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Donor Polymers Containing Benzothiadiazole and Four Thiophene Rings in Their Repeating Units with Improved Photovoltaic Performance

Ergang Wang, Ming Wang, Li Wang, Chunhui Duan, Jie Zhang, Wanzhu Cai, Chao He, Hongbin Wu, and Yong Cao*

Institute of Polymer Optoelectronic Materials and Devices, Key Lab of Specially Functional Materials, Ministry of Education, South China University of Technology, Guangzhou 510640, P. R. China

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ABSTRACT: A series of internal donor−acceptor type of copolymers containing benzothiadiazole and four thiophene rings (bis(2,2′-dithienyl)benzothiadiazole) in their repeating units were synthesized and characterized. The effect of the position of alkyl groups attached to different thiophene rings of the new polymers on their optical, electrochemical, and photovoltaic properties was investigated and compared with poly(2,7-(9,9-dioctylfluorene)-*alt*-5,5-(4′,7′-di-2-thienylbenzo[*c*][1,2,5]thiadiazole)) (PFO-DBT). One of the new polymers, poly(2,7-(9,9-dioctylfluorene)-*alt*-5′,5′-(4,7-bis(3′-hexyl-2,2′-bithiophen-5-yl)benzo[*c*][1,2,5]thiadiazole)) (PFO-M3), showed the best device performance with a power-conversion efficiency of 2.63%, an open-circuit voltage of 0.86 V, a short-circuit current density of 5.86 mA cm^{-2} and a fill factor of 0.52, which is better as compared with PFO-DBT. This work demonstrated that increasing the number of thiophene rings in the repeating units of the donor−acceptor polymers is a simple and effective method to red-shift their absorption spectra and also improve their solar cell performance.

Introduction

In recent years, polymer-based solar cells have been attracting considerable attention for their unique advantages over traditional silicon-based solar cells, such as low cost, light weight, and potential use in flexible devices.[1−5] At present, one of the most successful donor polymers is regioregular poly(3-hexylthiophene) (P3HT).[6,7] Several groups reported that the bulk heterojunction (BHJ) solar cells made from a blend of P3HT and [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) reached a power-conversion efficiency (PCE) of about 5.0%.[6,7] The PCE of P3HT:PCBM devices can be further improved by modifying the device architectures with a tandem configuration.[8]

The PCE of polymer solar cells was limited by at least two main factors from a view of materials: one is the mismatch between the absorption spectrum of the photoactive layer and the terrestrial solar radiation, which leads to only a small portion of solar energy can be utilized; the other is poor charge transport properties of organic donor and acceptor materials. Synthesis of low-bandgap donor polymers with absorption edge extended into the near-infrared region was considered as a feasible solution to enhance the absorbed solar radiation.[8−11] Thus, various classes of low-bandgap polymers have been synthesized and investigated.[10−14] Recently, the design of low-bandgap polymers by combining electron-rich unit (donor) and electron-deficient unit (acceptor) in their repeating units forming internal donor−acceptor structures has attracted more and more attention owing to their high open-circuit voltage (V_{oc}) and tunable optical, electrochemical, and electronic properties.[13−16] The benefit of this synthetic strategy was validated by low-bandgap conjugated copolymers such as PSBTBT,[17] APFO-15,[18] PFDTBT,[21,22] PSiF-DBT,[19] PCDTBT,[20] and PCPDTBT[12] (the structures are shown in Scheme 1). Throughout all the low-bandgap donor polymers, most of them contain thiophene rings in their repeating units. Thus, it is worth studying the influence of the number of thiophene rings in the repeating units of the polymers on their photophysical properties and performance in solar cells. 4,7-Bis(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (DBT) is one of the most successful electron-deficient units (acceptor), which can combine with many kinds of electron-rich units (donor), such as fluorene (PFDTBT,[21] PFO-DBT[22]), carbazole (PCDTBT),[20] and 4,4-dialkyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene-2,6-diyl (PCPDTBT).[23] The resulting polymers showed high PCE of 2.1−3.6% in polymer solar cells.[20−23] Considering the performance of PFO-DBT may be limited by its narrow absorption spectrum (absorption edge at 645 nm),[21,22] it will be interesting to modify the chemical structure of DBT by adding more thiophene rings to its unit aiming to red shift its absorption edge. In this study, a series of low-bandgap polymers containing benzo[*c*][1,2,5]thiadiazole and four thiophene rings in their repeating units were designed and synthesized. To increase the solubility of the resulting polymers, alkyl was introduced to the thiophene rings of the low bandgap units. It was found that the position of alkyl in thiophene rings has an obvious effect on the molecular weights and photovoltaic performance of the resulting polymers. The influence of the number of thiophene rings and the position of alkyl substituent on thiophene rings were compared and discussed. The photovoltaic performance with a PCE of 2.63%, a V_{oc} of 0.86 V, a short-circuit current density (J_{sc}) of 5.86 mA cm^{-2}, and a fill factor (FF) of 0.52 was achieved under illumination of AM 1.5 G (1000 W m^{-2}) from a solar simulator. As expected, the new polymer containing four thiophene rings in their repeating units with alkyl in a suitable position showed a red-shifted absorption spectrum and enhanced photovoltaic performance compared with PFO-DBT.[21,22]

