# Panchromatic Conjugated Polymers Containing Alternating Donor/Acceptor Units for Photovoltaic Applications

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ABSTRACT: We designed and synthesized a series of conjugated polymers containing alternating electron-donating and electron-accepting units based on (4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene), 4,7-(2,1,3)-benzothiadiazole, and 5,5′-[2,2′]bithiophene. These polymers possess an optical band gap as low as 1.4 eV (i.e., in the case of poly[2,6-(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)]), and their absorption characteristics can be tuned by adjusting the ratio of the two electron-donating units: (4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene) and 5,5′-[2,2′]bithiophene. The desirable absorption attributes of these materials qualify them as excellent candidates for light-harvesting materials in organic photovoltaic applications allowing for high short-circuit current. Electrochemical studies indicate sufficiently deep HOMO/LUMO levels that enable a high photovoltaic device open-circuit voltage when fullerene derivatives are used as electron transporters. Field-effect transistors made of these materials show hole mobility in the range of $5 \times 10^{-4}-3 \times 10^{-3}$ cm$^2$/(V s), which promises good device fill factor. Because of the combination of these characteristics, power conversion efficiencies up to 3.5% and an external quantum efficiency of at least 25% between 400 and 800 nm with a maximum of 38% around 700 nm were achieved on devices made of bulk heterojunction composites of these materials with soluble fullerene derivatives. Further improvement of the materials will include the modification of both the side chains and the backbone to effect change to the active layer morphology to maintain good charge carrier mobility in the composite.

## Introduction

An organic photovoltaic device[1,2] is fabricated by sandwiching a thin layer (or layers) of organic optoelectric materials between two conducting electrodes, one of which is transparent to allow incident light to reach the interior. In the active layer the organic materials absorb light, create separated charge carriers, and transport holes and electrons to the electrodes to furnish electric power. The solution processability of the conjugated polymers and the low cost of the fabrication process allow such devices to be easily produced into light weight, large area, and flexible panels. Their potential to contribute significantly to clean and renewable energy has attracted increasingly intensified attention.[3−5]

Among the various types organic photovoltaic devices investigated so far, one of the most heavily examined and the most promising employs a mixture of conjugated polymer and a fullerene derivative (i.e., [6,6]-phenyl-C61-butyric acid methyl ester, PCBM) as the active layer.[6−8] The bicontinuous intermixing of the donor and acceptor species in these devices allows the photogenerated electron−hole pairs to be efficiently separated throughout the bulk of the film and transported to the electrodes. Recently, such polymer cells with power conversion efficiency as high as 5% have been realized using a blend of regioregular poly(3-hexylthiophene) (P3HT) and PCBM as active layer.[9,10] However, the insufficient light absorption by P3HT (caused by a mismatch of its band gap, 2.2 eV, with the photon flux maximum of the solar spectrum at the standard air mass 1.5 conditions, which lies between 1.3 and 2.0 eV) limits the percentage of light absorption and thus restricts the power

conversion efficiency. Further improvement of polymer solar cells requires polymers that absorb more broadly and at longer wavelength to match the terrestrial solar radiation.

Besides band gap, several other characteristics of conjugated polymers, including HOMO/LUMO levels and carrier mobility, need to be optimized simultaneously in order to achieve high photovoltaic performance.[11] In general, the gap between the HOMO of the electron-donating polymer and the LUMO of the electron acceptor should be maximized in order to increase the open-circuit voltage, and at the same time the band gap of the polymer should be minimized to increase photon absorption and thus short-circuit current. In addition, the LUMO of the polymer (donor) should be positioned above the LUMO of the fullerene derivative (acceptor) by at least 0.2−0.3 eV to ensure efficient electron transfer. A high charge-carrier mobility of holes and electron is essential for efficient charge extraction and a good fill factor. To prevent significant photocurrent loss in cells with an active layer thickness of several hundred nanometers, a carrier mobility of $\geq 10^{-3}$ cm$^2$/(V s) is desired. A modeling study predicts that polymers with mobility in this range combined with a LUMO lower than −3.92 eV and a band gap smaller 1.74 eV should give energy conversion efficiency over 10% when blended with PCBM.[11]

## Results and Discussion

The employment of materials absorbing the red and near-IR part of the solar spectrum has been one of the fundamental strategies and main focus in improving the performance of organic solar cells.[12,13] It has been well-known that coupling together electron donors and acceptors leads to effective expansion of absorption wavelength. For example, the electron-withdrawing 2,1,3-benzothiadiazole when coupled with electron-donating thiophenes or pyrroles resulted in a number of low-

