^{\circ}$	0.81	6.24	0.46	2.3

 a The field-effect carrier mobilities of the polymers were investigated by fabricating thin film transistors (TFTs) with a bottom contact geometry using Au electrodes. b The device was fabricated with a layered structure of ITO/PEDOT:PSS/polymer:PC71BM/LiF/Al.



Figure 4. J-V characteristics of photovoltaic devices fabricated with P1:PC₇₁BM (black), P2:PC₇₁BM (red), and P3:PC₇₁BM (green) under AM 1.5 G irradiation (100 mW/cm²).

magnitude higher than that obtained with P3, which could explain the higher value of the short-circuit current measured for P2.



Figure 5. AFM images of films spin coated from $P1/PC_{71}BM$ (a, d), $P2/PC_{71}BM$ (b, e), and $P3/PC_{71}BM$ (c, f). (a–c) AFM topography of each film. (d–f) AFM phase images of each film.



Figure 6. External quantum efficiency of P1:PC₇₁BM (black), P2: PC₇₁BM (red), and P3:PC₇₁BM (green).

Figure 6 shows the external quantum efficiency (EQE) spectra of PSC devices fabricated with P2/PC₇₁BM and P3/PC₇₁BM under monochromatic light illumination. In both cases, the EQE spectra agree well with the optical-absorption curves, resulting in a close correlation with the photocurrents. Convolution of the spectral response with the photon flux of the AM 1.5 G spectrum provided an estimate of the value of J_{SC} under irradiation. The calculated J_{SC} value for the P2-based devices was 8.46 mA/cm². Because of the discrepancy between the EQE results and the photon flux under AM 1.5 illumination, an approximate mismatch of 15% was present between the convolution and the solar-simulator data.³⁶

Although the values of $V_{\rm OC}$ and $J_{\rm SC}$ were high, those of the fill factors were low. We believe that the value of FF could be improved by using different solvents,²² adding various additives,³⁷ and/or using a buffer layer.³⁸ With an enhancement of the FF, the performance of the polymer solar cells could be greatly improved.

CONCLUSIONS

In summary, we have synthesized a new series of conjugated polymers consisting of alternating carbazole and quinoxaline units by means of Suzuki coupling polymerization. Considering the polymer solubility, the ease of polymer characterization and photovoltaic-device fabrication, and the hole mobility, we were able to design conjugated polymers with the same polymer backbone but different side chains. The processability, hole mobility, and, film morphology of the copolymers were influenced by their size/shape. Interestingly, the new semiconducting copolymer P2 exhibited a field-effect carrier mobility of up to 1.4 imes 10^{-3} cm²/(V s). Bulk heterojunction solar cells fabricated from blends of P2 with PC71BM exhibited a power-conversion efficiency of 4.0% without any special treatments. Considering the field-effect carrier mobility and photovoltaic properties of P2, this polymer exhibits great potential as a candidate for new-generation solar-cell materials. Further modifications of the polymer structure and/or the device structure (for example by introducing an optical space such as titanium oxide) are currently underway to achieve even better performance.

EXPERIMENTAL SECTION

General Data. The synthesized compounds were characterized with ¹H NMR spectra obtained using a Bruker DPX-300 NMR spectrometer. UV–visible analysis was performed with a Lambda 20 (Perkin-Elmer) diode array spectrophotometer. The number- and weightaverage molecular weights of the polymers were determined by gel permeation chromatography (GPC; Viscotek) equipped with TDA 302 detector and PL-gel (Varian) column, using chloroform as the eluent and polystyrene as the standard. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed under a nitrogen atmosphere at a heating rate of 10 °C/min with a Dupont 9900 analyzer.

Fabrication of the Organic Thin Film Transistors (OTFTs). OTFT devices were fabricated in a bottom-contact geometry (channel length = 6 μ m, width = 120 μ m). The source and drain contacts consisted of gold (100 nm), and the dielectric was silicon oxide (SiO₂) with a thickness of 300 nm. The SiO₂ surface was cleaned, dried, and pretreated with a solution of 1.0 mM octyltrichlorosilane (OTS-8) in toluene at room temperature for 2 h under nitrogen to produce apolar and smooth surfaces onto which the polymers could be spin-coated. The polymers were dissolved to a concentration of 0.5 wt % in chlorobenzene. Films of the organic semiconductors were spin-coated at 1500 rpm for 50 s to a thickness of 50 nm, followed by an annealing process. All device fabrication procedures and measurements were carried out in air at room temperature.

