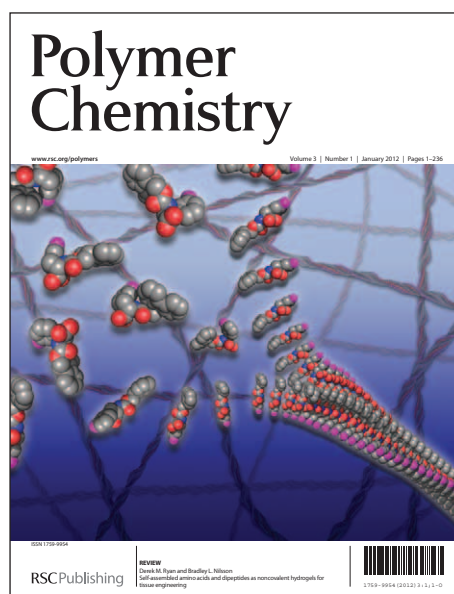


Polymer Chemistry

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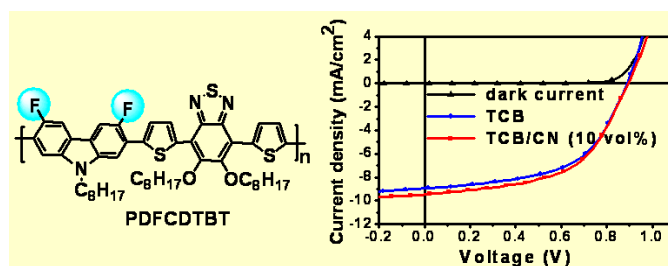
Conjugated Polymers with 2,7-Linked 3,6-Difluorocarbazole as Donor Unit for High Efficiency Polymer Solar Cells

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3,6-Difluorocarbazole based D-A type conjugated polymer **PDFCDTBT** was synthesized and used as donor materials for bulk heterojunction polymer solar cells.



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Conjugated Polymers with 2,7-Linked 3,6-Difluorocarbazole as Donor Unit for High Efficiency Polymer Solar Cells

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A novel donor-acceptor (D-A) copolymer **PDFCDTBT** with 3,6-difluoro substituted carbazole as the donor unit and dialkoxy substituted benzothiadiazole as the acceptor unit has been synthesized and used as donor materials for bulk heterojunction polymer solar cells (BHJ PSCs). **PDFCDTBT** possesses a band gap of 1.75 eV, a low-lying HOMO energy level of -5.23 eV, and a good thermal and electrochemical stability. In comparison with the corresponding non-fluoro substituted **HXS-1**, which has a HOMO energy level of 5.21 eV, a LUMO energy level of 3.35 eV, and an optical band gap of 1.86 eV, the incorporation of two fluoro atoms in the carbazole donor unit lowers the HOMO and the LUMO energy levels of polymer, results in simultaneous decreasing the band gap of polymer and increasing the V_{oc} of polymer solar cells. The fluoro-containing polymer **PDFCDTBT** also shows strong intramolecular interactions and forms close packing in solid state. Polymer solar cells based on **PDFCDTBT** and (6,6)-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) demonstrate a power conversion efficiency (PCE) of 4.8 % with a V_{oc} of 0.91 V, a J_{sc} of 9.5 mA/cm², and an FF of 0.55. In comparison with **HXS-1**, the better stability, higher V_{oc} , and narrower band gap indicate that **PDFCDTBT** is a very promising donor material for high efficiency polymer solar cells.

Introduction

As a method to use clean and renewable solar energy, bulk-heterojunction (BHJ) solar cells based on composites of electron-donating conjugated polymers (donor) and electron-accepting fullerene derivatives (acceptor) have been paid considerable attention for their obvious advantages over traditional silicon-based solar cells, such as low cost, light weight, and high-throughput manufacture.¹ (6,6)-Phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) and (6,6)-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) are commonly used acceptor materials and medium and low band gap conjugated polymers are commonly used donor materials.² Great effort has been devoted to developing novel polymer donor materials,^{2f,3} interfacial materials,⁴ and device structures.⁵ The power conversion efficiency (PCE) for polymer solar cells has been increased to around 10%.⁶

To fully exploit the solar energy, the absorption spectra of conjugated polymers need to cover a wider scope of the terrestrial solar spectrum in order to harvest sun light as more as possible to convert into J_{sc} .⁷ Therefore, it is highly desirable to develop conjugated polymers with a broader absorption through decreasing their optical band gap. An effective strategy in designing low band gap conjugated polymers is to alternate an electron-rich donor (D) unit and an electron-deficient acceptor (A) unit in the same conjugated polymer backbone.⁸ In the past several years, we have made a great effort to develop new low

band gap polymer materials for high efficiency polymer solar cells.⁹ In 2009, we have reported the design and synthesis of a planar narrow band gap conjugated polymer **HXS-1** for high efficiency polymer solar cells, and a PCE of 5.4% has been achieved.^{9a,10} **HXS-1** has a HOMO energy level of 5.21 eV, a LUMO energy level of 3.35 eV, and an optical band gap of 1.86 eV. Considering the ideal HOMO and LUMO energy levels of polymer donor are around 3.9 eV and 5.4 eV, respectively,¹¹ it would be of great importance to lower the HOMO and LUMO energy levels of **HXS-1**. Lowering the HOMO and LUMO energy levels of **HXS-1** will lead to narrower band gap and higher open-circuit voltage (V_{oc}). V_{oc} and short-circuit current (J_{sc}) are two most important parameters that determine the PCEs of PSCs. Recently, high efficiency donor polymers based on fluoro containing narrow band gap polymers have been reported by several groups.¹² In comparison with the corresponding non-fluoro substituted ones, the fluoro containing narrow band gap conjugated polymers exhibited deeper HOMO and LUMO energy levels. It is worthy noting that almost for all reported fluoro containing high efficiency polymers the fluoro atoms are located at the acceptor unit except one example reported by Yu et al.^{12c-f} According to the hybrid orbital theory and molecular orbital theory, the polymers' HOMO energy level should also be largely affected by the HOMO level of donor unit.¹³ Herein we report the design and synthesis of a D-A alternating conjugated polymer (**PDFCDTBT**) with 3,6-difluorocarbazole as the fluoro substituted donor unit. The chemical structures of **HXS-1** and

PDFCDTBT are shown in Chart 1. Due to the S-O supramolecular interaction, the two alkoxy chains on the benzothiadiazole unit can simultaneously increase the planarity and solubility of polymers.¹⁴ As expected, the fluorinated polymer PDFCDTBT exhibits markedly lower HOMO and LUMO energy level, forms closed packing in solid state, and shows higher thermal and electrochemical stability. Polymer solar cells with the blend of PDFCDTBT/PC₇₁BM (1:1.8) as the active layer showed a PCE of 4.8% under simulated solar illumination of AM 1.5G (100 mW/cm²). To the best of our knowledge, this is the first report that 3,6-difluorocarbazole can be a useful donor unit to construct narrow band gap conjugated polymers.

