# CHEMISTRY OF MATERIALS

## Significant Enhancement of Polymer Solar Cell Performance via Side-Chain Engineering and Simple Solvent Treatment

Yang Wang,<sup>†,‡</sup> Ying Liu,<sup>†</sup> Shaojie Chen,<sup>†</sup> Ruixiang Peng,<sup>†</sup> and Ziyi Ge\*<sup>,†</sup>

<sup>†</sup>Ningbo Institute of Material Technology and Engineering (NIMTE), Chinese Academy of Sciences (CAS), Zhuangshi Road 519, Ningbo, Zhejiang 315201, People's Republic of China

<sup>‡</sup>University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

**Supporting Information** 

**ABSTRACT:** Rational design and synthesis of polymeric semiconductors is critical to the development of polymer solar cells (PSCs). In this work, a new series of benzodithiophene–difuranylbenzooxadiazole-based donor–acceptor co-polymers—namely, PBDT-DFBO, PBDTT-DFBO, and PBDTF-DFBO, with various side groups—have been developed for bulk-heterojunction PSCs. These side-group substituents provide the opportunity to tailor the opto-electrical properties of the polymers. In addition, we show that the reduction of the bandgap of polymers and the enhancement of charge mobility in the devices can be accomplished concurrently by substituting the alkylthienyl side group with its furan counterpart. In the preliminary investigation, one could obtain PSCs with a power conversion efficiency (PCE) of 2.1% for PBDT-DFBO with an alkoxyl side chain, 2.2% for PBDTT-DFBO with an alkylthienyl side group. Further optimizing the performance of the devices was conducted via a simple solvent treatment. The PSCs based on PBDTF-DFBO:PC<sub>71</sub>BM could even achieve 7.0% PCE, which



exhibited an enhancement of 130%. To the best of our knowledge, the value of 7.0% is the highest efficiency for furan-containing PSCs to date and is also comparable with the hitherto reported highest efficiency of the single junction PSCs. Through a combination of testing charge transport by the space-charge limited current (SCLC) model and examining the morphology by atomic force microscopy (AFM), we found that the effects of solvent treatment on the improved performance originate from higher and more balanced charge transport and the formation of fiberlike interpenetrating morphologies, which are beneficial to the increase of short-circuit current density ( $J_{sc}$ ) and fill factor (FF). This work demonstrates a good example for tuning absorption range, energy level, charge transport, and photovoltaic properties of the polymers by side-chain engineering and the solvent treatment can offer a simple and effective method to improve the efficiency of PSCs.

KEYWORDS: polymer solar cells, side group engineering, solvent treatment, donor-acceptor conjugated copolymer

### **1.. INTRODUCTION**

Bulk-heterojunction (BHJ) solar cells, formed from a blend of electron-donating  $\pi$ -conjugated polymers and electron-accepting fullerene derivatives (such as PCBM), have received enormous academic and industrial enthusiasm, because of promising advantages such as low cost, light weight, flexibility, and large-area manufacturing compatibility.<sup>1</sup> The efficiency of polymer solar cells (PSCs) has now been enhanced by more than 10% through fundamental understanding, new materials synthesis, and device architecture innovation.<sup>2</sup>

New polymeric semiconductors are crucial in order for PSCs development. However, nearly all highly efficient PSCs (with a power conversion efficiency (PCE) of >5%) reported so far have been dependent on thiophene-based conjugated polymers. Only a small amount of research has been focused on nonthiophene heterocycles-based polymers. For instance, 2,1,3-benzooxadiazole (BO) is an electron-deficient heterocycle,<sup>3</sup> which is similar to the renowned 2,1,3-benzothiadiazole (BT), yet is much less explored than BT as an acceptor building block. To the best of our knowledge, several reports have described the photovoltaic properties of 4,7-dithiophene-

substituted BO-based conjugated polymers, which reached the highest PCE of 5.9%.<sup>4</sup> However, 4,7-difuran-substituted BO-based copolymers remain unexplored in PSCs. It has been shown that the substitution of furan for thiophene in the main chain of the polymer will improve polymer solubility, which is beneficial for obtaining higher molecular weight and the formation of high-quality films of active layer that provides efficient charge generation and collection for PSCs.<sup>5</sup> Besides, Li's work demonstrates that the replacement of thiophene in the backbone of polymers with furan is able to lower the HOMO energy level, thus increasing the open circuit voltage  $(V_{\rm oc})$  of solar cells.<sup>6</sup> Nonetheless, the photovoltaic performance of the furan-bridged copolymer (P(BDT-F-BT)) was lower than its thiophene counterpart (P(BDT-T-BT)), mainly because of its larger band gap, narrower absorption spectrum, and thus lower short-circuit current density  $(J_{sc})$  of the devices. On the other hand, we recently have found that poly[2,6-(4,8-

 Received:
 May 18, 2013

 Revised:
 July 7, 2013

ACS Publications © XXXX American Chemical Society



Figure 1. Chemical structures of furan containing donor-acceptor polymers in the literature<sup>8</sup> (top) and in this work (bottom).

bis(5-(2-ethylhexyl)furan-2-yl)benzo[1,2-b:4,5-b']dithiophene)-alt-3,6-(2,5-bis(2-ethylhexyl)-3,6-di(furan-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione)] (PBDTF-DPPF) with furan side group had smaller optical band gap, broader absorption range, deeper HOMO energy level in comparison with its corresponding alkoxy-substituted counterpart and a high PCE of 6.1% was achieved in a typical BHJ device, exceeding the performance of poly[2,6-(4,8-bis(5-(2ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene)-alt-3,6-(2,5-bis(2-ethylhexyl)-3,6-di(furan-2-yl)pyrrolo [3,4-*c*]pyrrole-1,4(2H,5H)-dione)] (PBDTT-FDPP) with thiophene side group; Meanwhile, Li and his co-workers have found that the furan side chain makes the lowest unoccupied molecular orbital (LUMO) level shift slightly downward. (All the structures are shown in Figure 1.)<sup>8</sup> In addition, furan-based materials are known to be biodegradable and can be prepared from biorenewable sources, which makes them more suitable for low-cost and large-scale applications. Based on the above results, more investigation of furan-based PSCs is definitely needed.

On the other hand, despite the advantages of the BHJ structure, the efficiency of PSCs can be limited by the unsatisfactory morphology of the polymer–fullerene blends.<sup>9</sup> Although thermal annealing and solvent vapor treatment are useful post-treatments to optimize the morphology of the blends,<sup>10</sup> these methods are time-consuming and require meticulous control of the experimental parameters. Inspiringly, several independent groups have found that the performance of PSCs could be improved simply through solvent treatment before deposition of the metal electrodes.<sup>11</sup> However, there are limited instances of employing this method to optimize PSCs, based on state-of-the-art donor–acceptor copolymers.