Experimental Section

Materials. All chemicals and reagents were used as received from Aldrich, ABCR, and Acros Chemical Co. unless otherwise specified. All solvents were dried and purified under nitrogen.

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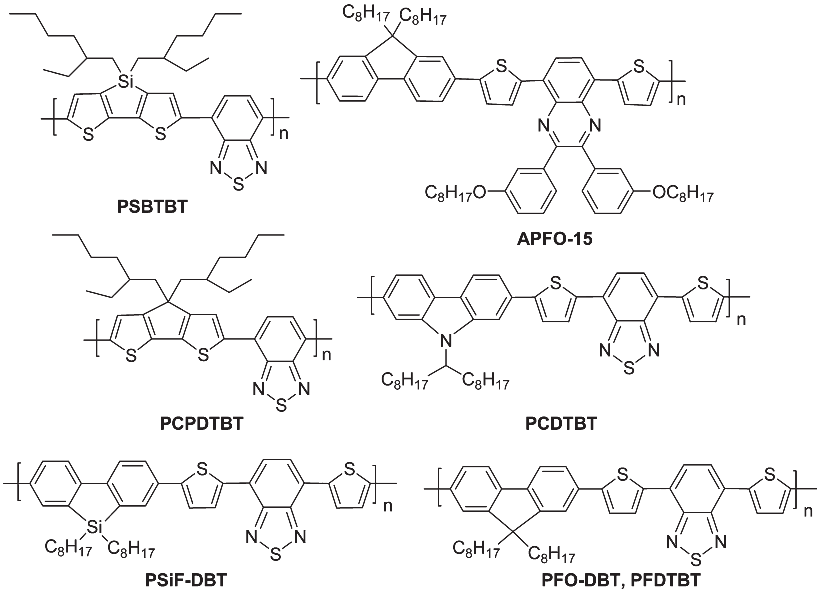
*Corresponding author. E-mail: poycao@scut.edu.cn.

Scheme 1. Structures of PSBTBT, APFO-15, PFDTBT, PSiF-DBT, PCDTBT, and PCPDTBT



All manipulations involving air-sensitive reagents were performed under a dry argon atmosphere.

Measurement and Characterization. ^{1}H NMR spectra were recorded on a Bruker AV-300 (300 MHz) in deuterated chloroform solution. Number-average (M_n) and weight-average (M_w) molecular weights were determined by a Waters GPC 2410 in tetrahydrofuran (THF) using a calibration curve with standard polystyrene as a reference. The elemental analysis was performed on a Vario EL elemental analysis instrument (ELEMENTAR Co.). UV−vis absorption spectra were recorded on an HP 8453 spectrophotometer. Cyclic voltammetry (CV) was performed on a CHI660B electrochemical workstation with platinum working electrodes at a scan rate of 50 mV s^{-1} against a saturated calomel reference electrode (SCE) with a nitrogen-saturated anhydrous solution of 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile (CH_3CN). The evaporation deposition of polymers onto the working electrode was conducted from a dilute chloroform solution.

Solar Cell Device Fabrication. The ITO-coated glass substrates were cleaned by ultrasonic treatment in deionized water, acetone, detergent, and isopropyl alcohol sequentially, followed by spin-coating of a 40 nm thin layer of poly(3,4-ethylenedioxythiopene):poly(styrenesulfonate) (PEDOT:PSS) (Bayer Baytron P 4083). After being dried, on top of this PEDOT:PSS film, a layer of a blend of polymer:PCBM (1:2, w/w) was spin-coated from chlorobenzene solution. The typical film thickness of the active layer was 100 nm. Onto the active layer, a 140 nm thick layer of aluminum was thermally evaporated under vacuum at a pressure below 3×10^{-4} Pa as the cathode. The active area of the device was 0.15 cm^2. PCE was measured under an AM 1.5 solar simulator (Oriel model 91192) (1000 W m^{-2}). The current density−voltage ($J-V$) characteristics were recorded with a Keithley 236 source meter. The spectral response was measured with a commercial photomodulation spectroscopic setup (Oriel). A calibrated Si photodiode was used to determine the photosensitivity.