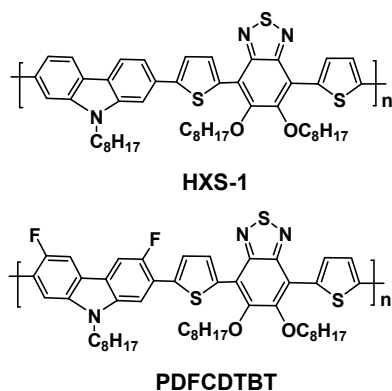
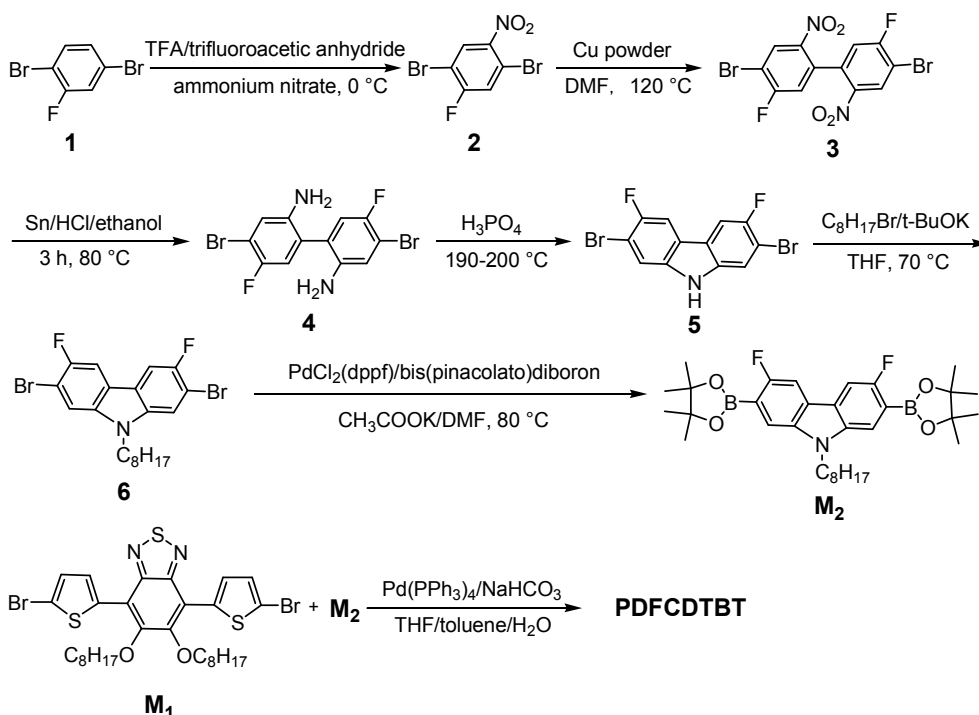


Chart 1. Chemical structures of HXS-1 and PDFCDTBT.



DSC curves. The gel permeation chromatography (GPC) measurements were performed at 150 °C on a PL-220 (Polymer

Experimental Section

Materials and instruments. Unless otherwise noted, all chemicals were purchased from commercial suppliers without further purification. Solvents were dried using standard procedures. The catalyst precursor Pd(PPh₃)₄ was prepared according to the literature¹⁵ and stored in a Schlenk tube under nitrogen. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium with benzophenone as an indicator under nitrogen atmosphere. Hexane and dichloromethane (CH₂Cl₂) were distilled from CaH₂. Chloroform (CF) 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 or 1,2-dichlorobenzene-D₄. UV-vis absorption spectra were obtained on a PerkinElmer Lambda 750 UV/VIS/NIR Spectrometer. Fluorescence spectra were recorded on a Horiba Scientific FluoroMax-4 spectrofluorometer. Matrix-assisted laser desorption ionization time of flight mass spectrum were performed on Bruker BIFLEXIII. 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

Laboratories) chromatography connected to a differential refractometer with 1,2,4-trichlorobenzene (TCB) 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 150 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 **PDFCDTBT** 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.¹⁶

Synthesis of 3,6-difluoro-9-octyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (M2**):** A mixture of 2,7-dibromo-3,6-difluoro-9-octyl-9H-carbazole (**6**) (0.30 g, 0.63 mmol), bis(pinacolato)diboron (0.40 g, 1.58 mmol), PdCl₂(dppf) (25.9 mg, 0.03 mmol), potassium acetate (0.37 g, 3.8 mmol) in dry N,N-dimethylformamide (DMF) (20 mL) was stirred at 80 °C for 3 days. The reaction mixture was allowed to cool to room temperature; water (200 mL) was added; the aqueous layer was extracted with diethyl ether (3 × 100 mL); and the combined organic layers were washed with brine, dried over Na₂SO₄, and evaporated to dryness. The residue was purified by flash column chromatography (SiO₂, petroleum ether (60-90 °C)/ethyl acetate = 4/1 by volume) and recrystallization from petroleum ether to afford **M2** as a white crystal (162 mg, 45%). ¹H NMR (400 MHz, CDCl₃) δ 7.72-7.71 (d, 2H), 7.66-7.64 (d, 2H), 4.35-4.32 (t, 2H), 1.88-1.85 (m, 2H), 1.41 (s, 24H), 1.36-1.26 (m, 10H), 0.88-0.85 (t, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 162.20, 159.80, 137.87, 125.31, 125.27, 125.21, 125.17, 116.41, 116.31, 106.38, 106.11, 83.91, 43.14, 31.76, 29.22, 29.13, 29.05, 27.01, 24.86, 22.59, 14.05. MALDI-TOF, m/z: calcd, 567.4; found, 567.4 (M⁺). Anal. calcd. for C₃₂H₄₅B₂F₂NO₄: C 67.75, H 7.99, N 2.47; Found: C 68.09, H 7.35, N 2.32

Synthesis of poly[3,6-difluoro-9-octyl-9H-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-5',6'-bis(octyloxy)-2',1',3'-benzothiadiazole)] (PDFCDTBT**):** A mixture of **M1** (200 mg, 0.28 mmol) and **M2** (159 mg, 0.28 mmol), THF (45 mL), toluene (15 mL), H₂O (4 mL), and NaHCO₃ (0.4 g, 4.8 mmol) was carefully degassed before and after Pd(PPh₃)₄ (3.6 mg, 3.2 μmol) was added. The mixture was stirred and refluxed under nitrogen for 3 days. Phenylboronic acid (10 mg) and Pd(PPh₃)₄ (1.8 mg, 1.6 μmol) were added; the reaction mixture was refluxed for 4 h to block the bromo endgroups; bromobenzene (100 μL) was added; and the reaction mixture was refluxed overnight to block the boronic endgroups. 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 solution was 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 resulted precipitates were collected by filtration and washed with acetone. The crude product was again dissolved in a minimum amount of

chlorobenzene, precipitated into a large amount of acetone, and the formed precipitates were collected by filtration and dried under high vacuum to afford **PDFCDTBT** as a dark red solid (220 mg, 91%). ¹H NMR (400 MHz, 1,2-dichlorobenzene-D₄) δ 8.97-8.79 (br, 2H), 7.93-7.67 (br, 6H), 4.39-4.27 (br, 6H), 2.28-0.92 (br, 45H); GPC (PS standards): M_w = 23.9 kg/mol, M_n = 9.1 kg/mol, and PDI = 2.64.

Polymer Solar Cell Fabrication and characterization. Polymer solar cells (PSCs) were fabricated with the device configuration of ITO/PEDOT:PSS/Polymer:PC₇₁BM /LiF/Al. The conductivity of ITO is 15 Ω/□ and PEDOT:PSS is Baytron Al 4083 from H.C.Starck. The ITO glass was cleaned and a thin layer of PEDOT:PSS was spin coated at 3000 rpm/s and dried subsequently at 120 °C for 10 min in an oven, and then transferred to a glove box. The blend of **PDFCDTBT** and PC₇₁BM was dissolved in different solvents 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 100 nm Al at a pressure of 1×10⁻⁶ mbar. Six cells were fabricated on one substrate with an effective area of 0.04 cm². Current-voltage characteristics were recorded using a Keithley 236 Source Meter under illumination of AM 1.5 G with intensity of 100 mW/cm² from a solar simulator (model XES-301S, AAA, SAN-EI).