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**Scheme 1. Synthesis of Poly[2,6-(4,4-dialkyl-4H-cyclopenta[2,1-b:3,4-b′]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)][a]**
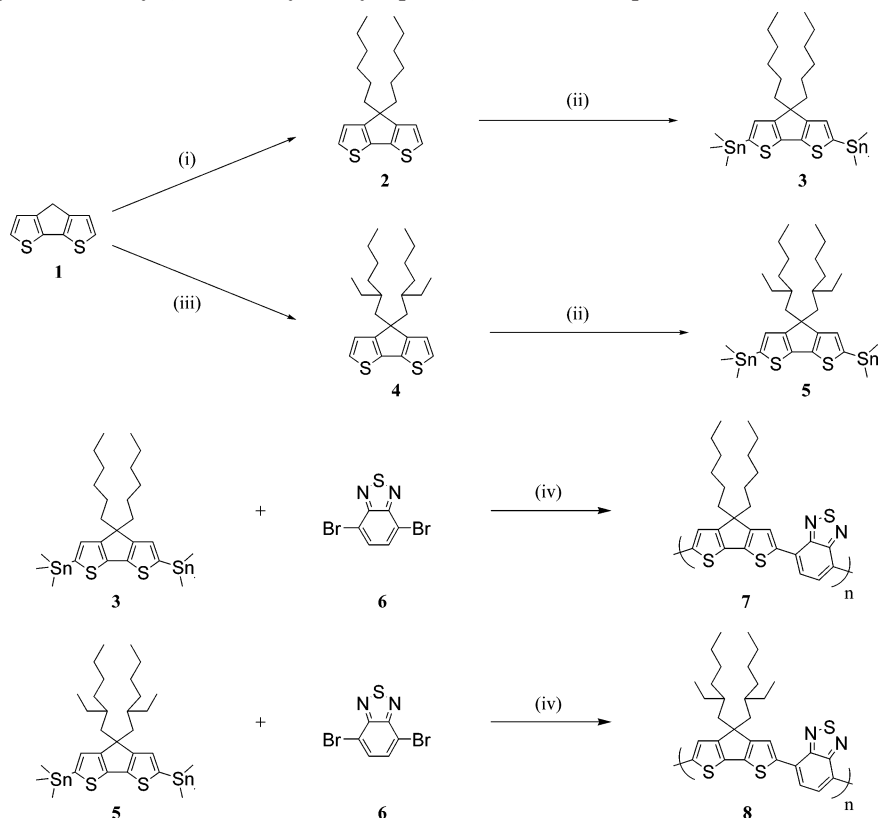


[a] Reagents and conditions: (i) KOH, *n*-hexyl bromide, DMSO; (ii) *n*-butyllithium, trimethyltin chloride, THF; (iii) KOH, 2-ethylhexyl bromide, DMSO; (iv) tris(dibenzylideneacetone)dipalladium, triphenylphosphine, toluene, 120 °C.

band-gap polymers.[14–25] Many structures have been designed and investigated, but most of them gave only very low device performance.[26–34] The photovoltaic performances of these polymers are typically lower than 1%, significantly inferior to what is realized with P3HT. One of the main reasons for this, we believe, is that these polymers usually lack solubility, and their building blocks do not provide suitable anchoring sites for solubilizing side chains without causing further twisting between adjacent repeating units so as to cause loss of conjugation. Recently, polymers containing low-band-gap donor−acceptor−donor segments connected by 9,9-dialkylfluorenes were synthesized which reach a band gap as low as 1.3 eV, but only a 0.7% power conversion efficiency was realized using these materials blended with a C70-fullerene derivative at AM1.5 conditions.[33,35] At the absorption maximum (840 nm) of the polymer, the device gave an external quantum efficiency only up to 8.4%. The carbon-bridged 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene was found to be a superior building block for conjugated polymers due to the forced coplanarity of the two thienyl subunits.[36,37] The 4-carbon of the 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene can be readily functionalized by alkyl groups to increase solubility without causing additional twisting of the repeating units in the resulting polymers. Soluble homo-polycyclopentadithiophenes containing alkyl side chains were found to have absorption maxima around 550−610 nm in solution, already a significantly longer wavelength than that of the absorption of P3HT.[38,39]