Synthesis. Tributyl(4-decylthiophen-2-yl)stannane (**1**),[24] tributyl(4-dodecylthiophen-2-yl)stannane (**7**),[24] 4,7-bis(5-bromothiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**8**),[25,26] and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**14**)[25] were prepared according to the published procedures. 4,7-Dibromobenzo[*c*][1,2,5]thiadiazole (**2**) and 2-bromo-3-hexylthiophene (**11**) were purchased from Pacific ChemSource Co.

*4,7-Bis(4-decylthiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**3**).* $PdCl_2(PPh_3)_2$ (0.05 g, 0.07 mmol) was added to a solution of 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (2.94 g, 10 mmol) and tributyl(4-decyl-2-thienyl)stannane (11.80 g, 23 mmol) in 50 mL of THF. The mixture was refluxed in a nitrogen atmosphere for 5 h. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel. Recrystallization from ethanol gave the title compound as red needles (5.34 g, 92%). ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si), δ (ppm): 7.98 (2H, d), 7.80 (2H, s), 7.04 (2H, d), 2.69 (4H, t), 1.65−1.75 (4H, m), 1.27−1.36 (28H, m), 0.86−0.90 (6H, t).

*4,7-Bis(5-bromo-4-decylthiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (**4**).* **3** (0.58 g, 1 mmol) was dissolved in 20 mL of THF, and then *N*-bromosuccinimide (NBS) (0.39 g, 2.2 mmol) was added in portions. The reaction mixture was stirred at room temperature for 2 h. After that, it was poured into water and extracted with ether. The organic layer was washed with brine and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure, affording the crude product as a red solid. Further purification with silica gel chromatography yielded the pure product (0.57 g, 77%). ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si), δ (ppm): 7.79 (2H, s), 7.76 (2H, s), 2.66 (4H, t), 1.64−1.71 (4H, m), 1.27−1.29 (28H, m), 0.90−0.92 (6H, t).

*4,7-Bis(3-decyl-2,2′-bithiophen-5-yl)benzo[*c*][1,2,5]thiadiazole (**5**).* **5** was synthesized by following the similar procedure of **3**. Yield: 82%. ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si), δ (ppm): 7.98 (2H, s), 7.82 (2H, s), 7.34−7.36 (2H, d), 7.23−7.24 (2H, d), 7.09−7.12 (2H, dd), 2.81−2.86 (4H, t), 1.69−1.79 (4H, m), 1.27−1.36 (28H, m), 0.88−0.90 (6H, t).

*4,7-Bis(5′-bromo-3-decyl-2,2′-bithiophen-5-yl)benzo[*c*][1,2,5]thiadiazole (**6**).* To the solution of **5** (2.05 g, 2.7 mmol) in 20 mL of THF was added dropwise the solution of NBS (1.06 g, 5.9 mmol) in 20 mL of THF at 0 °C in 20 min. After stirring for 15 min, the mixture was poured into water. The product was collected by extracting with dichloromethane and purified by silica gel chromatography (1.88 g, 77%). ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si), δ (ppm): 7.93 (2H, s), 7.77 (2H, s), 7.05 (2H, d), 6.96 (2H, d), 2.75−2.80 (4H, t), 1.68−1.74 (4H, m), 1.27−1.42 (28H, m), 0.86−0.90 (6H, t).

*4,7-Bis(4′-dodecyl-2,2′-bithiophen-5-yl)benzo[*c*][1,2,5]thiadiazole (**9**).* **9** was synthesized by following the similar procedure of **3**. Yield: 65%. ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si), δ (ppm): 7.99 (2H, d), 7.79 (2H, s), 7.21 (2H, d), 7.13 (2H, s), 6.85 (2H, s), 2.60 (4H, t), 1.60−1.67 (4H, m), 1.27−1.37 (36H, m), 0.86−0.93 (6H, m).