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 (30%), 2:1, by volume), pure water, pure ethanol and pure acetone, successively, then treated with a monolayer of trichloro(octadecyl)silane (OTS) by the normal vapor deposition method described elsewhere.¹⁷ Polymer films were spin-coated on the OTS modified Si/SiO₂ substrate from 1,2-dichlorobenzene (DCB) with the polymer concentration of 7 mg/mL. Electrodes of Au (25 nm) were vacuum deposited on films with width/length = 50 (channel width = 2.5 mm, channel length = 50 μm). *J-V* characteristics were obtained using a Keithley 4200 SCS with a Micromanipulator 6150 probe station in a clean and shielded box at room temperature in air. In order to confirm the reproducibility, about 10-20 transistors were examined at each condition.

Results and Discussion

Material Synthesis. The synthesis of **PDFCDTBT** is outlined in **Scheme 1**. Starting from commercially available 1,4-dibromo-2-fluorobenzene (**1**), its nitration with ammonium nitrate in the media of methylene chloride, trifluoroacetic acid, and trifluoroacetic anhydride (2:2:1, v/v) afforded 1,4-dibromo-2-fluoro-5-nitrobenzene (**2**).¹⁸ Ullmann coupling of 1,4-dibromo-2-fluoro-5-nitrobenzene (**2**) furnished 4,4'-dibromo-5,5'-difluoro-2,2'-dinitrobiphenyl (**3**) in 82% yield.¹⁹ The reduction of **3** with Sn/HCl/ethanol gave 4,4'-dibromo-5,5'-difluoro-biphenyl-2,2'-diamine (**4**) and the treatment of **4** with concentrated H₃PO₄ at 190 °C for 24 h furnished 2,7-dibromo-3,6-difluoro-9H-carbazole (**5**) in a total yield of 52%.²⁰ The reaction of **5** and 1-

bromooctance in THF with *t*-BuOK as the base afforded 2,7-dibromo-3,6-difluoro-9-octyl-9H-carbazole (**6**) in a yield of 89%. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-difluoro-9-octyl-9H-carbazole (**M2**) was accomplished in a yield of 45% by Miyaura reaction of **6** and bis(pinacolato)diboron at 80 °C with PdCl₂(dppf) as the catalyst precursor, potassium acetate as the base, and DMF as the solvent. The structure and purity of **M2** were confirmed by ¹H and ¹³C NMR spectroscopy and combustion analysis. The synthesis of monomer **M1** was reported in our previous paper.^{9a} Suzuki-Miyaura polymerization of **M1** and **M2** was carried out in a biphasic mixture of THF/toluene (3:1) and aqueous NaHCO₃ with Pd(PPh₃)₄ as the catalyst precursor. After polymerization for 72 hours, phenylboronic acid and then bromobenzene was consecutively added at a time interval of 4 hours to end cap the polymer. **PDFCDTBT** was obtained as a dark red solid in a yield of 91%. Although **PDFCDTBT** shows poor solubility in common organic solvents such as THF, CF, DCB, etc. at room temperature, it could be readily dissolved in chlorobenzene, DCB, TCB, etc. at elevated temperature., therefore its molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC) at elevated temperature (150 °C) using TCB as an eluent calibrated with polystyrene standards. **PDFCDTBT** shows a number-average molecular weight (*M_n*) of 9.1 kg/mol, a weight-average molecular weight (*M_w*) of 23.9 kg/mol, and a polydispersity index (PDI) of 2.63.

Optical Properties

The normalized UV-vis absorption spectra of **PDFCDTBT** and **HXS-1** in chlorobenzene and CF solutions at 20 °C are shown in Figure 1a. In chlorobenzene solutions, both **PDFCDTBT** and **HXS-1** show similar absorption spectra with two strong absorption peaks located at 383 and 517 nm. In CF solution, the absorption spectrum of **HXS-1** completely overlap with that in chlorobenzene; whereas in CF solution, the long wavelength absorption peak, which is originated from the internal charge transfer (ICT) of **PDFCDTBT**, red-shifted from 517 to 532 nm and an obvious absorption shoulder at 575 nm emerged, indicating the aggregation of **PDFCDTBT** molecules in CF solution. The film absorption spectra of **PDFCDTBT** and **HXS-1** are shown in Figure 1b. In comparison with their solution absorption ones, the absorption peaks of films are markedly red-shifted and broader due to the aggregation of polymer chains in films. The optical absorption onset of the **HXS-1** film is at 667 nm, corresponding to an optical band gap of 1.86 eV. The film absorption spectrum of **PDFCDTBT** is much broader than that of **HXS-1** with an absorption onset of 709 nm, indicating that in film the aggregation of **PDFCDTBT** is much stronger than that of **HXS-1**, and leading to an optical band gap of 1.75 eV. The close packing of **PDFCDTBT** in film is also confirmed by XRD results (vide infra). The photoluminescence spectra of **HXS-1** and **PDFCDTBT** in chlorobenzene solutions and in films with the excitation wavelength of 515 nm are shown in Figure S1. The emission spectra of **HXS-1** and **PDFCDTBT** in CB solutions are almost superimposed with their corresponding film emission ones. It is worthy noting that in both CB solutions and films the emission spectra of **PDFCDTBT** are red-shifted and narrowing in comparison with that of **HXS-1**.

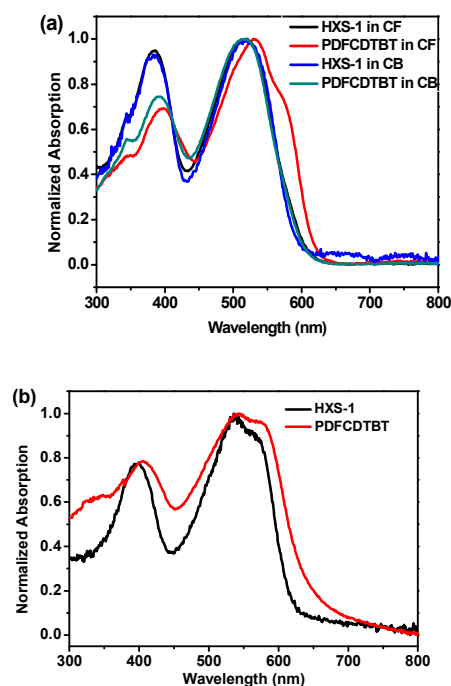


Figure 1. Normalized absorption spectra of **HXS-1** and **PDFCDTBT** in CF and CB solution (a) and in thin films (b).

Theoretical Calculations and Electrochemical Properties

The HOMO and LUMO energy level positions have pronounced influence on *V_{oc}*, offset (the driving force for charge separation), and the overall photovoltaic performance. We have estimated the HOMO and LUMO energy levels of the repeating units (the alkyl chains were simplified as methyls) of the corresponding alternating copolymers by using the density functional theory (DFT) calculations that were performed at the B3LYP/6-31+G(d) level. The electron distribution of HOMO and LUMO orbits of repeating units are shown in Figure 2 and the simulated data are summarized in Table 1. With two fluorine atoms on the donor unit, lower LUMO and HOMO energy levels and similar band gap of a repeating unit for **PDFCDTBT** were predicted.

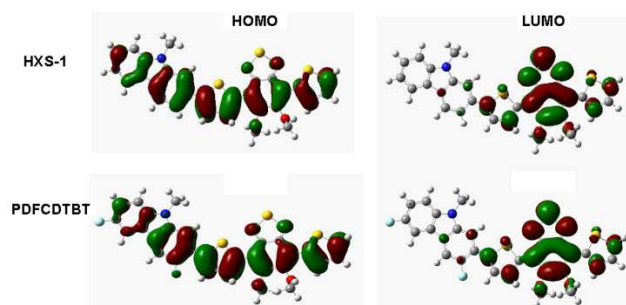


Figure 2. Simulated orbits of HOMO (left) and LUMO (right) of **HXS-1** and **PDFCDTBT** by DFT calculations.