Herein, we focus our attention on the effects of side-chain engineering and various polar solvent treatments to optimize the performance of furan-based PSCs. To carry out our studies, we first synthesized a series of new *p*-type semiconducting polymers with various side groups comprising benzodithiophene and difuranylbenzooxadiazole as the electron-donating and electron-accepting components, respectively. The three copolymers were named PBDT-DFBO, PBDTT- DFBO, and PBDTF-DFBO, as shown in Figure 1. We showed that the reduction of the bandgap of copolymers and the enhancement of charge mobility in the devices could be accomplished simultaneously by substituting the thiophene side group with its furan counterpart. The PSCs based on pristine polymers/ $PC_{71}BM$  blends showed a moderate PCE value of 2.1% for PBDT-DFBO with an alkoxyl side chain, 2.2% for PBDTT-DFBO with an alkylthienyl side group, and 3.0% for PBDTF-DFBO with an alkylfuranyl side group. Further optimizing the performance of the devices was conducted via a simple solvent treatment. Encouragingly, the PCE exhibited an enhancement of 130%–170% and PSCs based on PBDTF-DFBO: $PC_{71}BM$  reached the highest efficiency of 7.0% for furan-containing PSCs to date.<sup>12</sup>

#### 2.. EXPERIMENTAL SECTION

**2.1.** Materials. *n*-BuLi,  $Pd(PPh_3)_4$ , and  $Sn(C_4H_9)_3Cl$  were obtained from Tokyo Chemical Industry (TCI) and used as received. Tetrahydrofuran (THF) was dried over Na/benzophenone ketyl and freshly distilled prior to use. Other reagents and solvents were purchased commercially as analytical-grade quality and used without further purification. The synthesis of (4,8-bis((2-ethylhexyl)oxy)benzo-[1,2-*b*:4,5-*b*']dithiophene-2,6-diyl)bis(tributylstannane) (BDT), (4,8-bis(5-(2-ethylhexyl)furan-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(tributylstannane) (BDTF), (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis-(tributylstannane) (BDTT), 4,7-dibromo-5,6-bis(octyloxy)benzo[c]-[1,2,5]oxadiazole (compound 1); 2-(2-ethylhexyl)furan, 2-(2ethylhexyl)thiophene, and 4,8-dehydrobenzo[1,2-b:4,5-b']dithiophene-4,8-dione (compound 3); and 2-(tributylstannyl)furan was performed similarly to previous literature,<sup>8,13</sup> All of the other compounds were synthesized following the procedures described herein

4,7-Di(furan-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]oxadiazole(2). To a solution of 4,7-dibromo-5,6-bis(octyloxy)benzo[c][1,2,5]oxadiazole (2.20 g, 4 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.51 g, 0.44 mmol) in dry toluene (100 mL) was added 2-(tributylstannyl)furan (4.50 g, 12 mmol) and the reaction mixture was heated to reflux for 48 h under argon. The reaction mixture was concentrated directly on Celite under reduced pressure. The residue was chromatographically purified on a silica gel column eluting with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:10, *v:v*) to afford title compound as a yellow oil (1.8 g, yield 90%). <sup>1</sup>H NMR (400 MHz,

#### **Chemistry of Materials**

 $CDCl_3$ ): d (ppm) 7.73 (d, 2H, Ar–H), 7.42 (d, 2H, Ar–H), 6.65 (dd, 2H, Ar–H), 4.15 (t, 4H, CH<sub>2</sub>), 1.90 (m, 4H, CH<sub>2</sub>), 1.47 (m, 4H, CH<sub>2</sub>), 1.29–1.39 (m, 16H, CH<sub>2</sub>), 0.95 (t, 6H, CH<sub>3</sub>).

4,7-Bis(5-bromofuran-2-yl)-5,6-bis(octyloxy)benzo[c][1,2,5]oxadiazole (DFBO). A mixture of compound 2 (0.70 g, 3.8 mmol), Nbromosuccimide (NBS) (0.46 g, 7.8 mmol), chloroform (50 mL), and acetic acid (50 mL) was stirred at room temperature in darkness overnight. Then the reaction mixture was poured into water (200 mL) and extracted with chloroform  $(3 \times 50 \text{ mL})$ . The extracts were combined and washed with water and saturated sodium bicarbonate solution then dried over anhydrous sodium sulfate. After filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica, eluting with petroleum ether/ chloroform (from 20:0 to 20:1), to give a bright yellow solid (0.50 g, 60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): d (ppm) 7.38 (d, 2H, Ar-H), 6.54 (d, 2H, Ar-H), 4.11 (t, 4H, CH<sub>2</sub>), 1.94 (m, 4H, CH<sub>2</sub>), 1.52 (m, 4H, CH<sub>2</sub>), 1.24–1.36 (m, 16H, CH<sub>2</sub>), 0.90 (t, 6H, CH<sub>3</sub>). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub>): d (ppm) 152.42, 148.43, 145.14, 123.85, 116.51, 113.91, 108.54, 75.24, 31.86, 30.30, 29.59, 29.31, 26.09, 22.70, 14.14.

Polymerization for PBDT-DFBO. DFBO (133 mg, 0.20 mmol) and BDT (205 mg, 0.20 mmol) were dissolved into dry toluene (4 mL). The solution was flushed with argon for 10 min, and then  $Pd(PPh_3)_4$ (5 mg) was added into the flask. The flask was purged three times with successive vacuum and argon filling cycles. The polymerization reaction was heated to 120 °C, and the mixture was stirred for 36 h under argon atmosphere. Then, the reactant was cooled to room temperature and poured slowly into methanol (200 mL). The precipitate was filtered and washed with methanol, acetone, and hexane in a Soxhlet apparatus to remove the oligomers and catalyst residue. Finally, the polymer was extracted with chloroform. The solution was condensed by evaporation and precipitated into methanol. The title polymer was collected as a dark red solid. (205 mg, 61%,  $M_n = 36.1$  kg/mol, PDI = 2.07). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): 7.52-6.91 (br, 6H), 4.25 (br, 8H), 1.25-2.04 (br, 42H), 0.89-1.16 (br, 18H). Anal. Calcd for (C58H80N2O7S2)n (%): C, 70.98; H, 8.22; N, 2.85. Found: C, 70.27; H, 7.81; N, 2.68.