*4,7-Bis(5′-bromo-4′-dodecyl-2,2′-bithiophen-5-yl)benzo[*c*][1,2,5]thiadiazole (**10**).* **10** was synthesized by following the similar procedure of **6**. Yield: 94%. ^{1}H NMR (300 MHz; CDCl$_3$; Me$_4$Si), δ (ppm): 7.93 (2H, d), 7.76 (2H, s), 7.12 (2H, d), 6.96 (2H, s), 2.55 (4H, t), 1.58−1.61 (4H, m), 1.27−1.33 (36H, m), 0.85−0.90 (6H, m).

*4,7-Bis(3′-hexyl-2,2′-bithiophen-5-yl)benzo[*c*][1,2,5]thiadiazole (**12**).* To a suspension of magnesium powder (0.67 g, 28 mmol) in 15 mL of THF was added dropwise the solution of 2-bromo-3-hexylthiophene (5.50 g, 18 mmol) in 15 mL of THF. After refluxing for 3 h, the mixture was allowed cooling to rt. And then the mixture was added into the solution of 4,7-bis(5-bromothiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (2.75 g, 6 mmol) and dichloro[bis(1,3-diphenylphosphino)propane] nickel(II) (0.10 g) in 40 mL of THF. After refluxing for 18 h, the reaction mixture was quenched by water. The product was collected by extracting with dichloromethane and purified by silica gel chromatography (2.23 g, 59%). ^{1}H NMR (300 MHz; CDCl$_3$; Me$_4$Si), δ (ppm): 7.99 (2H, d), 7.79 (2H, s), 7.21 (2H, d), 7.13 (2H, s), 6.85 (2H, s), 2.60 (4H, t), 1.60−1.70 (4H, m), 1.25−1.42 (12H, m), 0.88−0.93 (6H, m).

*4,7-Bis(5′-bromo-3′-hexyl-2,2′-bithiophen-5-yl)benzo[*c*][1,2,5]thiadiazole (**13**).* **13** was synthesized by following the similar procedure of **6**. Yield: 93%. ^{1}H NMR (300 MHz; CDCl$_3$; Me$_4$Si), δ (ppm): 8.12 (2H, d), 7.86 (2H, s), 7.22 (2H, t), 6.98 (2H, d), 2.85 (4H, t), 1.65−1.72 (4H, m), 1.20−1.44 (12H, m), 0.88−0.92 (6H, t).

*Poly(2,7-(9,9-dioctylfluorene)-*alt*-5′,5′-(4,7-bis(3-decyl-2,2′-bithiophen-5-yl)benzo[*c*][1,2,5]thiadiazole)) (PFO-M1).* Monomer **6** (225 mg, 0.25 mmol), **14** (161 mg, 0.25 mmol), tris(dibenzylideneacetone)dipalladium(0) (1.5 mg), and tri(*o*-tolyl)phosphine (3 mg) were dissolved in a mixture of toluene (6 mL) and sodium carbonate (2 M, 2 mL) under argon. The resulting mixture was refluxed with vigorously stirring for 24 h, and then phenylboronic acid and bromobenzene were added orderly to end-cap the polymer chain. After cooling to room temperature, the resulting mixture was poured into methanol. The precipitated material was collected by filtration through a funnel and then purified by washing with acetone for 24 h to remove catalyst residues (198 mg, 70%). Found: C, 75.11; H, 8.33; N, 2.37; S, 14.27. Calcd for $C_{71}H_{90}N_2S_5$: C, 75.34; H, 8.01; N, 2.48; S, 14.17%.

*Poly(2,7-(9,9-dioctylfluorene)-*alt*-5′,5′-(4,7-bis(4′-dodecyl-2,2′-bithiophen-5-yl)benzo[*c*][1,2,5]thiadiazole)) (PFO-M2).* By following the similar methods, PFO-M2 was synthesized with monomers **10** and **14**. The final product, a deep red polymer, was obtained with a yield of 61%. Found: C, 75.51; H, 8.55; N, 2.17; S, 13.32. Calcd for $C_{75}H_{98}N_2S_5$: C, 75.83; H, 8.32; N, 2.36; S, 13.50%.

*Poly(2,7-(9,9-dioctylfluorene)-*alt*-5′,5′-(4,7-bis(3′-hexyl-2,2′-bithiophen-5-yl)benzo[*c*][1,2,5]thiadiazole)) (PFO-M3).* By following the similar methods, PFO-M3 was synthesized with monomers **13** and **14**. The final product, a deep green polymer, was obtained with a yield of 77%. Found: C, 73.91; H, 7.54; N, 2.67; S, 15.27. Calcd for $C_{63}H_{74}N_2S_5$: C, 74.21; H, 7.32; N, 2.75; S, 15.72%.