Cyclic voltammetry (CV) was used to determine the electrochemical properties of polymers. CV measurements were performed in a solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) in acetonitrile (0.10 M) with a scan rate of 100 mV/s at room temperature. A platinum electrode

($\sim 0.05 \text{ cm}^2$) coated with a thin polymer film was used as the working electrode. Pt wire and Ag/AgNO₃ electrode were used as the counter and reference electrode, respectively. And a standard ferrocene/ferrocenium (F_c) redox system was used as the internal standard for estimating the HOMO energy level of polymer films. The cyclic voltammograms are shown in Figure 3, and the oxidation onsets are summarized in Table 1. Taking 4.8 eV as HOMO level for the ferrocene/ferrocenium redox system, the HOMO energy levels of polymers were calculated according to the following equation:

$$E_{\text{HOMO}} = -(E_{\text{onset}}(\text{polymer vs. Ag/Ag}^+) - E_{\text{onset}}(\text{Fc/Fc}^+ \text{ vs. Ag/Ag}^+)) - 4.8 \text{ eV}$$

The oxidation onsets of **HXS-1** and **PDFCDTBT** were estimated to be 0.50 and 0.52 V, which correspond to HOMO energy levels of -5.21 and -5.23 eV.²¹ **HXS-1** exhibits an irreversible process in the oxidation scan; whereas **PDFCDTBT** is partially reversible. The unstability of polymers **HXS-1** is probably due to that the

3,6-positions of the carbazole ring in 2,7-linked carbazole polymers are highly active and can form radical-cations of carbazolic units.^{20,22} The carbazole polymers can form cross-linking structures during the CV measurements.²³ Because of the protection of active 3,6-positions of carbazole by fluorine atoms, **PDFCDTBT** is more stable than **HXS-1**.²⁴ Compared with **HXS-1**, a slightly lower HOMO energy level of **PDFCDTBT** will provide a slightly higher V_{oc} for photovoltaic device with a blend of **PDFCDTBT** and PC₇₁BM as the active layer. The LUMO energy levels of polymers were calculated to be -3.35 eV for **HXS-1** and -3.48 eV for **PDFCDTBT** by using the following equation: $E_{\text{LUMO}} - E_{\text{HOMO}} = E_{\text{g, opt}}$. The offsets (E_{LUMO} of polymer - E_{LUMO} of PC₇₁BM) are 0.85 eV for **HXS-1** and 0.72 eV for **PDFCDTBT**, which should provide an enough driving force for efficient exciton dissociation in bulk heterojunction polymer-fullerene solar cells.²⁵

Table 1. Electrochemical Potentials and Energy Levels of the Polymers.

Polymers	E_{HOMO}^a (eV)	E_{LUMO}^a (eV)	E_{onset}^b (V)	E_{HOMO}^c (eV)	E_{LUMO}^d (eV)	E_{gap}^e (eV)
HXS-1	-5.29	-3.05	0.50	-5.21	-3.35	1.86
PDFCDTBT	-5.46	-3.17	0.52	-5.23	-3.48	1.75

^a HOMO and LUMO energy levels simulated by DFT theory calculations. ^b Onset oxidation potential measured by cyclic voltammetry. ^c Determined by cyclic voltammetry measurements. ^d Determined by $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{gap}}$. ^e $E_{\text{gap}} = hc/\lambda_{\text{onset}}$.

Thermal stability of polymers is also a very important parameter for the performance of the BHJ polymer solar cell devices. Thermal properties of the two polymers were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA and DSC curves of **PDFCDTBT** are shown in Figure S2. The 5% weight loss temperatures (T_d) and the glass transition temperatures (T_g) of **PDFCDTBT** and **HXS-1**^{9a} are summarized in Table 2 for a comparison. Since molecular weight of polymers can have a significant influence on their thermal properties, the number- and weight-average molecular weights (M_n and M_w) of two polymers are also listed in Table 2. Although the molecular weight of **PDFCDTBT** is lower than **HXS-1**, the T_d of **PDFCDTBT** is about 30 °C higher than that of **HXS-1**. The deeper HOMO energy level and the protection of the active 3,6-positions of carbazole unit are probably responsible for the higher thermal stability of **PDFCDTBT**. In comparison with **HXS-1**, the glass transition temperature (T_g) of **PDFCDTBT** is also increased.

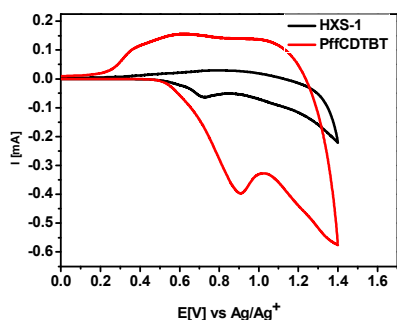


Figure 3. Cyclic voltammograms of the **HXS-1** and **PDFCDTBT** films in 0.1 M Bu₄NPF₆ acetonitrile solution at a scan rate of 100 mV/s.

X-ray Analyses

Close packing of polymer chains in the solid state is very crucial for the transportation of charge carriers and thus achieving high performance polymer solar cells.^{9a-c,26} X-ray diffraction (XRD) analyses on powdery polymers were performed and the diffraction patterns are shown in Figure S3. **HXS-1** exhibits two peaks, the first peak with a small angle of 5.2° reflects the distance of 17.0 Å between polymer backbones separated by alkyl side chains, and the second peak with a wide angle of 22.3° reflects a π - π stacking distance of 4.0 Å between the polymer backbones. **PDFCDTBT** shows five diffraction peaks ranging from 5.36° to 24.1°, the first peak at a wide angle of 24.1° reflects a much closer π - π stacking distance of 3.7 Å between the polymer backbones, and the sharp and intense peak at 5.36° reflects a much ordered packing of polymer chains with a distance of 16.5 Å between polymer backbones separated by alkyl side chains.²⁷ The data of X-diffraction are summarized in Table S1. The much closer and more ordered packing of **PDFCDTBT** in solid state is probably related to the highly favorable dipole-dipole interactions between conjugated polymer chains bearing fluoro atoms.²⁸

Transport Properties

The transport properties of the polymers were investigated by fabricating organic thin film field effect transistors (OFETs). Typical *p*-channel field-effect transistor behavior was obtained. The hole mobility (μ) was estimated in the saturated regime from the derivative plots of the square root of source-drain current (I_{SD}) versus gate voltage (V_G) through equation $I_{\text{SD}} = (W/2L)C_i\mu(V_G - V_T)^2$ where W is the channel width, L is the channel length, C_i is the capacitance per unit area of the gate dielectric layer (SiO₂, 500 nm, $C_i = 7.5 \text{ nF/cm}^2$), and V_T is the threshold voltage. The transfer characteristic curve of the spin-coated film of **PDFCDTBT** on OTS-treated Si/SiO₂ substrates are shown in Figure 4. The hole mobility of **PDFCDTBT** from DCB solution

Table 2. Number Average Molecular Weights (M_n), Weight Average Molecular Weights (M_w), Polydispersity Index (PDI), Degradation Temperatures (T_d) (5% weight loss), and Glass Transition Temperatures (T_g) of **HXS-1** and **PDFCDTBT**.

Sample	M_n (kg/mol)	M_w (kg/mol)	PDI	T_d (°C)	T_g (°C)
HXS-1 ^a	30.2	101.7	3.36	300	105
PDFCDTBT	9.1	23.9	2.63	328	112

^a Data from ref^{9a} and confirmed by experiment.

is $3.1 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with on/off ratio in the order of 10^5 by simple device fabrication without device optimization. Such high hole mobility is attributed to the strong π - π interactions between the planar polymer chains, especially the presence of fluoro atom can bring the polymer chain into closer proximity as evidenced by the XRD results. Closer distance between the polymer chains can facilitate the interchain charge hopping. Generally, mobility higher than $10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ is desired for high-efficiency PSCs. Therefore, **PDFCDTBT** with high hole mobility is expected to be

Table 3. Parameters of **PDFCDTBT**:PC₇₁BM based devices fabricated from TCB with or without different volume of CN.