Polymerization for PBDTT-DFBO. PBDTT-DFBO was prepared using the same procedure as PBDT-DFBO. The resulting co-polymer PBDTT-DFBO was obtained as a dark purple solid with a yield of 65%. ( $M_n = 29.3 \text{ kg/mol}$ , PDI = 2.01). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): 7.42–7.39 (br, 4H), 7.00 (br, 6H), 4.18 (br, 4H), 2.96 (br, 6H), 2.14–0.70 (br, 58H). Anal. Calcd for ( $C_{66}H_{84}N_2O_5S_4$ )<sub>n</sub> (%): C, 71.18; H, 7.60; N, 2.52. Found (%): C, 70.47; H, 7.30; N, 2.37.

Polymerization for PBDTF-DFBO. PBDTF-DFBO was prepared using the same procedure as PBDT-DFBO. The resulting copolymer PBDTF-DFBO was obtained as a dark blue solid, with a yield of 72%.  $(M_n = 38.4 \text{ kg/mol}, \text{PDI} = 2.24)$ . <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): 7.52–7.33 (br, 4H), 6.59–6.39 (br, 6H), 4.32–4.17 (br, 4H), 3.01–2.93 (br, 6H), 2.15–0.71 (br, 58H). Anal. Calcd for  $(C_{66}H_{84}N_2O_7S_2)_n$  (%): C, 73.30; H, 7.83; N, 2.59. Found (%): C, 72.57; H, 7.44; N, 2.46.

2.2. General Measurement and Characterization. <sup>1</sup>H and <sup>13</sup>C NMR spectra were measured using a Bruker DMX-400 spectrometer. Chemical shifts of NMR were reported in ppm relative to the singlet of CDCl<sub>3</sub> at 7.26 ppm for <sup>1</sup>H NMR spectroscopy and 77.6 ppm for <sup>13</sup>C NMR spectroscopy. Absorption spectra were collected on a Perkin-Elmer Lambda 950. The molecular weights of the polymers were measured by the GPC method on a Waters 1515, and polystyrene was used as the standard (room temperature, chloroform as the eluent). The electrochemical cyclic voltammetry (CV) of the polymer film was conducted in acetonitrile with 0.1 M of tetrabutylammonium hexafluorophosphate ( $Bu_4NPF_6$ ) using a scan rate of 100 mV s<sup>-1</sup> at room temperature. Platinum disk, Ag/AgCl, and platinum plate were used as the working electrode, reference electrode, and counter electrode, respectively. The polymer films for electrochemical measurements were coated from a chloroform solution, ca. 5 mg/ mL. For calibration, the redox potential of ferrocene/ferrocenium (Fc/ Fc<sup>+</sup>) was measured under the same conditions, and it is located at 0.40 V vs the Ag/AgCl electrode. It is assumed that the redox potential of Fc/Fc<sup>+</sup> has an absolute energy level of -4.80 eV to vacuum. The

energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) were then calculated according to the following equations:

 $E_{\text{HOMO}} (\text{eV}) = -e(\varphi_{\text{ov}} + 4.40)$ 

 $E_{\rm LUMO} (\rm eV) = -e(\varphi_{\rm re} + 4.40)$ 

where  $\varphi_{ox}$  is the onset oxidation potential vs Ag/AgCl and  $\varphi_{re}$  is the onset reduction potential vs Ag/AgCl.

2.3. Fabrication and Characterization of BHJ Devices. All organic photovoltaic devices had a conventional device architecture, ITO/PEDOT:PSS/polymer:PC71BM/Ca/Al. ITO/glass substrates were ultrasonically cleaned sequentially in detergent, water, acetone, and iso-propanol (IPA), followed by treating in an ultraviolet ozone chamber (Ultraviolet Ozone Cleaner, Jelight Company, USA) for 20 min. The cleaned substrates were covered by a 40-nm-thick layer of PEDOT:PSS(Baytron PV PAI 4083, Germany) by spin coating. After annealing in a glovebox at 140 °C for 20 min, the samples were cooled to room temperature. Polymers were dissolved in dichlorobenzene (DCB)/4% (v/v) 1-chloronaphthalene  $(CN)^{14}$  mixed solvent, and then PC71BM (purchased from American Dye Source) was added. The solution was then heated at 70 °C and stirred overnight at the same temperature. The solution of polymer:PC71BM was then spin-coated to form the active layer (~100 nm). After drying under vacuum, polar solvent exposure with various wetting time was carried out using the spin-coating methanol solvent on the top of active layers at 2500 rpm for 45 s. The devices were completed after the deposition of 20 nm Ca/100 nm Al as a cathode through a shadow mask under high vacuum ( $<10^{-6}$  Torr). The effective area of the device was measured to be 0.1257 cm<sup>2</sup>. The device characteristics were obtained using a xenon lamp at AM1.5 solar illumination (Oriel Instruments). The current-voltage (I-V) characterization of the devices was carried out on a computer-controlled Keithley 2440 Source Measurement system. The EQE measurements of the PSCs were performed using a Stanford Research Systems model SR830 DSP lock-in amplifier coupled with WDG3 monochromator and 500 W xenon lamp. The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

**2.4. Hole and Electron Mobility.** Hole and electron mobility was measured using the space charge limited current model (SCLC), using a diode configuration of ITO/PEDOT:PSS/polymer:PC<sub>71</sub>BM/MoO<sub>3</sub>/ $Al^{4a}$  for hole-only device and ITO/Al/polymer:PC<sub>71</sub>BM/Ca/ $Al^{15}$  for electron-only device, respectively, and taking current–voltage measurements in the range of 0–6 V and fitting the results to a space-charge-limited form, where the SCLC is described by the Mott–Gurney law:

$$J = \left(\frac{8}{9}\right) \varepsilon_{\rm r} \varepsilon_0 \mu \left(\frac{V^2}{L^3}\right)$$

where  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_r$  the dielectric constant of the polymer,  $\mu$  the charge mobility, V the voltage drop across the device ( $V = V_{appl} - V_{bi}$  where  $V_{appl}$  is the applied voltage to the device and  $V_{bi}$  is the built-in voltage, which we estimated from the difference between the work function and the HOMO energy level of polymers<sup>16</sup>), and L is the polymer thickness. The dielectric constant  $\varepsilon_r$  is assumed to be 3, which is a typical value for conjugated polymers. The thickness of films was measured using a Dektak 6 M surface profilometer.

**2.5. AFM Measurement.** AFM samples are prepared as follows. Films of polymer/ $PC_{71}BM$  blend are cast from solutions on clean glass slides. Both pristine and treated films are examined using a Veeco Dimension 3100 V atomic force microscopy (AFM) system.