Fabrication of the Polymer Solar Cells (PSCs). In this study, the devices were fabricated with the structure ITO/PEDOT:PSS/ polymer:PC₇₁BM/LiF/Al. The procedure for cleaning the ITO surface included sonication and rinsing in deionized water, methanol, and acetone. The hole-transporting PEDOT:PSS layer was spin-coated onto each ITO anode from a solution purchased from H. C. Starck. Each polymer:PC₇₁BM solution was then spin-coated onto the PEDOT:PSS layer. The polymer solution for spin-coating was prepared by dissolving

the polymer (1 wt %) in dichlorobenzene. LiF and aluminum contacts were formed by vacuum deposition at pressures below 3×10^{-6} Torr, providing an active area of 0.09 cm². Solar cell efficiencies were characterized under simulated 100 mW/cm² AM 1.5 G irradiation from a Xe arc lamp with an AM 1.5 global filter. Simulator irradiance was characterized using a calibrated spectrometer, and the illumination intensity was set using an NREL-certified silicon diode with an integrated KG1 optical filter: short-circuit currents were found to be within 15% of the values calculated using the integrated external quantum efficiency (EQE) spectra and the solar spectrum. The EQE was measured by underfilling the device area using a reflective microscope objective to focus the light output from a 100 W halogen lamp outfitted with a monochromator and optical chopper; the photocurrent was measured using a lock-in amplifier, and the absolute photon flux was determined using a calibrated silicon photodiode. All device fabrication procedures and measurements were carried out in air at room temperature.

MATERIALS

2,1,3-Benzothiadiazole, bromine, sodium borohydride, diethyl oxalate, 4-bromophenol, 1-bromooctane, 1-bromo-3,7-dimethyloctane, 2-(tribuylstannyl)thiophene, dimethylformamide (DMF), tetraethylammonium hydroxide solution, tetrakis(triphenylphosphine)palladium, and toluene (99.8%, anhydrous) were purchased from Aldrich. Palladium(II) acetate was purchased from Strem Chemicals Co. All chemicals were used without further purification. The monomer 4,7-dibromo-2,1,3-benzothiadiazole (1),³⁹ 3,6-dibromo-1,2-phenylenediamine (2),⁴⁰ 1,4-dimethylpiperazine-2,3-dione (3),⁴¹ 1-bromo-4-octyloxybenzene (4a),⁴² 1-(3,7dimethyloctyloxy)-4-bromobenzene (4b),43 4,4'-bis(2-octyloxy)benzil (5a),⁴¹ 5,8-dibromo-2,3-bis(4-octyloxyphenyl)quinoxaline (6a),⁴⁴ 5,8-bis(5'-bromodithien-2-yl)quinoxaline,²¹ 2,3-bis(4-octyloxyphenyl)-5,8-dithien-2-yl-quinoxaline (7a),⁴⁴ 2,3-bis(4-octyloxyphenyl)-5,8-bis(5'-bromodithien-2-yl)quinoxaline (8a),⁴⁴ and 2,7-bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-N-9"heptadecanylcarbazole²¹ were prepared with previously described methods.

1,2-Bis(4-(3,7-dimethyloctyloxy)phenyl)ethane-1,2-dione (5b). Into a solution of compound 4b (13.6 g, 43.3 mmol) in THF (100 mL) at -50 °C was added, by syringe, 30.0 mL (47.8 mmol) of *n*-BuLi (1.6 M in hexane). The mixture was stirred at -50 °C for 1 h. Compound 3 (3.00 g, 21.1 mmol) was added to the solution, and the resulting mixture was stirred at -50 °C for 1 h and then warmed to room temperature and stirred for a further 12 h. The mixture was poured into water, extracted with ether, and dried with anhydrous MgSO4. The solvent was removed via rotary evaporation, and the residue was precipitated in methanol. The product yield was 48% (5.29 g)¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.91 (d, 4H), 6.93 (d, 4H), 4.05(t, 4H), 1.85 (m, 2H), 1.74–1.12 (m, 18H), 0.92 (d, 6H), 0.87 (d, 12H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 193.77, 164.68, 132.56, 126.29, 114.92, 67.09, 39.41, 37.42, 36.11, 29.98, 28.17, 24.84, 22.90, 22.80, 19.80. Anal. Calcd for C₃₄H₅₀O₄: C, 78.12; H, 9.64. Found: C, 78.12; H, 9.68.