PDFCDTBT :PC ₇₁ BM	Solvent	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)	Thickness (nm)
1:1.8	TCB	0.91	8.9	0.56	4.56	78
1:1.8	TCB/CN (2%)	0.89	9.2	0.55	4.52	74
1:1.8	TCB/CN (6%)	0.88	9.1	0.55	4.40	102
1:1.8	TCB/CN (10%)	0.91	9.5	0.55	4.80	80

Photovoltaic Properties

Photovoltaic properties of polymers were investigated in devices with the structure of ITO/PEDOT:PSS (40 nm)/**PDFCDTBT**:PC₇₁BM/LiF (0.5 nm)/Al (100 nm). The active layer is a blend of **PDFCDTBT** donor and PC₇₁BM acceptor. PC₇₁BM is chosen as the acceptor because it has similar electronic properties as PC₆₁BM, but a higher absorption coefficient in the visible region with a broad peak from 440 to 530 nm, which compensates the absorption valley of the polymers. The device performance was screened by using different processing solvents, different ratios of **PDFCDTBT** to PC₇₁BM, different concentration, different spin-coating speeds, and different additives. The results are shown in Table S2-4 in the supporting information. Solar cells fabricated with a blend of **PDFCDTBT** and PC₇₁BM in a weight ratio of 1:1.8 using TCB as the solvent gave the best performance with a PCE of 4.56%, a V_{oc} of 0.91 V, a J_{sc} of 8.9 mA/cm², and an FF of 0.56. The typical current density-voltage (J - V) curves of photovoltaic cells with the blend of **PDFCDTBT** and PC₇₁BM (1:1.8, by weight) as the active layer under 1 sun of simulated AM 1.5G solar radiation (100 mW/cm²) are shown in Figure 5. Without using the additive 1,8-diiodooctane (DIO), **HXS-1**/PC₇₁BM based devices exhibited a PCE of 3.60% with a V_{oc} of 0.85 V, a J_{sc} of 8.3 mA/cm², and an FF of 0.51. Significantly, **PDFCDTBT** based devices exhibited a higher V_{oc} than **HXS-1**, which can be attributed to the lower HOMO energy level of **PDFCDTBT** than that of **HXS-1**. Additionally, Compared with **HXS-1**, the lower PC₇₁BM ratio

a promising material for solar cell applications. For **HXS-1**, it has been reported that the hole mobility was $1.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ without device optimization. We expect that the hole mobility of **PDFCDTBT** can be improved after further device optimization.

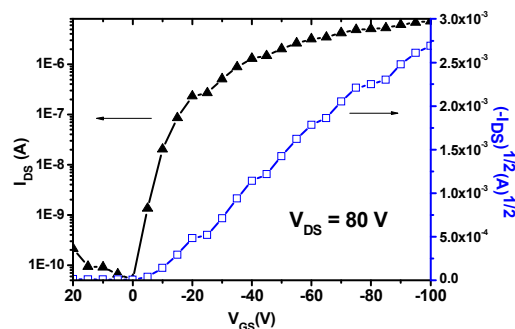


Figure 4. The transfer characteristics of the spin-coated film of **PDFCDTBT** transistor based on OTS-modified Si/SiO₂ substrate

and the higher FF for the optimized **PDFCDTBT** based devices indicated that **PDFCDTBT** probably possesses higher hole mobility, which can balance the electron mobility.

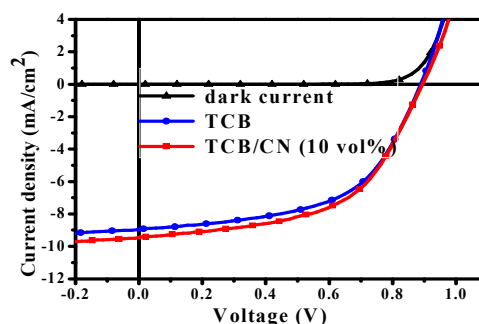


Figure 5. J - V curves of BHJ solar cells fabricated from the blend of **PDFCDTBT**:PC₇₁BM (1:1.8, by weight) in TCB and TCB containing 10 vol% CN.

1,8-Diiodooctane (DIO) is a most commonly used additive to enhance photovoltaic performance in PSCs.^{5f,10,29} Using 2.5 vol% DIO as the additive, PCE of **HXS-1** based solar cells was increased from 3.6 to 5.9%.^{9b} However, the use of DIO as additive for the fabrication of **PDFCDTBT** based solar cells did not show any positive effect on their photovoltaic performances. 1-Chloronaphthalene (CN) has been reported as a processing additive to increase the compatibility of polymers and PC₇₁BM and to decrease the domain size.³⁰ Therefore, TCB containing different amount of CN was used for the fabrication of

PDFCDTBT based solar cells. The device results are summarized in Table 3. The best photovoltaic performance with a PCE of 4.80%, a V_{oc} of 0.91 V, a J_{sc} of 9.5 mA/cm², and an FF of 0.55 was achieved by using TCB containing 10 vol% CN as the processing solvent. Obviously, the increase of J_{sc} from 8.9 to 9.5 mA/cm² contributes to the enhancement of the overall photovoltaic performance. Although the photovoltaic performance of **PDFCDTBT** based solar cells is inferior to that of **HXS-1** based ones, **PDFCDTBT** is still considered a very promising donor materials for high performance solar cells because of its lower HOMO energy level, narrower band gap, and higher hole mobility. The lower molecular weight and the poor film morphology (vide infra) of **PDFCDTBT** may responsible for the poor photovoltaic performance. To evaluate the accuracy of measurements, the external quantum efficiency (EQE) of the PSC devices fabricated from the blend of the polymer and PC₇₁BM were measured under illumination of monochromatic light. As shown in Figure 6, a significant photo-to-current response can be observed in nearly the entire visible range of 370 to 600 nm with EQE value of 45% for the **PDFCDTBT** based devices with CN (10 vol%). It is worthy noting that the EQE curve of the **PDFCDTBT**:PC₇₁BM based polymer solar cell is quite consistent with the corresponding absorption spectrum of the blend film. The current intensity (J_{sc}) calculated from the integration of the EQE of device agrees roughly with the J_{sc} values obtained from the J - V measurements.

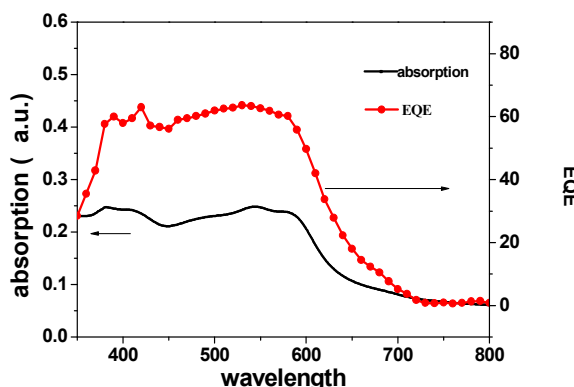
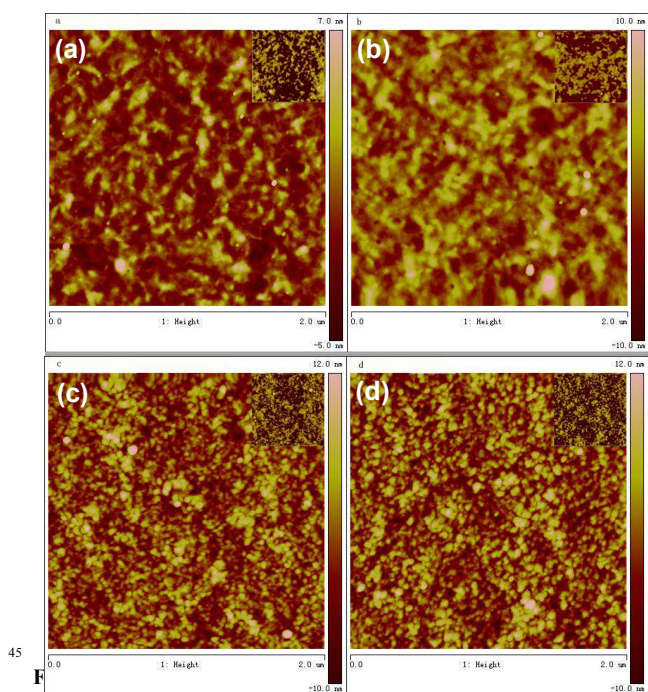


Figure 6. Incident photon to current efficiency and solid film absorption of blend of **PDFCDTBT**: PC₇₁BM = 1:1.8.