### 3.. RESULTS AND DISCUSSION

**3.1. Material Design and Synthesis.** The synthetic routes of the new monomer (4,7-bis(5-bromofuran-2-yl)-5,6-bis-(octyloxy)benzo[c][1,2,5]oxadiazole) (DFBO) and three copolymers are shown in Scheme 1. In our synthetic design, the

Article

Scheme 1. Synthetic Routes of the Monomers and Polymers



Figure 2. (a) Absorption spectra of PBDT-DFBO, PBDTT-DFBO, and PBDTF-DFBO in thin films. (b) HOMO and LUMO energy levels of the polymers; energy levels of  $PC_{71}BM$  are listed for comparison.

 $\pi$ -conjugating bridge (furan) was first attached to the electronaccepting BO unit. It was synthesized from 2-stannylated furan by a Stille cross-coupling reaction with compound 1 to give compound 2, which was then subjected to bromination to afford DFBO. Consequently, three new furan- $\pi$ -bridged donor-acceptor copolymers—namely, PBDT-DFBO, PBDTT-DFBO, and PBDTF-DFBO—were synthesized via Stille-coupling polymerization (Scheme 1). All three copolymers were purified by Soxhlet extraction with a washing solvent sequence of methanol, acetone, hexane, and finally chloroform. The resulting copolymers showed excellent solubility in common organic solvents, such as chloroform, toluene, chlorobenzene, and 1,2-dichlorobenzene. Gel permeation chromatography (GPC) studies (using polystyrene as the standard and chloroform as the eluent) showed that these polymers were purified by successive reprecipitation and Soxhlet extraction had a number-average molecular weight  $(M_n)$ : PBDT-DFBO  $(M_n = 36.1 \text{ kg/mol}, \text{PDI} = 2.07)$ , PBDTT-DFBO  $(M_n = 29.3 \text{ kg/mol}, \text{PDI} = 2.01)$ , and PBDTF-DFBO  $(M_n = 38.4 \text{ kg/mol}, \text{PDI} = 2.24)$ , respectively.

**3.2.** Properties of Newly Designed Benzodithiophene–Difuranylbenzooxadiazole Co-polymers. The UV–vis absorption spectra of all three co-polymers as thin films are shown in Figure 2a (UV absorption in dilute chloroform solution shown in Figure S1 in the Supporting Information), and the photophysical data of polymers are summarized in Table 1. One could observe that PBDTT-

# Table 1. Optical and Electrochemical Properties of the Polymers

	$\lambda_{\mathrm{onset}}$ (r	nm)						
polymer	solution <sup>a</sup>	film <sup>b</sup>	$E_{g}^{opt}$ (eV)	HOMO (eV)	LUMO (eV)	$E_{g}^{ec}$ (eV)		
PBDT- DFBO	645	672	1.85	-5.34	-3.43	1.91		
PBDTT- DFBO	661	686	1.81	-5.44	-3.59	1.85		
PBDTF- DFBO	672	700	1.77	-5.40	-3.61	1.79		
$^a$ Measured in chloroform solution. $^b$ Cast from chloroform solution.								

DFBO and PBDTF-DFBO had broader absorption range than PBDT-DFBO, which could be ascribed to the enhanced intermolecular  $\pi - \pi$  interaction that was originated from the extended conjugation by replacing alkoxyl group with alkylaromatic unit. Furthermore, it should be noted that PBDTF-DFBO with a furan side group showed red-shifted absorption onset (11 and 14 nm), compared with thiophene counterpart in both solution and thin film. Thus, an increased light harvesting by the film of PBDTF-DFBO was expected because of absorption over a broader spectral range (see Figure 2a), and the film color was close to blue. From the onset of the thin film absorptions ( $\lambda_{onset}$ ), one could estimate the optical band gaps of the copolymers. The band gap of PBDTF-DFBO was 1.77 eV, which was reduced by 0.04 eV in comparison with that of PBDTT-DFBO (1.81 eV). The reduction of the band gap energy can be mainly attributed to a more planar structure of the BDTF unit than that of the BDTT unit.<sup>17</sup>

Meanwhile, the HOMO and LUMO energy levels of the polymers are determined by cyclic voltammetry (CV), and the results are summarized in Figure 2b and Table 1 (the original data can be found in the Figure S2 in the Supporting Information). When the alkoxy side chain is replaced by aromatic conjugated side chains (such as alkylfuranyl or alkylthienyl), the HOMO and LUMO levels of the polymers are shifted to lower energy levels, implying that the weak electron-donating ability of aromatic side groups is favorable to reducing the HOMO level of the polymer. For example, the HOMO and LUMO of PBDTF-DFBO were 0.06 and 0.18 eV lower than those of PBDT-DFBO, respectively. On the other hand, PBDTT-DFBO had deeper HOMO level than PBDTF-DFBO. This is because the oxygen atom is known to be a richer electron donor, compared to the sulfur atom, because of the better overlap of its orbitals with the  $\pi$ -system;<sup>18</sup> therefore, the alkylfuranyl group has relatively stronger electron-donating ability than does the alkylthienyl unit. Consequently, by replacing the alkylthienyl with alkylfuranyl, the HOMO values of the resulting polymers were expected to be higher, which would lead to lower open-circuit voltage ( $V_{oc}$ ) in photovoltaic devices.<sup>8</sup> Overall, the results of the UV/vis absorption spectra and the CV measurements agreed quite well.

3.3. Characteristics and Optimization of Photovoltaic Devices. To characterize the photovoltaic properties for these polymers, BHJ PSCs were fabricated with a general device structure of ITO/PEDOT: PSS/polymer:PC71BM/Ca/Al, and their performances were measured under 100 mW/cm<sup>2</sup> AM 1.5 G illumination. The ratio of polymer to PC<sub>71</sub>BM was adjusted from 1:1 to 1:3 (by weight) and the optimized condition was 1:2 for all of them. The polymer active layers were spin-coated from solutions in dichlorobenzene (DCB)/1-chloronaphthalene (CN) mixed solvent. Moreover, the optimized condition was 4 vol % CN in DCB solution, and the typical current density-voltage (J-V) curves of PSCs based on PBDTF-DFBO with varying CN concentration in DCB are shown in Figure S3a in the Supporting Information. The J-V curves of all PSCs are shown in Figure 3a (and Figure S3b in the Supporting Information), and the device performances are summarized in Table 2. In the initial investigation, it was found that the solar cells exhibited moderate performance with PCE of 2.0%  $\pm$  0.1% for PBDT-DFBO with alkoxyl chains, 2.1%  $\pm$ 0.1% for PBDTT-DFBO with alkylthienyl groups and a relative high efficiency of 2.8% ± 0.2% for PBDTF-DFBO with alkylfuranyl side moiety.