In order to further increase the absorption wavelength and lower the band gap of the polymer, a polymer containing the combination of cyclopentadithiophene as electron-donating units and 2,1,3-benzothiadiazole as electron-accepting units (**7**, Scheme 1) was designed and synthesized. The starting 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (**1**) was synthesized from
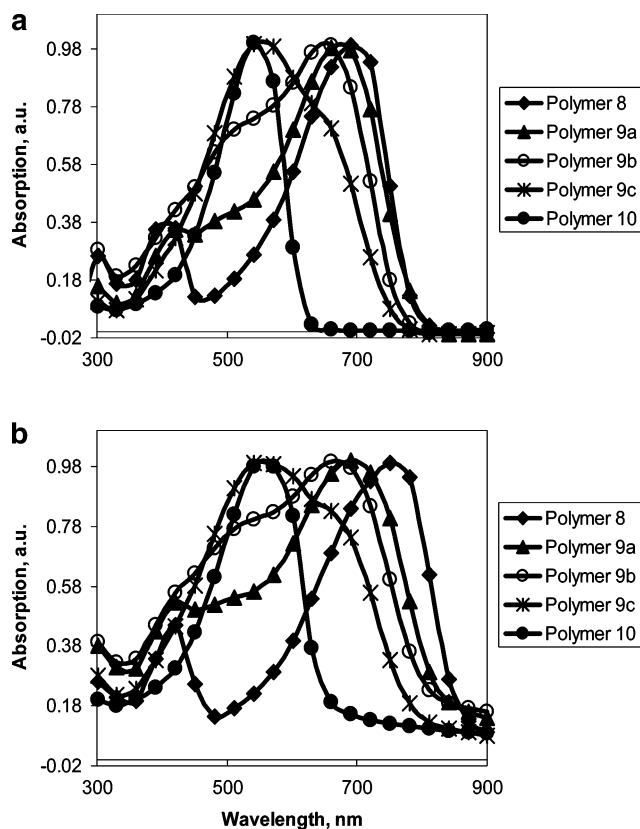


**Figure 1.** Normalized absorption spectra of the polymers in chloroform (a) and in solid state (b).

cyclopenta[2,1-*b*:3,4-*b*′]dithiophen-4-one[40] using a reduction procedure described by Turner et al.[41] Cyclopentadithiophene **1** was alkylated to form both 4,4-dihexylhexyl-4*H*-cyclopenta-

**Scheme 2. Synthesis of Both [2,2′]bithiophene- and Cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-Containing Copolymers***a*

**9a**, m : n = 2 : 1
**9b**, m : n = 1 : 1
**9c**, m : n = 1 : 2

**10**
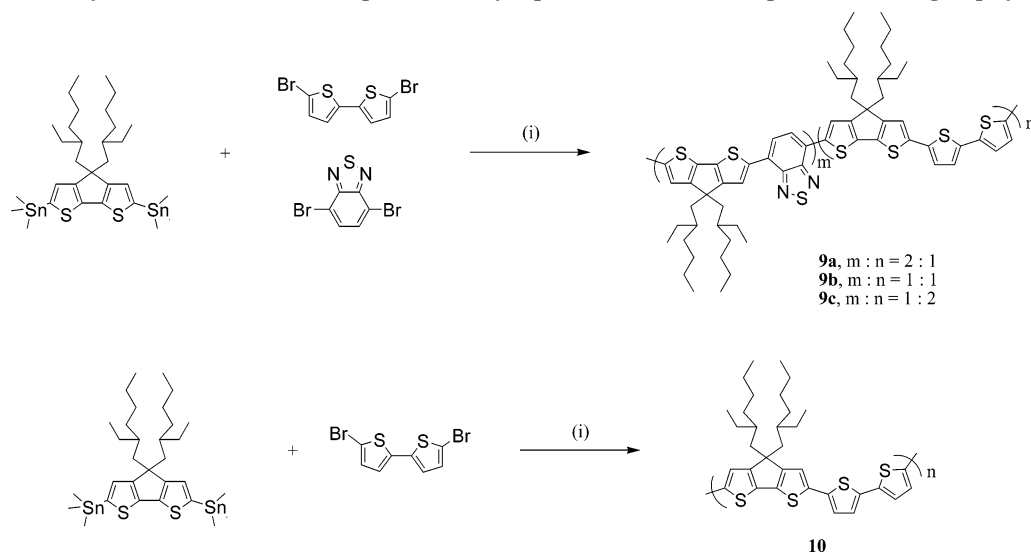
*a* Reagents and conditions:  (i) tris(dibenzylideneacetone)dipalladium, triphenylphosphine, toluene, 120 °C.

**Table 1. GPC and Spectroscopic Data of Polymers 8−10**

| polymer | m:n | $M_n{}^a$ (kDa) | $d^a$ | $\lambda_{max}$ (in CHCl₃/film, nm) | $\lambda_{max,film} - \lambda_{max,solution}$ (nm) |
|---|---|---|---|---|---|
| **8** | *m*:0 | 28 | 1.5 | 721/760 | 39 |
| **9a** | 2:1 | 28 | 1.4 | 670/693 | 23 |
| **9b** | 1:1 | 30 | 1.6 | 652/668 | 16 |
| **9c** | 1:2 | 23 | 1.4 | 543/553 | 10 |
| **10** | 0:*n* | 15 | 1.6 | 548/554 | 6 |

*a* Determined by GPC against polystyrene standards.