Film Morphologies. The morphology of active layer, which is spontaneously formed during the solution processing, has a large influence on the performance of PSC, because it strongly affects the charge carrier generation, recombination, and transportation.³¹ Atomic force microscopy (AFM) was used to investigate the surface morphology of **PDFCDTBT**:PC₇₁BM blend (1:1.8) spin-coated from TCB solutions with and without the additive CN.³² As shown in Figure 7, the blend film from pure TCB solution showed a rough surface with a large domain size, and the root-mean-square (rms) roughness is 0.326 nm. As the increase of volume of CN additive from 2 to 10%, the domain size of films became smaller and the surface morphology became less rough and more uniform. This result indicates that the additive CN can be used to modify the morphology of the active layer to achieve better photovoltaic performance.



coated from TCB solutions containing different amount of CN: (a) 0% vol, (b) 2% vol, (c) 6% vol, and (d) 10%. The inset shows the images after executing particle analysis.

Conclusions

In summary, a novel difluoro substituted carbazole based D-A alternating conjugated polymer **PDFCDTBT** was successfully designed and synthesized. The introduction of two fluoro atoms at the 3,6-positions of carbazole donor unit endowed the polymer **PDFCDTBT** with lower HOMO and LUMO energy levels and better thermal and electrochemical stability. In comparison with **HXS-1**, the fluoro containing **PDFCDTBT** showed stronger intermolecular interactions and formed closer π - π stacking and more ordered packing in solid state. Photovoltaic devices with **PDFCDTBT**:PC₇₁BM (1:1.8) as the active layer gave a PCE of 4.8% with a V_{oc} of 0.91 V, a J_{sc} of 9.5 mA/cm², and an FF of 0.55. The good thermal and electrochemical stability, narrower band gap, and lower HOMO energy level made **PDFCDTBT** a promising donor material for practical photovoltaic applications. The reason why **PDFCDTBT** based solar cells exhibited lower PCE than **HXS-1** is probably due to the lower molecular weight of the polymer and poorer film morphology of the active layer. Molecular weight and film morphology have been proved to be critical to the photovoltaic performance of polymer solar cells. By further optimization of the chemical structure, for example, incorporating longer branched alkoxy side chains to the polymer backbone, we expect to synthesize high molecular weight **PDFCDTBT** to achieve high PCE. Further optimizations of the chemical structure, molecular weight, the morphology of active layer, and the condition for device fabrication are currently underway.

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5 Notes and references

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† Electronic Supplementary Information (ESI) available: [Molar extinction coefficient data, XRD patterns, DSC and TGA curves, cyclic voltammograms, PL spectra]. See DOI: 10.1039/b000000x/