Inspired by recent work on post-solvent treatment,<sup>11</sup> we tried to employ a variety of polar solvents, including methanol, ethanol, and propanol, to optimize the performance of PSCs with a modified procedure: (i) spin-coated the active layer and dried under vacuum; (ii) methanol (or other polar solvents) was added atop the active layer and a short wait time (such as 2 min) was allowed; (iii) solvent was removed by spin coating at high speed (such as 2500 rpm); (iv) the cathode was evaporated (as shown in Figure S4 in the Supporting



Figure 3. (a) Current density–voltage (J-V) curves of the PSCs based on polymer/PC<sub>71</sub>BM (1:2, w/w) with and without solvent exposure, under the illumination of AM1.5G, 100 mW cm<sup>-2</sup>. (b) J-V characteristics of devices with (circles) and without polar solvent treatment (squares) in darkness.

Table 2. Performance of the Polymer:  $PC_{71}BM$  BHJ Solar Cells before and after Various Polar Solvent Treatments with a Wetting Time of 2 min, at a Blend Ratio of  $1:2^a$ 

solvent treatment	$J_{\rm sc}  [{\rm mA \ cm^{-2}}]^b$	$V_{\rm oc} \left[ { m V}  ight]^b$	FF $[\%]^b$	PCE $[\%]^b$				
		PBDT-DFBO						
none	$5.2 \pm 0.1$	$0.78 \pm 0.01$	$50.2 \pm 0.1$	$2.0 \pm 0.1$				
methanol	$9.3 \pm 0.1$	$0.82 \pm 0.01$	$52.9 \pm 0.2$	$4.0 \pm 0.2$				
ethanol	$10.6 \pm 0.2$	$0.83 \pm 0.01$	$64.7 \pm 0.4$	$5.6 \pm 0.3$				
propanol	$9.0 \pm 0.4$	$0.80 \pm 0.02$	$48.7 \pm 0.6$	$3.7 \pm 0.1$				
PBDTT-DFBO								
none	$5.5 \pm 0.1$	$0.83 \pm 0.01$	$46.5 \pm 0.1$	$2.1 \pm 0.1$				
methanol	$9.1 \pm 0.3$	$0.86 \pm 0.01$	$58.6 \pm 0.5$	$4.5 \pm 0.3 (5.0)^c$				
ethanol	$7.3 \pm 0.5$	$0.83 \pm 0.02$	$39.4 \pm 0.7$	$2.6 \pm 0.1$				
propanol	$7.4 \pm 0.6$	$0.82 \pm 0.01$	$46.6 \pm 0.5$	$3.0 \pm 0.1$				
PBDTF-DFBO								
none	$6.9 \pm 0.1$	$0.79 \pm 0.01$	$53.4 \pm 0.1$	$2.8 \pm 0.2$				
methanol	$12.7 \pm 0.1$	$0.83 \pm 0.01$	$62.0 \pm 0.1$	$6.5 \pm 0.1 \ (7.0)^c$				
ethanol	$11.0 \pm 0.2$	$0.81 \pm 0.01$	$53.0 \pm 0.4$	$4.7 \pm 0.2$				
propanol	$10.7 \pm 0.4$	$0.84 \pm 0.01$	$48.1 \pm 0.3$	$4.4 \pm 0.2$				

<sup>*a*</sup>Boldface font indicates the best solvent treatment for each polymer solar cell. <sup>*b*</sup>Photovoltaic properties of co-polymer/PC<sub>71</sub>BM-based devices spincoated from a DCB/4% (v/v) CN mixed solution. Only the optimized recipes were considered for the estimation of the average PCE. Data have been averaged on eight devices. <sup>*c*</sup>The efficiency was achieved with a wetting time of 3 min.



**Figure 4.** Wetting time dependence of PSCs performance of PBDT-DFBO, PBDTT-DFBO, and PBDTF-DFBO: (a) short-circuit current density  $(J_{sc})$ , (b) open-circuit voltage  $(V_{oc})$ , (c) fill factor (FF), and (d) power conversion efficiency (PCE).

Information). From Table 2, Figure 3a, and Figure S3b in the Supporting Information, one could observe that different materials had different appropriate solvent options. Cheerfully, after the solvent exposure, the performance of all PSCs had been enhanced dramatically. For PBDT-DFBO, the most appropriate solvent was ethanol and the PCE values achieved ranged from 2.0%  $\pm$  0.1% to 5.6%  $\pm$  0.3%, with a largely increased short-circuit current density ( $J_{sc}$ ), from 5.2  $\pm$  0.1 mA cm<sup>-2</sup> to 10.6  $\pm$  0.2 mA cm<sup>-2</sup>, a open-circuit voltage ( $V_{oc}$ ) ranging from 0.78  $\pm$  0.01 V to 0.83  $\pm$  0.01 V, and a fill factor (FF) from 50.2%  $\pm$  0.1% to 64.7%  $\pm$  0.4%. For PBDTT-DFBO, the most appropriate solvent is methanol and the PCE value reached ranged from 2.1%  $\pm$  0.1% to 4.5%  $\pm$  0.3%, with J s<sub>c</sub> ranging from 5.5  $\pm$  0.1 mA cm<sup>-2</sup> to 9.1  $\pm$  0.3 mA cm<sup>-2</sup>, a V<sub>oc</sub> value ranging from 0.83  $\pm$  0.01 V to 0.86  $\pm$  0.01 V, and a FF

ranging from 46.5%  $\pm$  0.1% to 58.6%  $\pm$  0.5%. For PBDTF-DFBO, the most appropriate solvent is also the methanol, and the PCE achieved ranged from 2.8%  $\pm$  0.2% to 6.5%  $\pm$  0.1%, with  $J_{\rm sc}$  ranging from 6.9  $\pm$  0.1 mA cm<sup>-2</sup> to 12.7  $\pm$  0.1 mA cm<sup>-2</sup>, a  $V_{\rm oc}$  ranging from 0.79  $\pm$  0.01 V to 0.83  $\pm$  0.01 V, and a FF from 53.4%  $\pm$  0.1% to 62.0%  $\pm$  0.1%. The  $J_{\rm sc}$  value (12.32 mA cm<sup>-2</sup>) calculated by integrating the EQE data (see Figure S5 in the Supporting Information) with the AM 1.5G spectrum agreed rather well with the directly measured  $J_{\rm sc}$  value (PCE estimated from the calculated  $J_{\rm sc}$  value: 6.43%) and the EQE curve revealed a broad photoresponse, from 300 nm to 700 nm, with two maximum peak values of 74% at ~450 nm and ~570 nm. Moreover, as shown in the J-V curves (obtained in darkness) in Figure 3b and Figure S6 in the Supporting Information), all BHJ solar cells with polar solvent exposure



**Figure 5.**  $J^{0.5}-V$  plots for PBDT-DFBO:PC<sub>71</sub>BM devices without (squares) and with (circles) ethanol treatment: (a) hole-only devices and (b) electron-only devices. The solid lines represent the fit using a model of single carrier SCLC with field-independent mobility. The J-V characteristics are corrected for the built-in voltage ( $V_{bi}$ ).