[2,1-*b*:3,4-*b*′]dithiophene (**2**)[41] and 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (**4**). Deprotonation of the 4,4-dialkyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene using *n*-buthyllithium followed by treatment with trimethyltin chloride afforded the corresponding 4,4-dialkyl-2,6-bis(trimethylstannanyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene monomers **3** and **5**, respectively. Stille coupling **3** with 4,7-dibromo-2,1,3-benzothiadiazole resulted in a blue polymer (**7**). However, this material was found to be only sparingly soluble in all solvents. To help increase the solubility, a 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]-dithiophene monomer carrying two 2-ethylhexyl side chains (**5**) was synthesized. Stille coupling of the bis-stannane **5** with 4,7-dibromo-2,1,3-benzothiadiazole (**6**) afforded polymer **8**, which is sufficiently soluble in both chloroform and chlorobenzene. Polymer **8** was purified by preparative GPC using chlorbenzene as a solvent, and polymers with a number-average molecular ($M_n$) of between 28 and 50 kDa (determined by GPC based on polystyrene standards) were obtained as separated fractions. High-quality films of polymer **8** can be prepared by coating the polymer from chlorobenzene or *o*-dichlorobenzene solution.

The absorption spectra of the polymer **8** ($M_n$ = 28 kDa) was recorded in both solution and solid state (Figure 1). This polymer has an absorption maximum of 721 nm in chloroform, and this maximum shifts further to 760 nm in the solid state, indicating significant interchain association in the solid state. The optical band gap at solid state was estimated to be 1.4 eV from its absorption edge. It has a HOMO level of −5.3 eV, a LUMO level of −3.55 eV, and band gap of 1.75 eV as determined by cyclic voltammetry.[42] Field effect transistors made of this material indicates a hole mobility as high as $1.5 \times 10^{-2}$ cm²/(V s). These physical parameters make this polymer a very promising material for high-performance organic solar cells.

It was noted that there is a transmission window in the solid state absorption spectrum of **8** around 500 nm which will reduce

light harvesting and, consequently, cell performance. To increase light harvesting across the solar spectrum and further improve this low-band-gap polymer, copolymers comprising combinations of 5,5′-[2,2′]bithiophene and cyclopenta[2,1-*b*:3,4-*b*′]-dithiophene as electron-donating units and 2,1,3-benzothiadiazole as electron-accepting moieties were synthesized (Scheme 2). By coupling 4,4-bis(2-ethylhexyl)-2,6-bis(trimethylstannanyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (**4**) with a mixture of various ratios of 5,5′-dibromo-[2,2′]bithiophene and 4,7-dibromo-2,1,3-benzothiadiazole, several three-component random copolymers **9a**−**9c** were prepared. The copolymer of bithiophene and cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (**10**) was also synthesized for comparison purposes.

The absorption spectra of the polymers are compiled in Figure 1, and the absorption maxima are listed in Table 1 along with the polymer molecular weight data determined by GPC. With the incorporation of unbridged [2,2′]bithiophene, the absorption maxima shift to the shorter wavelength region. With a ratio of the two electron-donating units, (4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene) and 5,5′-[2,2′]bithiophene, between 2:1 and 1:2, the copolymer absorption covers broad range of the visible spectrum. A comparison of the absorption spectra of **8** and **10** clearly demonstrates the significance of the electron-withdrawing 2,1,3-benzothiadiazole in the shifting the absorption to longer wavelength. The polymer films generally have longer absorption maxima than the corresponding solutions due to interchain association in the solid state, and this spectral shift is more significant when larger ratios of 2,1,3-benzothiadiazole are present in the polymer (Table 1).

An additional attractive feature of these polymers is that they have significantly higher absorptivity than the well-known regioregular P3HT polymer. The optical densities of these polymers in chlorobenzene are normalized to the same polymer concentration (1 g/L), and their comparison is shown in Figure
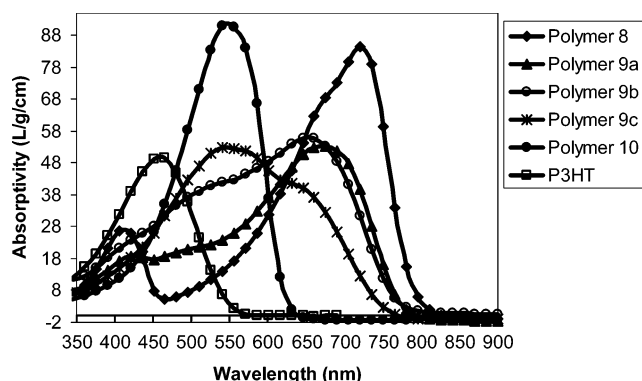
**Figure 2.** Comparison of the absorptivity of the polymers with that of regioregular P3HT. All spectra were recorded in chlorobenzene.
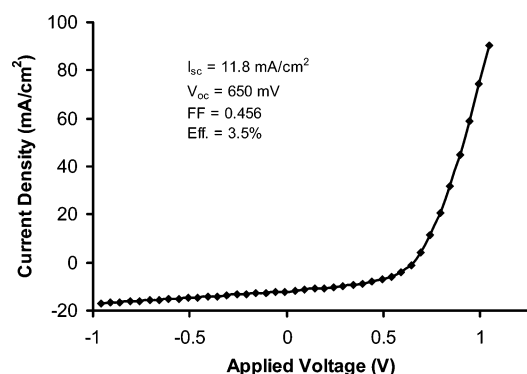