- 1 (a) K. M. Coakley, M. D. McGehee, *Chem. Mater.* 2004, **16**, 4533. (b) G. Dennler, M. C. Scharber, C. J. Brabec, *Adv. Mater.* 2009, **21**, 1323. (c) S. Gunes, H. Neugebauer, N. S. Sariciftci, *Chem. Rev.* 2007, **107**, 1324. (d) H. Hoppe, N. S. Sariciftci, *J. Mater. Res.* 2004, **19**, 1924. (e) J. Y. Kim, K. Lee, N. E. Coates, D. Moses, T. Q. Nguyen, M. Dante, A. J. Heeger, *Science* 2007, **317**, 222. (f) G. Li, V. Shrotriya, J. S. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *Nat. Mater.* 2005, **4**, 864. (g) W. L. Ma, C. Y. Yang, X. Gong, K. Lee, A. J. Heeger, *Adv. Funct. Mater.* 2005, **15**, 1617. (h) G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science* 1995, **270**, 1789. (i) X. B. Huang, C. L. Zhu, S. M. Zhang, W. W. Li, Y. L. Guo, X. W. Zhan, Y. Q. Liu, Z. Z. Bo, *Macromolecules* 2008, **41**, 6895. (j) E. Bundgaard, O. Hagemann, M. Manceau, M. Jorgensen, F. C. Krebs, *Macromolecules* 2010, **43**, 8115. (k) F. C. Krebs, *Sol. Energy Mater. Sol. Cells* 2009, **93**, 484.
- 2 (a) Y. J. He, Y. F. Li, *PCCP* 2011, **13**, 1970. (b) H. J. Jiang, X. Y. Deng, W. Huang, *Progress in Chemistry* 2008, **20**, 1361-1374. (c) X. Y. Meng, W. Q. Zhang, Z. A. Tan, Y. F. Li, Y. H. Ma, T. S. Wang, L. Jiang, C. Y. Shu and C. R. Wang, *Adv. Funct. Mater.*, 2012, **22**, 2187. (d) J. G. Muller, J. M. Lupton, J. Feldmann, U. Lemmer, M. C. Scharber, N. S. Sariciftci, C. J. Brabec and U. Scherf, *Physical Review B*, 2005, **72**. (e) I. Riedel, E. von Hauff, H. Parisi, N. Martin, F. Giacalone and V. Dyakonov, *Adv. Funct. Mater.*, 2005, **15**, 1979. (f) S. H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee and A. J. Heeger, *Nat. Photonics*, 2009, **3**, 297.
- 3 (a) E. G. Wang, Z. F. Ma, Z. Zhang, K. Vandewal, P. Henriksson, O. Inganäs, F. L. Zhang and M. R. Andersson, *J. Am. Chem. Soc.*, 2011, **133**, 14244. (b) R. Uy, L. Q. Yang, H. X. Zhou, S. C. Price and W. You, *Macromolecules*, 2011, **44**, 9146. (c) L. J. Huo, S. Q. Zhang, X. Guo, F. Xu, Y. F. Li and J. H. Hou, *Angew. Chem. Int. Ed.*, 2011, **50**, 9697. (d) L. J. Huo, J. H. Hou, S. Q. Zhang, H. Y. Chen and Y. Yang, *Angew. Chem. Int. Ed.*, 2010, **49**, 1500. (e) J. W. Chen and Y. Cao, *Acc. Chem. Res.*, 2009, **42**, 1709. (f) H. Y. Chen, J. H. Hou, S. Q. Zhang, Y. Y. Liang, G. W. Yang, Y. Yang, L. P. Yu, Y. Wu and G. Li, *Nat. Photonics*, 2009, **3**, 649. (g) J. H. Hou, H. Y. Chen, S. Q. Zhang, G. Li and Y. Yang, *J. Am. Chem. Soc.*, 2008, **130**, 16144. (h) J. H. Hou, Z. A. Tan, Y. Yan, Y. J. He, C. H. Yang and Y. F. Li, *J. Am. Chem. Soc.*, 2006, **128**, 4911. (i) N. Blouin, A. Michaud and M. Leclerc, *Adv. Mater.*, 2007, **19**, 2295.
- 4 (a) Y. X. Zhu, X. F. Xu, L. J. Zhang, J. W. Chen and Y. Cao, *Sol. Energy Mater. Sol. Cells*, 2012, **97**, 83. (b) Z. A. Tan, W. Q. Zhang, Z. G. Zhang, D. P. Qian, Y. Huang, J. H. Hou and Y. F. Li, *Adv. Mater.*, 2012, **24**, 1476. (c) J. M. Sun, Y. X. Zhu, X. F. Xu, L. F. Lan, L. J. Zhang, P. Cai, J. W. Chen, J. B. Peng and Y. Cao, *J. Phys. Chem. C*, 2012, **116**, 14188. (d) Z. C. He, C. M. Zhong, X. Huang, W. Y. Wong, H. B. Wu, L. W. Chen, S. J. Su and Y. Cao, *Adv. Mater.*, 2011, **23**, 4636. (e) Z. C. He, C. Zhang, X. F. Xu, L. J. Zhang, L. Huang, J. W. Chen, H. B. Wu and Y. Cao, *Adv. Mater.*, 2011, **23**, 3086. (f) Y. J. Cheng, F. Y. Cao, W. C. Lin, C. H. Chen and C. H. Hsieh, *Chem. Mater.*, 2011, **23**, 1512. (g) J. H. Seo, A. Gutacker, Y. M. Sun, H. B. Wu, F. Huang, Y. Cao, U. Scherf, A. J. Heeger and G. C. Bazan, *J. Am. Chem. Soc.*, 2011, **133**, 8416.
- 5 (a) X. F. Xu, Y. X. Zhu, L. J. Zhang, J. M. Sun, J. Huang, J. W. Chen and Y. Cao, *J. Mater. Chem.*, 2012, **22**, 4329. (b) L. M. Kozycz, D. Gao, J. Hollinger and D. S. Seferos, *Macromolecules*, 2012, **45**, 5823. (c) L. T. Dou, J. Gao, E. Richard, J. B. You, C. C. Chen, K. C. Cha, Y. J. He, G. Li and Y. Yang, *J. Am. Chem. Soc.*, 2012, **134**, 10071. (d) S. Sista, M. H. Park, Z. R. Hong, Y. Wu, J. H. Hou, W. L. Kwan, G. Li and Y. Yang, *Adv. Mater.*, 2010, **22**, 380. (e) J. Y. Kim, S. H. Kim, H. H. Lee, K. Lee, W. L. Ma, X. Gong and A. J. Heeger, *Adv. Mater.*, 2006, **18**, 572. (f) J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger and G. C. Bazan, *Nat. Mater.*, 2007, **6**, 497. (g) J. Gilot, M. M. Wienk and R. A. J. Janssen, *Adv. Mater.*, 2010, **22**, E67.
- 6 Z. C. He, C. M. Zhong, S. J. Su, M. Xu, H. B. Wu and Y. Cao, *Nat. Photonics*, 2012, **6**, 591.
- 7 (a) M. C. Scharber, D. Wuhlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger and C. L. Brabec, *Adv. Mater.*, 2006, **18**, 789. (b) G. Dennler, M. C. Scharber, T. Ameri, P. Denk, K. Forberich, C. Waldauf and C. J. Brabec, *Adv. Mater.*, 2008, **20**, 579. (c) C. H. Duan, F. Huang and Y. Cao, *J. Mater. Chem.*, 2012, **22**, 10416. (d) Y. F. Li, *Acc. Chem. Res.*, 2012, **45**, 723.
- 8 (a) D. Wuhlbacher, M. Scharber, M. Morana, Z. G. Zhu, D. Waller, R. Gaudiana and C. Brabec, *Adv. Mater.*, 2006, **18**, 2884. (b) C. Winder and N. S. Sariciftci, *J. Mater. Chem.*, 2004, **14**, 1077. (c) Y. Liu, H. F. Wang, H. L. Dong, J. H. Tan, W. P. Hu and X. W. Zhan, *Macromolecules*, 2012, **45**, 1296. (d) J. C. Bijleveld, V. S. Gevaerts, D. Di Nuzzo, M. Turbiez, S. G. J. Mathijssen, D. M. de Leeuw, M. M. Wienk and R. A. J. Janssen, *Adv. Mater.*, 2010, **22**, E242.
- 9 (a) R. P. Qin, W. W. Li, C. H. Li, C. Du, C. Veit, H. F. Schleiermacher, M. Andersson, Z. S. Bo, Z. P. Liu, O. Inganäs, U. Wuerfel and F. L. Zhang, *J. Am. Chem. Soc.*, 2009, **131**, 14612. (b) C. Du, C. H. Li, W. W. Li, X. Chen, Z. S. Bo, C. Veit, Z. F. Ma, U. Wuerfel, H. F. Zhu, W. P. Hu and F. L. Zhang, *Macromolecules*, 2011, **44**, 7617. (c) J. S. Song, C. Du, C. H. Li and Z. S. Bo, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 4267. (d) M. Wang, C. H. Li, A. F. Lv, Z. H. Wang and Z. S. Bo, *Macromolecules*, 2012, **45**, 3017.
- 10 W. W. Li, Y. Zhou, B. V. Andersson, L. M. Andersson, Y. Thomann, C. Veit, K. Tvingstedt, R. P. Qin, Z. S. Bo, O. Inganäs, U. Wuerfel and F. L. Zhang, *Org. Electron.*, 2011, **12**, 1544.
- 11 B. C. Thompson and J. M. J. Frechet, *Angew. Chem. Int. Ed.*, 2008, **47**, 58.
- 12 (a) H. Z. Chen, M. M. Ling, X. Mo, M. M. Shi, M. Wang and Z. Bao, *Chem. Mater.*, 2007, **19**, 816. (b) A. Iyer, J. Bjorgaard, T. Anderson and M. E. Kose, *Macromolecules*, 2012, **45**, 6380. (c) Y. Y. Liang, Z. Xu, J. B. Xia, S. T. Tsai, Y. Wu, G. Li, C. Ray and L. P. Yu, *Adv. Mater.*, 2010, **22**, E135. (d) S. C. Price, A. C. Stuart, L. Q. Yang, H. X. Zhou and W. You, *J. Am. Chem. Soc.*, 2011, **133**, 4625. (e) H. J. Son, W. Wang, T. Xu, Y. Y. Liang, Y. E. Wu, G. Li and L. P. Yu, *J. Am. Chem. Soc.*, 2011, **133**, 1885. (f) H. X. Zhou, L. Q. Yang, A. C. Stuart, S. C. Price, S. B. Liu and W. You, *Angew. Chem. Int. Ed.*, 2011, **50**, 2995.
- 13 (a) C. Kitamura, S. Tanaka and Y. Yamashita, *Chem. Mater.*, 1996, **8**, 570. (b) N. Blouin, A. Michaud, D. Gendron, S. Wakim, E. Blair, R. Neagu-Plesu, M. Belletete, G. Durocher, Y. Tao and M. Leclerc, *J. Am. Chem. Soc.*, 2008, **130**, 732. (c) Y.-J. Cheng, S.-H. Yang and C.-S. Hsu, *Chem. Rev.*, 2009, **109**, 5868.
- 14 (a) J. A. Irvin, I. Schwendeman, Y. Lee, K. A. Abboud and J. R. Reynolds, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 2164. (b) W. Jiang, Y. Zhou, H. Geng, S. D. Jiang, S. K. Yan, W. P. Hu, Z. H. Wang, Z. G. Shuai and J. A. Pei, *J. Am. Chem. Soc.*, 2011, **133**, 1.
- 15 C. A. Tolman, W. C. Seidel and D. H. Gerlach, *J. Am. Chem. Soc.*, 1972, **94**, 2669.
- 16 J. Pommerehne, H. Vestweber, W. Guss, R. F. Mahrt, H. Bässler, M. Porsch and J. Daub, *Adv. Mater.*, 1995, **7**, 551.
- 17 L. Li, Q. Tang, H. Li, X. Yang, W. Hu, Y. Song, Z. Shuai, W. Xu, Y. Liu and D. Zhu, *Adv. Mater.*, 2007, **19**, 2613.
- 18 G. S. Chen, A. D. Konstantinov, B. G. Chittim, E. M. Joyce, N. C. Bols and N. J. Bunce, *Environ. Sci. Technology*, 2001, **35**, 3749.
- 19 H. Kun, H. Yi, R. G. Johnson and A. Iraqi, *Polym. Adv. Technol.*, 2008, **19**, 299.
- 20 M. Sonntag and P. Stroehriegel, *Chem. Mater.*, 2004, **16**, 4736.