Results and Discussion

Synthesis and Characterization. The synthetic routes to generate the monomers and polymers are shown in Schemes 2 and 3, respectively. We have tried to synthesize 4,7-di(2,2′-bithiophen-5-yl)benzo[*c*][1,2,5]thiadiazole without alkyl, yet its solubility was poor. To improve the solubility of the resulting polymers, alkyl was introduced to the thiophene rings of the monomers. Considering that the position of alkyl groups in thiophene rings of the monomers may have an impact on the properties of the resulting polymers, three monomers (**M1**, **M2**, and **M3**, Scheme 2) with alkyl in different positions of the thiophene rings were synthesized.

Compound **3** was synthesized from **1** and **2** by Stille coupling in high yield. Bromination of **3** with NBS yielded **4** successfully. Stille coupling was carried out again to yield **5** via coupling **4** with tributyl(thiophen-2-yl)stannane. Unlike the bromination of **3**, the bromination of **5** is very fast and should be carried out in the ice bath to avoid formation of polybromide. Monomer **6** (**M1**) was polymerized with **14** to yield PFO-M1 via a modified Suzuki coupling reaction with tris(dibenzylideneacetone)dipalladium(0) and tri(*o*-tolyl) phosphine, which was proved to be one of the best catalysts for Suzuki reaction.[26] By using this catalyst, a polymer of PFO-M1 with M_n = 107 000 and PDI = 1.6 was obtained.

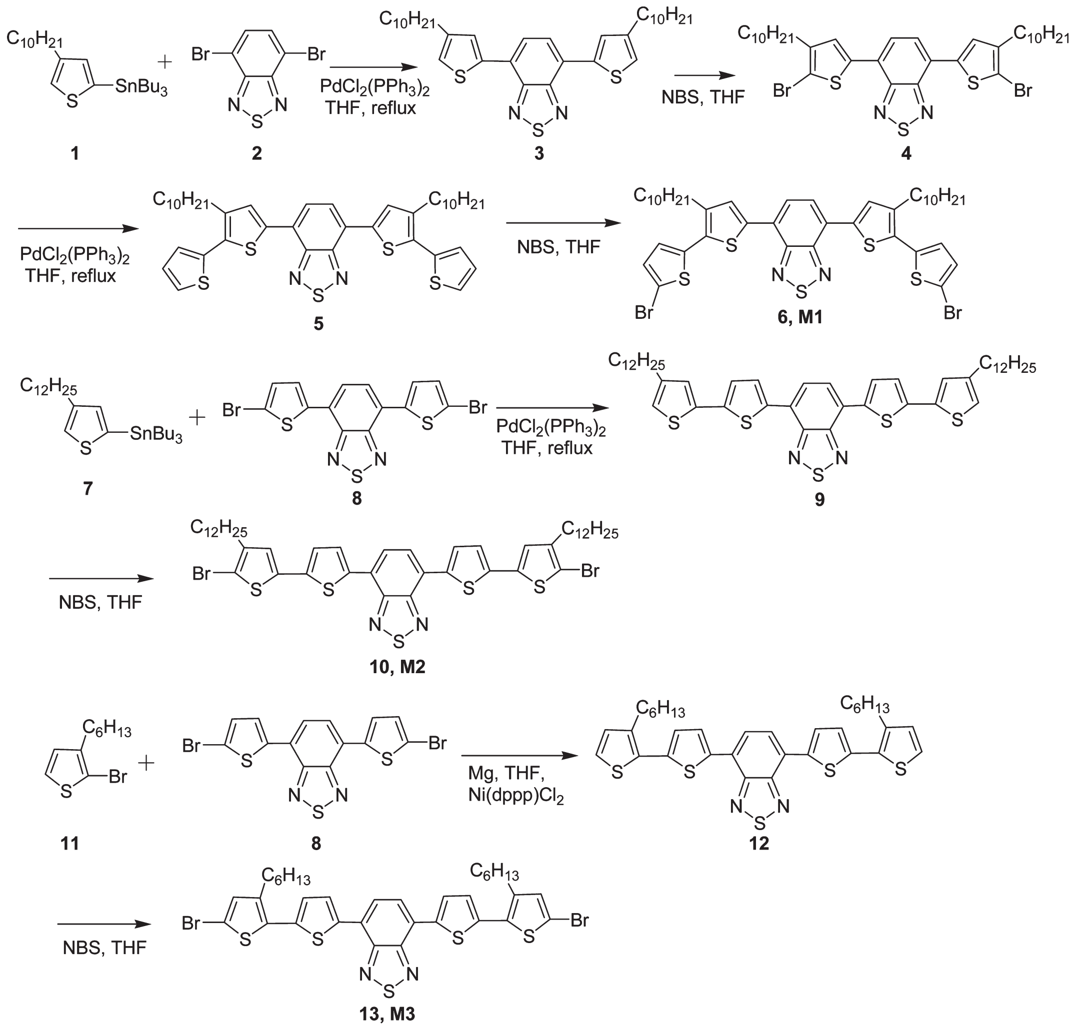
Monomer **10** (**M2**) was prepared using the same procedure as monomer **6**. As compared with monomer **6** which has the alkyls in the thiophene rings connected to benzo[*c*][1,2,5]-thiadiazole, the alkyl groups of the monomer **10** are attached to the peripheral thiophene rings. The M_n of the resulting polymer PFO-M2 is 9000. The rather low molecular weight of PFO-M2 is probably due to the steric hindrance effect of the 4′-alkyl in the thiophene rings of the monomer in the polymerization reaction. To verify our hypothesis, the monomer **13** (**M3**) was synthesized where the alkyl of **13** was moved to 3′-position of the thiophene rings. In this case, there should be much less steric hindrance effect in Suzuki coupling reaction for monomer **13** compared with monomer **10**. The resulting polymer PFO-M3 showed a high M_n of 62 000 with a DPI of 2.3, which confirmed our hypothesis.