**Figure 3.** $I-V$ characteristics of an organic PV cell prepared from polymer **8** and PCBM (1:3 by weight) under AM 1.5 irradiation (100 mW/cm$^2$).

**Table 2. Summary of Representative Electrochemical Characterization Data of the Polymers**

| polymer | HOMO (eV)[a] | LUMO (eV)[a] | $E_g$ (eV)[a] | $\mu_h$[b] (cm$^2$/(V s)) |
|---|---|---|---|---|
| **8** | −5.3 | −3.55 | 1.75 | $1 \times 10^{-3}$ |
| **9a** | −5.25 | −3.55 | 1.70 | $3 \times 10^{-3}$ |
| **9b** | −5.38 | −3.55 | 1.83 | $5 \times 10^{-4}$ |
| **9c** | −5.3 | −3.55 | 1.75 | $2.4 \times 10^{-3}$ |
| **10** | −5.35 | −3 | 2.35 | $2 \times 10^{-3}$ |

[a] Determined by cyclic voltammetry measurements. [b] Determined by field effect transistor evaluation.

2. As can be seen from the spectra, polymers **8−10** not only absorb at longer wavelength but also exhibit higher absorptivity than P3HT. Electrochemical analysis (cyclic voltammetry) was conducted on these polymers, and a summary of the representative characterization data is included in Table 2. All the polymers (**8−10**) have a HOMO of between −3.25 and −3.38 eV. The LUMOs of all the benzothiodiazole-containing polymers (**8, 9a− c**) are around −3.55 eV. The LUMO of polymer **10** is around −3.0 eV. Hole mobility values between $5 \times 10^{-4}$ and $3 \times 10^{-3}$ cm$^2$/(V s) were also determined for all the polymers in field effect transistors. All these characteristics are within the desirable range for an ideal polymer for organic photovoltaic applications.

A conventional single-junction photovoltaic device made of the bulk heterojunction composite of **8** with soluble fullerene derivatives (PC$_{60}$PM and PC$_{70}$BM) gives power conversion efficiencies up to 3.5%. Typical external quantum efficiency is found to be higher than 25% in the wavelength range between 400 and 800 nm, and its maximum is found to be 38% around 700 nm.[42,43] The $I-V$ characteristics of a representative cell prepared with polymer **8** and PCBM are shown in Figure 3. It has an open-circuit voltage of 0.65 V and gives a current density of 11.8 mA/cm$^2$ and a power conversion efficiency of 3.5%

under the standard AM1.5 conditions. This power conversion efficiency value represents one of the highest among known low-band-gap polymers. However, it is still significantly lower than what is predicted on the basis of electrooptical properties of the polymer.[11] The deficit is mainly caused by a low fill factor. Preliminary AFM and field effect transistor studies on the polymer and PCBM blends indicate a lack of continuity in the polymer phase, which might have been caused by the almost complete intermixing of the polymer with PCBM at the molecular level resulting in hindered charge transport. Film morphology, the way in which the polymers and the fullerene derivative are organized relative to each other, has been found to be one of the key elements in determining the power conversion efficiency of organic solar cells.[45−47] Further improvements to the polymer will include modification of the side chains to help optimize bicontinuous phase separation. Initial cell testing on polymers **9a−9c** blended with PCBM already resulted in up to 3% power conversion efficiency. Further optimization of device performance of these materials is also in process.

## Conclusions

Polymers containing alternating electron-donating 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene and electron-accepting (2,1,3)-benzothiadiazole moieties have been synthesized. The 4-carbon of 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene allows for easy attachment of alkyl groups to increase solubility without causing additional twisting between the donor and the acceptor units. The absorption spectra of these polymers can be tuned to cover broad range of the visible spectrum. Electrochemical studies reveal that these materials possess desirable HOMO/LUMO levels for polymer photovoltaic applications. Hole mobility values (FET) for these materials are high. Because of the combination of these desirable properties, photovoltaic devices made of these new polymers demonstrated high power conversion efficiency. A high open-circuit voltage and large short-circuit current but a low fill factor indicates the possibility of further device performance improvements by the optimization of film morphology of the polymer/PCBM blends and/or device architecture.