**Figure 6.** Tapping-mode atomic force microscopy (AFM) topography image of the blend film of PBDTF-DFBO/PC<sub>71</sub>BM (1:2, w/w): (a) without solvent treatment, (b) with methanol treatment, (c) with ethanol treatment, (d) with propanol treatment, (e) three-dimensional (3D) surface plot without solvent treatment, and (f) 3D surface plot with methanol treatment. (All image sizes are 2.0  $\mu$ m × 2.0  $\mu$ m.)

exhibited a higher shunt resistance  $(R_{\rm sh})$  and a reduced series resistance  $(R_{\rm s})$ , compared without solvent treatment. For example, the  $R_{\rm sh}$  values were calculated to be  $1.4 \times 10^5 \ \Omega \ {\rm cm}^2$ and  $1.0 \times 10^4 \ \Omega \ {\rm cm}^2$  for the methanol-treated PSCs and the pristine PSCs based on PBDTF-DFBO, respectively. These data are in agreement with the slightly increased  $V_{\rm oc}$  values in the PSCs. Moreover, the series resistance  $(R_{\rm s})$  of the methanol-treated PSCs is 3  $\Omega$  cm<sup>2</sup>, which was lower than that of the

pristine device (10  $\Omega$  cm<sup>2</sup>). These results demonstrated that better diode characteristics were obtained after solvent exposure. In addition, note that the  $J_{\rm sc}$  value of the PBDTF-DFBO/PC<sub>71</sub>BM solar cell (12.7 ± 0.1 mA cm<sup>-2</sup>) was remarkably improved from 9.1 ± 0.3 mA cm<sup>-2</sup> of the PBDTT-DFBO based devices, but accompanied by a slight reduction in  $V_{\rm oc}$ . This phenomenon is consistent with that which is predicted by theory and the experimental results of the UV/vis absorption spectra and the CV measurements. The improved photocurrent of PBDTF-DFBO from PBDTT-DFBO is attributed to its higher charge carrier mobility (see Table S2 in the Supporting Information) and broader absorption range. The slightly decreased  $V_{\rm oc}$  value of PBDTF-DFBO from PBDTT-DFBO is, to a certain degree, caused by its higher HOMO energy level.

To further optimize the performance of all PSCs, we examine the wetting time effect (the time that polar solvent is present on top of the active layer before the substrate is spun), since it is relevant for the observed improvements.<sup>11a</sup> Figure 4 presented the wetting time dependence of  $J_{sc}$ ,  $V_{oc}$ , FF, and overall PCE of 1:2 polymer/PC<sub>71</sub>BM devices on their most appropriate solvent treatment (ethanol for PBDT-DFBO, methanol for PBDTT-DFBO and PBDTF-DFBO) (see also Table S1 in the Supporting Information. A wetting time of 2 min was found to work best for PBDT-DFBO, whereas PSCs based on PBDTT-DFBO and PBDTF-DFBO achieved the highest PCEs of 5.0% and 7.0%, respectively, with a wetting time of 3 min. Although there were slight decreases of PCE with wetting time longer than 3 min, the  $V_{oc}$  and  $J_{sc}$  values remained almost the same.

3.4. Effects of Solvent Treatment on Charge-Transport Properties. In order to explore the origin of the largely enhanced performance, especially the dramatically increased  $J_{sc}$ and FF values after polar solvent exposure, the charge-transport properties were investigated by examining the charge carrier mobility of polymer:PC71 BM using single-carrier diodes and the space-charge limited current (SCLC) model. The photocurrent in the BHJ solar cells combines contributions of both the hole and the electron; therefore, we must assist the injection of one type of the charges and suppress the other by choosing suitable electrodes to manufacture electron-only or hole-only devices<sup>19</sup> (details can be found in the Experimental Section). The J-V curves were fit using the Mott–Gurney law (see Figure 5 and Figure S7 in the Supporting Information), and the data were collected in Table S2 in the Supporting Information. The hole mobilities of all polymer:PC71BM devices were enhanced dramatically after polar solvent exposure. For instance, in pristine PBDT-DFBO:PC71BM devices, the hole mobility of 5.4  $\times$  10<sup>-5</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> was almost 1 order of magnitude lower than the electron mobility of  $3.1 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . After methanol treatment, the hole mobility increased to  $1.8 \times 10^{-4}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, while the electron mobility almost remained unaltered  $(3.4 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1})$ . As a consequence, on one hand, the larger  $J_{sc}$  value of the polar solvent-treated devices from prestine devices was, to a certain degree, attributed to its higher charge carrier mobility; on the other hand, with the more balanced charge transport in the devices, one may increase the FF of the PSCs by restricting the buildup of space charges, and consequently, reducing charge recombination.15

**3.5. Modification of Solvent Treatment on the Active Layer surface.** Since the morphology of the photoactive layer played a key role in the photovoltaic performance of PSCs, we directly examined the surface morphology with and without

polar solvent exposure via tapping-mode atomic force microscopy (AFM). The AFM topography images are shown in Figure 6 and Figure S8 in the Supporting Information). In the case of PBDTF-DFBO:PC71BM blends, it could be observed that the blend film without solvent exposure exhibited relatively course phase separation between the polymer and PC71BM with a root-mean-square (RMS) surface roughness of 5.2 nm (see Figure 6a). The relatively large (100-300 nm) globular clusters that can be attributed to PC71BM domains may originate from the fact that, during the drying of the film, PC<sub>71</sub>BM crystallizes before the polymer is solidifying.<sup>20</sup> In contrast, after solvent treatment, the surface of the blend film demonstrated a more uniform distribution of PBDTF-DFBO and  $PC_{71}BM$  (see Figures 6b, 6c, and 6d) and the formation of fiberlike interpenetrating morphologies at the length scale of ~20 nm with decreasing roughness of RMS = 2.1 nm for the methanol-treated device, RMS = 0.7 nm for the ethanol-treated device, and RMS = 1.4 nm for the propanol-treated device. According to Park's work,<sup>11c</sup> tens of seconds of polar solvent treatment did not provide an adequate driving force for reconstructing the morphologies of the polymer films, possibly because polymers are relatively bulky and weighty, compared to the small molecules. However, as some of the polar solvent molecules penetrated the active layer, PC71BM particles could be redistributed to reduce the contact areas with the polar solvents,<sup>21</sup> and after some appropriate wetting time, PC<sub>71</sub>BM particles aggregated to the tens-of-nanometers length domains, thus, the formation of nanoscale phase separation of the blend films (see Figures 6a, 6b, 6e, and 6f). This relatively smooth surface and more ordered structure are beneficial to the charge transportation,<sup>8b</sup> thus leading to an increase in  $J_{sc}$  as well as the device efficiency. The cases of PBDT-DFBO/PC71BM and PBDTT-DFBO/PC71BM blends are similar to that of PBDTF-DFBO/PC<sub>71</sub>BM blend (see Figure S8 in the Supporting Information).