Absorption Spectra. The absorption spectra for films of the novel reported polymers are shown in Figure 1. For comparison, the absorption spectrum of PFO-DBT is also included in Figure 1. All of the four polymers showed two absorption peaks, which is a common feature of internal donor−acceptor polymers.[13,27,28] The absorption peak at short wavelength (388−428 nm) originates from $\pi-\pi^*$ transition of fluorene units, while the absorption peak at long wavelength (558−589 nm) is due to $\pi-\pi^*$ transition of the low-bandgap units.[29] It was noted that the absorption peaks at short wavelength of PFO-M2 and PFO-M3 are red-shifted about 30−40 nm as compared with PFO-DBT. The red shift may be due to the strong electron-donating alkyl side chains on thiophene rings that change the ionization potential of fluorene units through the push−pull effect.[16] The absorption bands at long wavelength of all three new polymers are also red-shifted as compared to PFO-DBT. This behavior can be attributed to the longer conjugation length of the low-bandgap units of the new polymers by increasing the number of thiophene rings in the repeating units. Overall, by comparison with PFO-DBT, the absorption spectra of the three new reported polymers containing four thiophene rings in their repeating units are red-shifted. Thus, increasing the number of thiophene rings in the repeating units of polymers should be a simple and effective method to spread the absorption spectra of the polymers. The maximum absorption peaks of the polymers are summarized in Table 1.

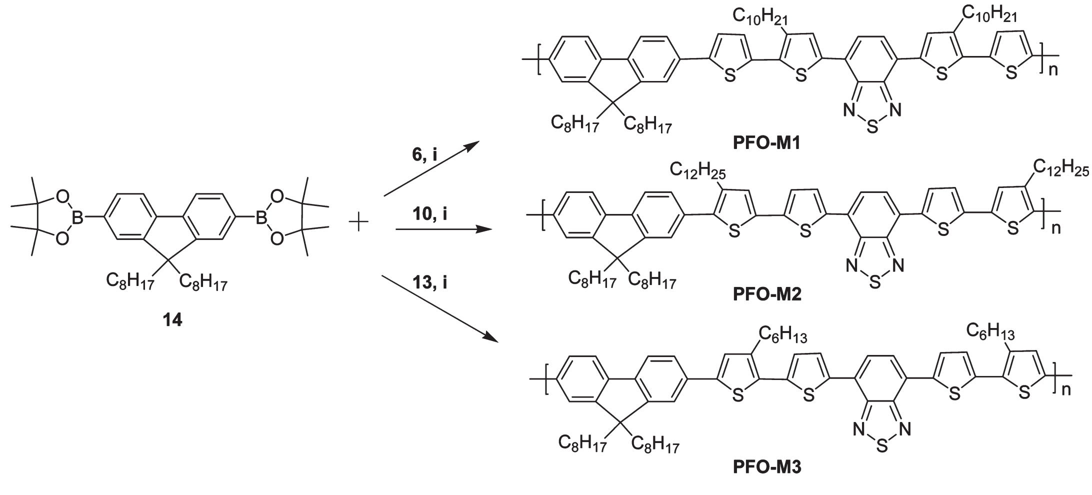
The optical bandgaps (E_{op}) of the polymers deduced from their absorption onset in solid state are summarized in Table 1. The three new polymers showed slightly smaller optical bandgaps compared to PFO-DBT, which is in accordance with their red-shifted absorption spectra.