## Experimental Section

**General Methods.** The 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (**1**) and 4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophen (**2**) were synthesized according to a literature procedure.[41] Regioregular poly-(3-hexylthiophene-2,5-diyl) (P3HT) was purchased from Rieke Metals, Inc. All other starting materials were purchased from Sigma-Aldrich and used as received. NMR ($^1$H and $^{13}$C) spectra were recorded on a Bruker 200 MHz or 250 MHz spectrometer. Chemical shifts were recorded in parts per million (ppm), and splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). Coupling constants, $J$, are reported in hertz (Hz). The residual proton signal of the solvent was used as an internal standard for spectra recorded in chloroform-*d* (7.27 for $^1$H, 77 for $^{13}$C). Mass spectra were determined by M-Scan Inc. on either a Micromass Q-Tof API US hybrid quadrupole/time-of-flight mass spectrometer or a VG Analytical ZAB 2-SE high field mass spectrometer. The molecular weights of polymers were determined using a Plgel 5 $\mu$m Mixed-B (600 × 7.5 mm) column and a diode array detector at 300 nm at a flow rate of 1.0 mL/min. Polymer molecular weights are reported relative to polystyrene standards purchased from Aldrich.

**Optical and Electrochemical Characterizations.** UV absorption spectra were recorded on a Perkin-Elmer Lambda 35 UV/vis spectrometer. Solid-state absorption spectra were obtained on thin films coated on quartz prepared by spin-coating of the polymer

solution in chlorobenzene. Electrochemical characteristics were determined by cyclovoltametry experiments carried out on drop-cast polymer films at room temperature in a glovebox. The supporting electrolyte was tetrabutylammonium hexafluorophosphate (TBAPF$_6$, electrochemical grade, Aldrich) in anhydrous acetonitrile (~0.1 M). The working electrode (WE) as well as the counter electrode (CE) was a platinum foil. A silver wire coated with AgCl was used as the reference electrode (RE). After each measurement the RE was calibrated with ferrocene ($E^0$ = 400 mV vs NHE), and the potential axis was corrected to NHE (using −4.75 eV for NHE) according to the difference of $E^0$ (ferrocene) and the measured $E^{1/2}$ (ferrocene). The onset for oxidation and reduction was determined as the point where the CV trace differed from the baseline by more than 1 $\mu$A relative to the baseline.

**Polymer Solar Cell Fabrication and Analysis.** Conductive indium tin oxide (ITO) coated glass was purchased from Merck. The ITO−glass substrate was cleaned by ultrasonification sequentially in acetone, isopropyl alcohol, and deionized water. On top of the conductive side was coated a layer of PEDOT:PSS (Baytron PH from H.C. Starck, ~60 nm thick) applied by doctorblading. After being dried, this PEDOT:PSS film is covered by a layer of a blend of the polymers (**8** or **9a**−**9c**)/PC$_{61}$BM or PC$_{71}$BM (purchased from Nano-C) in a 1:3 w/w ratio by doctorblading method from *o*-dichlorobenzene solution. The active layer thickness was determined by AFM to be between 150 and 250 nm. As the cathode, a thin layer of LiF (ca. 1 nm thick) and a film of aluminum (ca. 80 nm thick) were thermally evaporated. Device characterization was carried out under AM 1.5G irradiation (100 mW/cm$^2$) on an Oriel Xenon solar simulator with a spectral mismatch of 0.83 for the spectral range down to 1000 nm. $I-V$ characteristics were recorded with a Keithley 2400. Active areas were in the range 15−20 mm$^2$.

**Synthesis. 4,4-Dihexyl-2,6-bis(trimethylstannanyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene.** Starting material 4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (1.5 g, 0.004 33 mol) was dissolved in dry THF (30 mL). The solution was cooled to −78 °C, and butyllithium (6.1 mL, 0.0130 mol) was added dropwise. The reaction was stirred at this temperature for 2 h, warmed to room temperature, and stirred for 3 h. Again the reaction was cooled to −78 °C, and trimethyltin chloride (1 M in hexanes, 16.0 mL, 16.0 mmol) was added dropwise. The reaction was allowed to warm to room temperature and stirred for 17 h. Water was added, and the reaction was extracted with toluene. The organic layer was washed with water and dried over sodium sulfate. Solvent was removed under vacuum, and the residue was dissolved in toluene and quickly passed through a plug of silica gel pretreated with triethylamine. Solvent was removed, and the residue dried under vacuum to afford 2.65 g (91% yield) of the bis(trimethyltin) monomer. $^1$H NMR (CDCl$_3$, 200 MHz): 6.97 (m, 2H), 1.84 (m, 4H), 1.20 (m, 16H), 0.88 (m, 6H), 0.42 (m, 18H). $^{13}$C NMR (CDCl$_3$, 62.9 MHz): 160.88, 142.71, 140.36, 129.88, 52.60, 38.01, 32.04, 25.05, 23.08, 14.54, −7.57. HRMS (EIS) *m/z*, calcd for C$_{27}$H$_{46}$S$_2$Sn$_2$ (M$^+$): 674.1085; found: 674.1094.