#### 4.. CONCLUSION

In summary, a series of furan-based donor-acceptor copolymers with various side groups have been developed. These side-group substituents offer the opportunity to tailor the optical and electronic properties of the polymers. In the preliminary investigation, one can obtain solar cells with power conversion efficiency (PCE) values of 2.1% for PBDT-DFBO, 2.2% for PBDTT-DFBO, and 3.0% for PBDTF-DFBO. Inspiringly, after simply polar solvent exposure (such as methanol or ethanol), the PCE could reach up to 5.9%, 5.0%, and 7.0%, respectively, which showed an improvement of 130%-170%. The effects of polar solvent treatment on the simultaneous enhancement in the open-circuit voltage, shortcircuit current density, and fill factor of the PSCs are shown to originate from the increased hole mobilities, more-balanced charge transport, and the formation of fiberlike interpenetrating morphologies. Furthermore, this strategy obviates laborious synthesis of interlayer materials, time-consuming thermal annealing, and solvent vapor treatment. This work demonstrates a good example for tuning the absorption range, energy level, charge transport, and photovoltaic properties of the polymers by side-chain engineering and the solvent treatment can offer a simple and effective method to improve the efficiency of polymer solar cells (PSCs).

#### **Chemistry of Materials**

#### ASSOCIATED CONTENT

#### **S** Supporting Information

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectrum of DFBO and co-polymers. UV–visible absorption spectra, CV, SCLC results, J-V characteristics of the polymer:PC<sub>71</sub>BM devices, and EQE of PBDTF-DFBO:PC<sub>71</sub>BM devices. This material is available free of charge via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

### **Corresponding Author**

\*E-mail: geziyi@nimte.ac.cn.

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

We would like to thank the financial support of the National Natural Science Foundation of China (Nos. 21074144, 51273209, and 21102156), and the External Cooperation Program of the Chinese Academy of Scieces (No. GJHZ1219).

#### REFERENCES

(1) (a) Sariciftci, N. S.; Smilowitz, L.; Heeger, A. J.; Wudl, F. Science 1992, 258, 1474. (b) Yu, G.; Ga, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. Science 1995, 270, 1789. (c) Heeger, A. J. Angew. Chem., Int. Ed. 2001, 40, 2591. (d) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. Adv. Funct. Mater. 2001, 11, 15. (e) Günes, S.; Neugebauer, H.; Sariciftci, N. S. Chem. Rev. 2007, 107, 1324. (f) Park, S. H.; Roy, A.; Beaupré, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. Nat. Photonics 2009, 3, 297. (h) Cheng, Y.-J.; Yang, S.-H.; Hsu, C.-S. Chem. Rev. 2009, 109, 5868. (i) Boudreault, P.-L.; Najari, T. A.; Leclerc, M. Chem. Mater. 2011, 23, 456. (j) Li, G.; Zhu, R.; Yang, Y. Nat. Photonics 2012, 6, 153. (k) Li, X.; Choy, W. C. H.; Huo, L.; Xie, F.; Sha, W. E. I.; Ding, B.; Guo, X.; Li, Y.; Hou, J.; You, J.; Yang, Y. Adv. Mater. 2012, 24, 3046. (l) Li, Y. Acc. Chem. Res. 2012, 45, 723.

(2) (a) Wang, D. H.; Kim, D. Y.; Choi, K. W.; Seo, J. H.; Im, S. H.; Park, J. H.; Park, O. O.; Heeger, A. J. Angew. Chem., Int. Ed. 2011, 50, 5519. (b) Huo, L.; Zhang, S.; Guo, X.; Xu, F.; Li, Y.; Hou, J. Angew. Chem., Int. Ed. 2011, 50, 9697. (c) Zhou, H. X.; Yang, L. Q.; Stuart, A. C.; Price, S. C.; Liu, S. B.; You, W. Angew. Chem., Int. Ed. 2011, 50, 2995. (d) Small, C. E.; Chen, S.; Subbiah, J.; Amb, C. M.; Tsang, S.-W.; Lai, T.-H.; Reynolds, J. R.; So, F. Nat. Photonics 2012, 6, 115. (e) Gevaerts, V. S.; Furlan, A.; Wienk, M. M.; Turbiez, M.; Janssen, R. A. J. Adv. Mater. 2012, 24, 2130. (f) Dou, L.; You, J.; Yang, J.; Chen, C.-C.; He, Y.; Murase, S.; Moriarty, T.; Emery, K.; Li, G.; Yang, Y. Nat. Photonics 2012, 6, 180. (g) Dou, L.; Chang, W.-H.; Gao, J.; Chen, C.-C.; You, J.; Yang, Y. Adv. Mater. 2013, 25, 825. (h) Son, H. J.; Lu, L.; Chen, W.; Xu, T.; Zheng, T.; Carsten, B.; Strzalka, J.; Darling, S. B.; Chen, L. X.; Yu, L. Adv. Mater. 2013, 25, 838. (i) You, J.; Dou, L.; Yoshimura, K.; Kato, T.; Ohya, K.; Moriarty, T.; Emery, K.; Chen, C.-C.; Gao, J.; Li, G.; Yang, Y. Nat. Commun. 2013, 4, 1446. (j) You, J.; Chen, C.-C.; Hong, Z.; Yoshimura, K.; Ohya, K.; Xu, R.; Ye, S.; Gao, J.; Li, G.; Yang, Y.; Adv. Mater., 2013, 25, DOI: 10.1002/ adma.201300964.

(3) (a) Hoven, C. V.; Dang, X. D.; Coffin, R. C.; Peet, J.; Nguyen, T. Q.; Bazan, G. C. *Adv. Mater.* **2010**, *22*, E63. (b) Wang, X.; Jiang, P.; Chen, Y.; Luo, H.; Zhang, Z.; Wang, H.; Li, X.; Yu, G.; Li, Y. *Macromolecules* **2013**, *46*, 4805.