Electrochemical Study. To investigate the band diagram of the polymers, and then understand the performance of the resulting solar cell devices, it is necessary to determine the energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the polymers. Thus, the electrochemical behaviors of the polymers were investigated by CV. The HOMO (E_{HOMO}) and LUMO (E_{LUMO}) levels of the polymers were

Scheme 2. Synthesis of the Monomers



Scheme 3. Synthesis of the Polymers[a]



[a] Key: (i) $Pd_2(dba)_3$, $(o\text{-tolyl})_3P$, toluene, Na_2CO_3.

calculated according to the empirical formulas $E_{HOMO} = -(E_{ox} + 4.40)$ eV and $E_{LUMO} = -(E_{re} + 4.40)$ eV,[30] respectively, where E_{ox} and E_{re} are the onset oxidation potential and the onset reduction potential of the polymers vs SCE, respectively. As shown in Table 1, the E_{HOMO} and E_{LUMO} of the three polymers are close to those of PFO-DBT, respectively. This result indicates there is no obvious influence on the HOMO or LUMO levels of the resulting polymers by increasing the number of thiophene rings in their repeating units. The low HOMO levels of the new polymers are favorable for keeping a high V_{oc}.[8] The electrochemical bandgaps (E_{ec}) of the polymers are summarized in Table 1,

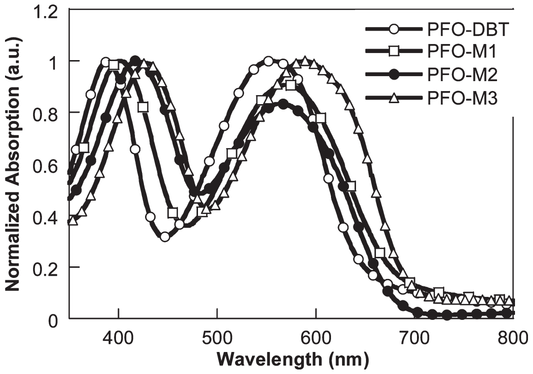


Figure 1. Absorption spectra of PFO-M1, PFO-M2, PFO-M3, and PFO-DBT in films.

Table 1. Electrochemical and Optical Properties of the Polymers

polymers	λ_{max}/nm	$M_n \times 10^4$	DPI	E_{op}/eV	HOMO/eV	LUMO/eV	E_{ec}/eV
PFO-DBT	388, 555	0.8	2.0	1.89	−5.43	−3.20	2.23
PFO-M1	402, 571	10.7	1.6	1.79	−5.40	−3.13	2.27
PFO-M2	417, 565	0.9	1.5	1.81	−5.37	−3.17	2.37
PFO-M3	428, 589	6.2	2.3	1.77	−5.34	−3.22	2.12

Table 2. Performance of the Solar Cell

polymers	V_{oc}/V	J_{sc}/mA cm^{-2}	FF	PCE (%)
PFO-DBT	0.90	5.07	0.44	2.02
PFO-M1	0.90	3.97	0.41	1.82
PFO-M2	0.70	2.80	0.38	0.74
PFO-M3	0.86	5.86	0.52	2.63

which are higher than those of E_{op}. The poor agreement may be originated from the interface barrier present between the polymer film and the electrode surface.[31] Moreover, the HOMO or LUMO levels of polymers estimated by different methods also resulted in different E_{ec}.[32,33] It was observed that the position of alkyl of the polymers has only a slight influence on their HOMO or LUMO levels.

Since V_{oc} of polymer solar cells is linearly correlated with the difference between the HOMO level of electron donor and the LUMO level of electron acceptor, the lower HOMO levels of the three new polymers can result in higher V_{oc} of the resulting polymer solar cells.[8] The LUMO levels of the three polymers are much higher than those of PCBM (−4.3 eV),[8] which indicates the photoinduced electron transfer from the polymers (as donor) to PCBM (as acceptor) is allowed.[34,35] Judging from the CV results, the new polymers showed promising electrochemical properties as polymer donor materials.