**4,4-Bis(2-ethyl-hexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene.** 4*H*-Cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (1.5 g, 0.008 43 mol) was dissolved in DMSO (50 mL). The solution was purged with nitrogen, and ground KOH (1.89 g, 0.0337 mol) and sodium iodide (50 mg) were added, followed by 2-ethylhexyl bromide (3.25 g, 0.0169 mol). The reaction was stirred overnight under nitrogen (ca. 16 h). Water was added, and the reaction was extracted with *tert*-butyl methyl ether. The organic layer was separated and dried over magnesium sulfate. Solvent was removed under vacuum, and the residue was purified by chromatography using hexanes as eluent. Fractions containing pure 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene product were combined, and the solvents were evaporated. The product was obtained as a colorless oil after drying under vacuum. Yield: 2.68 g (79%). $^1$H NMR (CDCl$_3$, 250 MHz): 7.13 (m, 2H), 6.94 (m, 2H), 1.88 (m, 4H), 0.94 (m, 16H), 0.78 (t, 6.4 Hz, 6H), 0.61 (t, 7.3 Hz, 6H). $^{13}$C NMR (CDCl$_3$, 50.3 MHz): 158.01, 137.26, 124.39, 122.76, 53.67, 43.69, 35.43, 34.70, 29.03, 27.71, 23.18, 14.52, 11.08. HRMS (FAB) *m/z*, calcd for C$_{25}$H$_{38}$S$_2$ (M$^+$): 402.2415; found: 402.2417.

**4,4-Bis(2-ethylhexyl)-2,6-bis(trimethylstannanyl)-4*H*-cyclopenta-[2,1-*b*:3,4-*b*′]dithiophene.** Starting material 4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (1.5 g, 0.003 72 mol) was dissolved in dry THF (30 mL). The solution was cooled to −78 °C, and butyllithium (5.96 mL, 0.0149 mol) was added dropwise. The reaction was stirred at this temperature for 1 h and allowed to warm to room temperature over 3 h, at which point it was stirred for an additional hour. The reaction was then cooled to −78 °C, and trimethyltin chloride (1 M in hexanes, 18 mL, 18 mmol) was added dropwise. The reaction was allowed to warm to room temperature and stirred overnight (ca. 20 h). Water was added, and the reaction was extracted with methyl *tert*-butyl methyl ether. The organic layer was washed with water and dried over sodium sulfate. Solvent was removed under vacuum, and the residue was dissolved in toluene and quickly passed through a plug of Celite pretreated with triethylamine. Solvent was removed, and the residue dried under vacuum at 80 °C overnight. The distannyl compound was dissolved in hexanes and filtered through a plug of densely packed Celite. Solvent was removed, and the residue dried under vacuum overnight. The bis(trimethyltin) monomer was obtained as a light brownish viscous oil (2.52 g, 93%). $^1$H NMR (CDCl$_3$, 250 MHz): 6.96 (m, 2H), 1.85 (m, 4H), 1.29 (m, 2H), 0.92 (m, 16H), 0.78 (t, 6.8 Hz, 6H), 0.61 (t, 7.3 Hz, 6H), 0.38 (m, 18H). $^{13}$C NMR (CDCl$_3$, 62.9 MHz): 160.11, 143.09, 136.60, 130.52, 52.78, 43.57, 35.56, 34.91, 29.18, 28.07, 23.28, 14.63, 11.26, −7.79. HRMS (EIS) *m/z*, calcd for C$_{31}$H$_{54}$S$_2$Sn$_2$ (M$^+$): 730.1711; found: 730.1722.