(4) (a) Jiang, J.-M.; Yang, P.-A.; Chen, H.-C.; Wei, K.-H. *Chem. Commun.* **2011**, 47, 8877. (b) Ding, P.; Zhong, C.; Zou, Y.; Pan, C.; Wu, H.; Cao, Y. *J. Phys. Chem. C* **2011**, 115, 16211. (c) Liu, B.; Chen, X.; He, Y.; Li, Y.; Xu, X.; Xiao, L.; Li, L.; Zou, Y. *J. Mater. Chem. A* **2013**, 1, 570.

(5) (a) Woo, C. H.; Beaujuge, P. M.; Holcombe, T. W.; Lee, O. P.; Frechet, J. M. J. J. Am. Chem. Soc. **2010**, 132, 15547. (b) Coffin, R. C.; Peet, J.; Rogers, J.; Bazan, G. C. Nat. Chem. **2009**, 1, 657. (c) Li, W.; Roelofs, W. S. C.; Wienk, M. M.; Janssen, R. A. J. J. Am. Chem. Soc. 2012, 134, 13787.

(6) Wang, X.; Chen, S.; Sun, Y.; Zhang, M.; Li, Y.; Li, X.; Wang, H. Polym. Chem. 2011, 2, 2872.

(7) Wang, X.; Sun, Y.; Chen, S.; Guo, X.; Zhang, M.; Li, X.; Li, Y.; Wang, H. *Macromolecules* **2012**, *45*, 1208.

(8) (a) Yuan, J.; Huang, X.; Zhang, F.; Lu, J.; Zhai, Z.; Di, C.; Jiang, Z.; Ma, W. J. Mater. Chem. 2012, 22, 22734. (b) Wang, Y.; Yang, F.; Liu, Y.; Peng, R.; Chen, S.; Ge, Z. Macromolecules 2013, 46, 1368. (c) Dou, L.; Gao, J.; Richard, E.; You, J.; Chen, C. C.; Cha, C. C.; He, Y.; Li, G.; Yang, Y. J. Am. Chem. Soc. 2012, 134, 10071. (d) Zhang, Y.; Gao, L.; He, C.; Sun, Q.; Li, Y. Polym. Chem. 2013, 4, 1474.

(9) (a) Moulé, A. J.; Meerholz, K. Adv. Funct. Mater. 2009, 19, 3028.
(b) Clarke, T. M.; Durrant, J. R. Chem. Rev. 2010, 110, 6736.

(10) (a) Peet, J.; Kim, J. Y.; Coates, N. E.; Ma, W. L.; Moses, D.; Heeger, A. J.; Bazan, G. C. *Nat. Mater.* **2007**, *6*, 497. (b) Li, G.; Shrotriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat. Mater.* **2005**, *4*, 864. (c) Miller, S.; Fanchini, G.; Lin, Y.-Y.; Li, C.; Chen, C.-W.; Su, W.-F.; Chhowalla, M. J. Mater. Chem. **2008**, *18*, 306.

(11) (a) Liu, X.; Wen, W.; Bazan, G. C. Adv. Mater. 2012, 24, 4505.
(b) Li, H.; Tang, H. W.; Li, L. G.; Xu, W. T.; Zhao, X. L.; Yang, X. N. J. Mater. Chem. 2011, 21, 6563. (c) Nam, S.; Jang, J.; Cha, H.; Hwang, J.; An, T. K.; Park, S.; Park, C. E. J. Mater. Chem. 2012, 22, 5543.
(d) Wang, Q.; Zhou, Y.; Zheng, H.; Shi, J.; Li, C. Z.; Su, C. M. Q.; Wang, L.; Luo, C.; Hu, D. G.; Pei, J.; Wang, J.; Peng, J. B.; Cao, Y. Org. Electron. 2011, 12, 1858. (e) Zhou, H.; Zhang, Y.; Seifter, J.; Collins, S. D.; Luo, C.; Bazan, G. C.; Nguyen, T.-Q.; Heeger, A. J. Adv. Mater. 2013, 25, 1646.

(12) Yiu, A. T.; Beaujuge, P. M.; Lee, O. P.; Woo, C. H.; Toney, M. F.; Frechet, J. M. J. J. Am. Chem. Soc. **2012**, 134, 2180.

(13) (a) Wang, M.; Hu, X.; Liu, P.; Li, W.; Gong, X.; Huang, F.; Cao, Y. J. Am. Chem. Soc. **2011**, 133, 9638. (b) Huo, L.; Hou, J.; Chen, H. Y.; Zhang, S.; Jiang, Y.; Chen, T. L.; Yang, Y. Macromolecules **2009**, 42, 6564. (c) Jiang, J. M.; Yang, P. A.; Chen, H. C.; Wei, K. H. Chem. Commun. **2011**, 47, 8877.

(14) (a) Woo, C.; Beaujuge, P.; Holcombe, T.; Lee, O.; Fréchet, J. M.
J. J. Am. Chem. Soc. 2010, 132, 15547. (b) Guo, X.; Cui, C.; Zhang, M.;
Huo, L.; Huang, Y.; Hou, J.; Li, Y. Energy Environ. Sci. 2012, 5, 7943.
(15) Zhou, H.; Zhang, Y.; Seifter, J.; Collins, S. D.; Luo, C.; Bazan, G.

C.; Nguyen, T. Q.; Heeger, A. J. Adv. Mater. 2013, 25, 1646.

(16) Chan, S. H.; Hsiao, Y. S.; Hung, L. I.; Hwang, G. W.; Chen, H. L.; Ting, C.; Chen, C. P. *Macromolecules* **2010**, *43*, 3399.

(17) Chen, H. Y.; Yeh, S. C.; Chen, C. T.; Chen, C. T. J. Mater. Chem. 2012, 22, 21549.

(18) Lee, D.; Stone, S. W.; Ferraris, J. P. Chem. Commun. 2011, 47, 10987.

(19) (a) Zhang, Y.; Blom, P. W. M. Appl. Phys. Lett. 2010, 97.
(b) Zhang, Y.; Blom, P. W. M. Appl. Phys. Lett. 2011, 98.

(20) (a) Wienk, M. M.; Kroon, J. M.; Verhees, W. J. H.; Knol, J.; Hummelen, J. C.; Van Hal, P. A.; Janssen, R. A. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3371. (b) Bijleveld, J. C.; Karsten, B. P.; Mathijssen, S. G. J.; Wienk, M. M.; Leeuw, D. M.; Janssen, R. A. J. *J. Mater. Chem.* **2011**, *21*, 1600.

(21) Nam, S.; Chung, D. S.; Jang, J.; Kim, S. H.; Yang, C.; Kwon, S.-K.; Park, C. E. J. Electrochem. Soc. **2010**, 157, H90.