- 21 D. A. M. Egbe, L. H. Nguyen, H. Hoppe, D. Muhlbacher and N. S. Sariciftci, *Macromol. Rapid. Commun.*, 2005, **26**, 1389.
- 22 (a) J. F. Ambrose, L. L. Carpenter and R. F. Nelson, *J. Electrochem. Soc.*, 1975, **122**, 876. (b) A. Siove, D. Ades, E. Ngbilo and C. Chevrot, *Synth. Met.*, 1990, **38**, 331.
- 23 Y. Q. Fu and Z. S. Bo, *Macromol. Rapid. Commun.*, 2005, **26**, 1704.
- 24 A. Szucs and M. Novak, *J. Electroanal. Chem.*, 1995, **383**, 75.
- 25 T. Erb, U. Zhokhavets, G. Gobsch, S. Raleva, B. Stühn, P. Schilinsky, C. Waldauf and C. J. Brabec, *Adv. Funct. Mater.*, 2005, **15**, 1193.
- 26 (a) Y. Kim, S. Cook, J. Kirkpatrick, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, M. Heeney, R. Hamilton and I. McCulloch, *J. Phys. Chem. C*, 2007, **111**, 8137. (b) H. Y. Chen, J. H. Hou, A. E. Hayden, H. Yang, K. N. Houk and Y. Yang, *Adv. Mater.*, 2010, **22**, 371. (c) J. S. Lee, S. K. Son, S. Song, H. Kim, D. R. Lee, K. Kim, M. J. Ko, D. H. Choi, B. Kim and J. H. Cho, *Chem. Mater.*, 2012, **24**, 1316. (d) W. Shin, M. Y. Jo, D. S. You, Y. S. Jeong, D. Y. Yoon, J. W. Kang, J. H. Cho, G. D. Lee, S. S. Hong and J. H. Kim, *Synth. Met.*, 2012, **162**, 768. (e) Y. Zou, Z. Q. Guan, Z. Y. Zhang, Y. Huang, N. N. Wang, Z. Y. Lu, Q. Jiang, J. S. Yu, Y. Liu and X. M. Pu, *J. Mater. Sci.*, 2012, **47**, 5535.
- 27 (a) T. Yamamoto, D. Komarudin, M. Arai, B.-L. Lee, H. Suganuma, N. Asakawa, Y. Inoue, K. Kubota, S. Sasaki, T. Fukuda and H. Matsuda, *J. Am. Chem. Soc.*, 1998, **120**, 2047. (b) C. Du, C. Li, W. Li, X. Chen, Z. Bo, C. Veit, Z. Ma, U. Wuerfel, H. Zhu, W. Hu and F. Zhang, *Macromolecules*, 2011, **44**, 7617.
- 28 (a) K. Reichenbacher, H. I. Suss and J. Hulliger, *Chem. Soc. Rev.*, 2005, **34**, 22. (b) Y. Wang, S. R. Parkin, J. Gierschner and M. D. Watson, *Org. Lett.*, 2008, **10**, 3307.
- 29 (a) D. Di Nuzzo, A. Aguirre, M. Shahid, V. S. Gevaerts, S. C. J. Meskers and R. A. J. Janssen, *Adv. Mater.*, 2010, **22**, 4321. (b) X. Guo, C. H. Cui, M. J. Zhang, L. J. Huo, Y. Huang, J. H. Hou and Y. Li, *Energy Environ. Sci.*, 2012, **5**, 7943. (c) L. G. Kaake, G. C. Welch, D. Moses, G. C. Bazan and A. J. Heeger, *J. Phys. Chem. Lett.*, 2012, **3**, 1253. (d) S. J. Lou, J. M. Szarko, T. Xu, L. P. Yu, T. J. Marks and L. X. Chen, *J. Am. Chem. Soc.*, 2011, **133**, 20661. (e) J. K. Park, C. Kim, B. Walker, T. Q. Nguyen and J. H. Seo, *Rsc Advances*, 2012, **2**, 2232. (f) G. Q. Ren, E. Ahmed and S. A. Jenekhe, *Adv. Energy Mater.* 2011, **1**, 946. (g) Y. M. Sun, G. C. Welch, W. L. Leong, C. J. Takacs, G. C. Bazan and A. J. Heeger, *Nat. Mater.*, 2012, **11**, 44. (h) J. Peet, M. L. Senatore, A. J. Heeger and G. C. Bazan, *Adv. Mater.*, 2009, **21**, 1521.
- 30 (a) B. R. Aich, J. P. Lu, S. Beaupre, M. Leclerc and Y. Tao, *Org. Electron.*, 2012, **13**, 1736. (b) F. C. Chen, H. C. Tseng and C. J. Ko, *Appl. Phys. Lett.*, 2008, **92**. (c) C. V. Hoven, X. D. Dang, R. C. Coffin, J. Peet, T. Q. Nguyen and G. C. Bazan, *Adv. Mater.*, 2010, **22**, E63. (d) H. M. Ko, H. Choi, S. Paek, K. Kim, K. Song, J. K. Lee and J. Ko, *J. Mater. Chem.*, 2011, **21**, 7248. (e) J. A. Mikroyannidis, A. N. Kabanakis, P. Suresh and G. D. Sharma, *J. Phys. Chem. C*, 2011, **115**, 7056. (f) J. S. Moon, C. J. Takacs, S. Cho, R. C. Coffin, H. Kim, G. C. Bazan and A. J. Heeger, *Nano Lett.*, 2010, **10**, 4005. (g) G. D. Sharma, J. A. Mikroyannidis and S. P. Singh, *Mater. Chem. Phys.*, 2012, **135**, 25.
- 31 (a) M. Campoy-Quiles, T. Ferenczi, T. Agostinelli, P. G. Etchegoin, Y. Kim, T. D. Anthopoulos, P. N. Stavrinou, D. D. C. Bradley and J. Nelson, *Nat. Mater.*, 2008, **7**, 158. (b) D. Chirvase, J. Parisi, J. C. Hummelen and V. Dyakonov, *Nanotechnology*, 2004, **15**, 1317. (c) H. Hoppe, M. Niggemann, C. Winder, J. Kraut, R. Hiesgen, A. Hinsch, D. Meissner and N. S. Sariciftci, *Adv. Funct. Mater.*, 2004, **14**, 1005. (d) X. Yang and J. Loos, *Macromolecules*, 2007, **40**, 1353. (e) X. N. Yang, J. Loos, S. C. Veenstra, W. J. H. Verhees, M. M. Wienk, J. M. Kroon, M. A. J. Michels and R. A. J. Janssen, *Nano Lett.*, 2005, **5**, 579.
- 32 (a) J. K. Lee, W. L. Ma, C. J. Brabec, J. Yuen, J. S. Moon, J. Y. Kim, K. Lee, G. C. Bazan and A. J. Heeger, *J. Am. Chem. Soc.*, 2008, **130**, 3619. (b) G. Dennler, A. J. Mozer, G. Juska, A. Pivrikas, R. Osterbacka, A. Fuchsbaier and N. S. Sariciftci, *Org. Electron.*, 2006, **7**, 229.