**Polymerization of Bis(trimethylstannyl)-4,4-bis(2-ethylhexyl)-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene and 4,7-Dibromo-2,1,3-benzothiadiazole To Afford Polymer 8.** Bis(trimethylstannyl)-4,4-di(2-ethylhexyl)-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (0.291 g, 0.399 mmol) and 4,7-dibromo-2,1,3-benzothiadiazole (0.115 g, 0.391 mmol) were dissolved in toluene (30 mL). The reaction was purged with nitrogen, and tris(dibenzylideneacetone)dipalladium (0.0072 g, 0.0078 mmol) and triphenyphosphine (0.0164 g, 0.0625 mmol) were added. The reaction was further purged with nitrogen for 10 min and heated to 120 °C under nitrogen for 48 h. The reaction was poured into methanol (500 mL), and the blue precipitates were collected by filtration, washed with methanol, and dried. The solid was dissolved in chlorobenzene (150 mL), and an aqueous solution of sodium diethyldithiocarbamate trihydrate (6.3 g in 84 mL water) was added. The mixture was stirred at 80 °C under nitrogen overnight. The organic layer was separated and was passed through a column packed with alumina, Celite, and silica gel. The column was eluted with chlorobenzene. The combined polymer solution was concentrated to 50 mL and was poured into methanol (500 mL). The precipitates were collected and dissolved in chlorobenzene (30 mL). Purification by prep GPC using chlorobenzene as solvent afforded the polymer as a dark blue solid (138 mg, $M_n$ = 28 kDa, $d$ = 1.5). Polymers of higher molecular weights were obtained by further fractionation with prep GPC. $^1$H NMR (CDCl$_3$, 200 MHz): 8.16 (s, br, 2H), 7.91 (s, br, 2H), 2.10 (s, br, 2H), 1.08 (m, 20H), 0.74 (m, 12H).

**Representative Preparation of Polymers 9a−9c: Polymerization of Bis(trimethylstannyl)-4,4-bis(2-ethylhexyl)cyclopenta-[2,1-*b*:3,4-*b*′]dithiophene and 5,5′-Dibromo-[2,2′]bithiophene and 4,7-Dibromo-2,1,3-benzothiadiazole in a Mole Ratio of 3:1:2 To Afford Polymer 9a.** Bis(trimethylstannyl)-4,4-bis(2-ethylhexyl)-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (0.250 g, 0.343 mmol), 5,5′-dibromo[2,2′]bithiophene (0.0367 g, 0.113 mmol), and 4,7-dibromo-2,1,3-benzothiadiazole (0.0666 g, 0.227 mmol) were dissolved in toluene (20 mL). The reaction was purged with nitrogen, and tris-(dibenzylideneacetone)dipalladium (3.14 mg, 3.43 $\mu$mol) and triphenylphosphine (7.20 mg, 27.5 $\mu$mol) were added. The reaction was further purged with nitrogen and heated to 120 °C under nitrogen for 30 h. The reaction was poured into methanol (250 mL), and the precipitate was collected by filtration, washed with methanol, and dried. The solid was dissolved in chlorobenzene (150 mL), and a solution of sodium diethyldithiocarbamate trihydrate (2 g in 20 mL of water) was added. The mixture was stirred at 80 °C under nitrogen for 18 h. The organic layer was separated and was passed through a column packed with alumina, Celite,

and silica gel. The column was eluted with chlorobenzene. The combined polymer solution was concentrated to 10 mL and was poured into methanol (100 mL). The precipitates were collected. The polymer was dissolved in cholrobenzene and purified by prep GPC to afford the pure polymer (85 mg, 28 kDa, $d = 1.4$). $^1$H NMR (CDCl$_3$, 200 MHz): 8.16 (s, br, 4H), 7.91 (s, br, 6H), 7.14 (s, br, 4H), 2.04 (s, br, 6H), 0.7−1.1 (m, 96H).

**Polymerization of Bis(trimethylstannyl)-4,4-bis(2-ethylhexyl)-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene and 5,5′-Dibromo[2,2′]-bithiophene To Afford Polymer 10.** Bis(trimethylstannyl)-4,4-bis(2-ethylhexyl)cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (0.198 g, 0.000 272 mol) and 5,5′-dibromo[2,2′]bithiophene (0.0873 g, 0.000 269 mol) were dissolved in toluene (20 mL). The reaction was purged with nitrogen, and tris(dibenzylideneacetone)dipalladium (2.46 mg, 2.69 $\mu$mol) and triphenylphosphine (5.65 mg, 21.6 $\mu$mol) were added. The reaction was further purged with nitrogen for 10 min and heated to 120 °C under nitrogen for 48 h. The reaction was poured into methanol (250 mL), and the red precipitates were collected by filtration, washed with methanol, and dried. The solid was dissolved in chlorobenzene (150 mL), and a solution of sodium diethyldithiocarbamate trihydrate (2 g in 20 mL water) was added. The mixture was stirred at 80 °C under nitrogen overnight. The organic layer was separated and was passed through a column packed with alumina, Celite, and silica gel. The column was eluted with chlorobenzene. The combined polymer solution was concentrated to 10 mL and was poured into methanol (100 mL). Prep GPC afforded the purified polymer ($M_n$ 15 kDa, 121 mg). $^1$H NMR (CDCl$_3$, 200 MHz): 7.15 (m, 6H), 1.94 (s, br, 2H), 1.07 (m, 20H), 0.74 (m, 12H).

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