5,8-Dibromo-2,3-bis(4-(3,7-dimethyloctyloxy)phenyl)quinoxaline (6b). Compound **2** (2.50 g, 9.34 mmol) and **5b** (4.48 g, 8.57 mmol) were dissolved in 60 mL of MeOH, then 5,5 mL of acetic acid was added, the mixture was heated under reflux for 4 h. After evaporation of the solvent, the mixture was poured into water (100 mL) and extracted with CHCl₃. After the reaction had finished, the reaction mixture was extracted three times with chloroform and brine. The organic layer was separated and dried with anhydrous magnesium sulfate, and then the solvent was removed by using a rotary evaporator. The crude product was precipitated in methanol. The product yield was 95% (6.47 g) ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.83 (s, 2H), 7.64 (d, 4H), 6.86 (d, 4H), 4.02 (t, 4H), 1.83 (m, 2H), 1.74–1.12 (m, 18H), 0.94 (d, 6H), 0.87 (d, 12H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 160.67, 153.78, 139.22, 132.69, 131.87, 130.54, 123.64, 114.58, 66. 64, 39.77, 37.49, 36.33, 30.06, 28.17, 24.87, 22.92, 22.82, 19.87. Anal. Calcd for C₄₀H₅₄Br₂N₂O₂: C, 63.66; H, 7.21; N, 3.71. Found: C, 63.61; H, 7.17; N, 3.68.

2,3-Bis(4-(3,7-dimetyloctyloxy)phenyl)-5,8-dithien-2-ly-quinoxaline (7b). In a 250 mL three neck flask, compound 6b (5.40 g, 7.18 mmol) and tetrakis (triphenylphosphine)palladium(0) (0.194 g, 0.168 mmol) were mixed, and the flask was evacuated and filled with nitrogen. After addition of tolene (50 mL) the mixture was heated to 110 °C. Then, 2-(tri-nbutylstannyl)thiophene (5.90 g, 15.7 mmol) was added via a syringe and the reaction mixture was stirred for 24 h. The mixture was poured into water (100 mL) and extracted with CHCl₃. The extract was then successively washed with water and brine. After drying over anhydrous MgSO₄, the solvent was evaporated and the residue was precipitated with MeOH several times to give 4.50 g (83%) of red-yellow solid. ¹H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.09 (s, 2H), 7.85 (d, 2H), 7.72 (d, 4H), 7.50 (d, 2H), 7.18 (t, 2H), 6.90 (d, 4H), 4.05 (t, 4H), 1.83 (m, 2H), 1.75-1.11 (m, 18H), 0.94 (d, 6H), 0.87 (d, 12H). ¹³C NMR (75 MHz, $CDCl_3$): δ (ppm) 159.99, 151.32, 138.95, 136.98, 131.88, 131.04, 130.22, 128.74, 127.16, 126.55, 126.22, 114.25, 66.42, 39.27, 37.33, 36.22, 29.91, 28.01, 24.70, 22.75, 22.65, 19.72. Anal. Calcd for $C_{48}H_{58}N_2O_2S_2$: C, 75.95; H, 7.70; N, 3.69; S, 8.45. Found: C, 75.91; H, 7.68; N, 3.62; S, 8.36.

2,3-Bis(4-(3,7-dimetyloctyloxy)phenyl)-5,8-bis(5'-bromodithien-2-ly)quinoxaline (8b). A solution of compound 7b (3.80 g, 4.98 mmol) in CHCl₃ was protected from light and cooled to 0 °C. Then N-bromosuccinimide (1.79 g, 9.96 mmol) was added in small portions over 20 min and then the mixture was stirred for 3 h. The mixture was poured into water (100 mL) and extracted with CHCl₃. The organic layer was dried over anhydrous MgSO₄ and the solvent removed by rotary evaporation. The crude product was purified by crystallization with MeOH to yield compound 8b as a red-yellow solid (4.26 g, 93%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.94 (s, 2H), 7.66 (d, 4H), 7.49 (d, 2H), 7.08 (d, 2H), 6.91 (d, 4H), 4.05 (t, 4H), 1.85 (m, 2H), 1.77–1.15 (m, 18H), 0.97 (d, 6H), 0.88 (d, 12H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 160.34, 151.99, 139.96, 136.58, 132.13, 130.85, 130.52, 129.25, 125.54, 125.41, 117.16, 114.48, 66.65, 39.48, 37.55, 36.45, 30.11, 28.21, 24.90, 22.95, 22.85, 19.93. Anal. Calcd for C48H56Br2N2O2S2: C, 62.88; H, 6.16; N, 3.06; S, 6.99. Found: C, 62.81; H, 6.16; N, 3.03; S, 6.99.