Photovoltaic Properties. In order to investigate the potential application of the three new polymers in solar cells, the devices with a sandwich structure of ITO/PEDOT:PSS/polymer:PCBM/Al were fabricated. To investigate the influence of the number of thiophene rings in the repeating units of the polymers on the performance of the solar cells, PFO-DBT was also tested in the same device configurations. The performances of the polymers are summarized in Table 2. Although the absorption spectra of the three new polymers are red-shifted compared with PFO-DBT, the PCE of PFO-M1 and PFO-M2 is lower than that of PFO-DBT. PFO-M3 ranked the best performance, which is in accordance with its large red-shifted absorption spectrum.

The $J-V$ characteristics of the devices prepared from PFO-DBT, PFO-M1, PFO-M2, and PFO-M3 measured under the illumination of AM 1.5 G (1000 W m^{-2}) from a solar simulator are shown in Figure 2. The PCE up to 2.63% was observed from the solar cells made by PFO-M3:PCBM with a V_{oc} of 0.86 V, a J_{sc} of 5.86 mA cm^{-2}, and a FF of 0.52, which is higher than that of PFO-DBT (2.0%) fabricated and measured in the same conditions. It is worth noting that the V_{oc} of PFO-M1 and PFO-M3 are almost the same as that of PFO-DBT (Table 2), which is in accordance with their close HOMO levels. The PCE and V_{oc} of PFO-M2 are much lower than those of the others, which is probably due to its low molecular weight.[36,37] It has been reported that the low efficiency of solar cells fabricated from low-molecular-weight polymers originates mainly from the reduced charge carriers mobility in the donor phase of the heterojunction.[36,37]

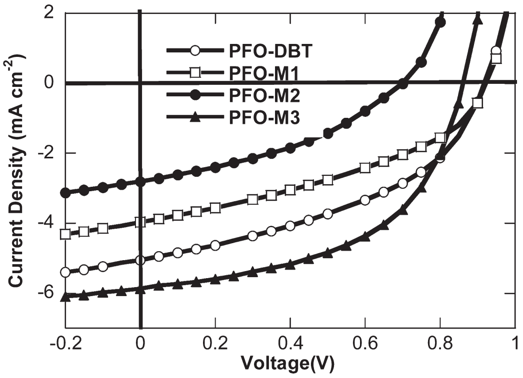


Figure 2. $J-V$ characteristics of the device with the structure of ITO/PEDOT:PSS/polymer:PCBM (1:2, w/w)/Al under the illumination of AM 1.5 G from a solar simulator (1000 W m^{-2}).

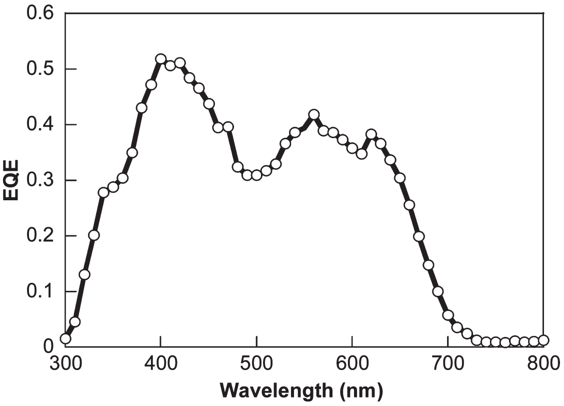


Figure 3. EQE of the device from PFO-M3 illuminated by monochromatic light.

To validate the PCE, the external quantum efficiency (EQE) of the device from PFO-M3 illuminated by monochromatic light was determined. The EQE profile is shown in Figure 3. The integral of the EQE is in accordance with the J_{sc} measured from the devices. Almost identical profiles between the EQE of the devices and the absorption spectrum of PFO-M3 (Figure 1) indicate that excitons are mainly generated in the polymer phase.

The photovoltaic study of PFO-M3 showed that this copolymer is a promising donor material for BHJ solar cells.

Conclusions

In summary, a series of new polymers containing benzothiadiazole and four thiophene rings in their repeating units were synthesized and characterized. PFO-M3 showed the best performance with a PCE of 2.63%, a V_{oc} of 0.86 V, a J_{sc} of 5.86 mA cm^{-2}, and a FF of 0.52, which is better than that of PFO-DBT. Moreover, the solubility and molecular weight of PFO-M3 are much better than those of PFO-DBT, which is in favor of the process of solar cells. This work demonstrated that increasing the number of thiophene rings in the repeating units of the donor−acceptor type of polymers is a simple and effective method to red-shift the absorption spectra of them and then improve their device performance. This method is anticipated to apply to other donor−acceptor type of polymers besides PFO-DBT.

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