General Procedure for the Synthesis of Polymers with the Suzuki Reaction. Synthesis of Poly[N-9''-heptadecanyl-2,7-carbazole-alt-5,5-(5',8'-di-2-thienyl-2,3-bis(4-octyloxyl)phenyl)quinoxaline] (**P2**). This is presented in detail as a representative example. 2,7-Bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-N-9''-heptadecanylcarbazole (0.263 g, 0.400 mmol), 2,3-bis(4-octyloxyphenyl)-5,8-bis(5'-bromodithien-2-yl)quinoxaline (**8a**) (0.344 g, 0.400 mmol), tricyclohexylphosphine (3.4 mg, 0.0120 mmol), and palladium(II) acetate (0.0080 mmol, 5.4 mg) were dissolved in 4 mL of anhydrous toluene. To the solution, tetraethylammonium hydroxide solution (1.30 g) degassed by sonicator was added under argon flow. The mixture was heated under reflux for 24 h, and then, the reaction mixture was cooled to about 50 °C and

added slowly to a vigorously stirred mixture consisting of 230 mL methanol and 13 mL 1 N aqueous HCl. The polymer fibers were collected by filtration and reprecipitation from methanol. The polymer was purified by washing for 2 days in a Soxhlet apparatus with acetone to remove oligomers and catalyst residues, and column chromatographed with a chloroform/toluene solution of the polymer. The reprecipitation procedure in toluene/methanol was then repeated several times. The final product was obtained after drying in vacuo at 40 °C (60%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.29–6.70 (m, 20H); 4.75 (br, 1H); 4.03 (br, 4H); 2.61–0.61 (m, 64H). Anal. Calcd: C, 79.39; H, 8.44; N, 3.70; S, 5.65. Found: C, 79.26; H, 8.35; N, 3.62; S, 5.53.

Poly[*N*-9"-heptadecanyl-2,7-carbazole-alt-5,5-(5',8'-di-2thienylquinoxaline)] (**P1**). was synthesized with the procedure described for **P2**. The copolymerization of the monomers 2,7bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-*N*-9"-heptadecanylcarbazole (0.263 g, 0.400 mmol), and 5,8-bis(5'-bromodithien-2-yl)quinoxaline (0.181 g, 0.400 mmol) gave **P1** (68%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.75 (br, 2H); 8.19- 7.38 (m, 12H); 4.73 (br, 1H); 2.61- 0.61 (m, 34H). Anal. Calcd: C, 77.75; H, 7.63; N, 5.79; S, 8.83. Found: C, 77.69; H, 7.54; N, 5.64; S, 8.75.

Poly[N-9"-heptadecanyl-2,7-carbazole-alt-5,5-(5',8'-di-2thienyl-2,3-bis(4-(3,7-dimethyloctyloxy)phenyl)quinoxaline] (**P3**). This was synthesized with the procedure described for **P2**. The copolymerization of the monomers 2,7-bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-N-9"-heptadecanylcarbazole (0.263 g, 0.400 mmol), and 2,3-bis(3,7-dimetyloctyloxyphenyl)-5,8-bis(5'-bromodithien-2-yl)quinoxaline (0.367 g, 0.400 mmol) gave **P3** (65%). **P3** was extracted again with acetone and hexane successively using a Soxhlet apparatus to remove oligomers and inpurity. ¹H NMR (300 MHz, CDCl₃): δ (ppm): 8.30–6.70 (m, 20H); 4.73 (br, 1H); 4.07 (br, 4H); 2.62–0.60 (m, 72H). Anal. Calcd: C, 79.68; H, 8.72; N, 3.53; S, 5.39. Found: C, 79.55; H, 8.60; N, 3.46; S, 5.33.

ASSOCIATED CONTENT

Supporting Information. Density functional theory (DFT) calculations for the model compound using the DMol 3 software, figures showing the structure of model compounds, output characteristics of OTFT devices, J-V characteristics of OPV composed of P2:PC₇₁BM with and without postannealing treatment, and photovoltaic performance. This material is available free of charge via the Internet at http://pubs.acs.org.

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