

Fluorene-Based Copolymers with Donor–Acceptor Units on the Side Chain and Main Chain: Synthesis and Application in Polymer Solar Cells

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ABSTRACT: Two narrow band gap fluorene-based copolymers with donor–acceptor (D–A) structure on the polymer side chain and/or main chain are synthesized by Pd-catalyzed Stille coupling reactions. The two copolymers have excellent thermal stability. The effects of D–A structure on the main and side chains on the absorption and electrochemical properties are studied. The copolymer PF-BTh-DBT with D–A structure both on the main and side chains has broader and stronger absorption and narrower band gap than the copolymer PF-BTh with only a pendent D–A structure. The power conversion efficiency of the assembled solar cell using PF-BTh-DBT as donor and PC₇₁BM as acceptor is 1.6% with open-circuit voltage (V_{oc}) 0.84 V under simulated AM 1.5 G solar irradiation (100 mW/cm²). © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 3276–3281, 2013

KEYWORDS: copolymers; optical and photovoltaic applications; optical properties

Received 9 April 2013; accepted 19 May 2013; Published online 14 June 2013

DOI: 10.1002/app.39563

INTRODUCTION

Polymer solar cells (PSCs) have potential applications in general industrial and consumer electronics because of their simple large-area preparation by spin-coating, printing, and other methods.^{1–3} Many different low band gap conjugated polymers have been designed and developed over the years, enhancing the power conversion efficiency (PCE) more than 9%.^{4–6} Although the progress has been impressive, much work still need to be done before practical applications of PSCs can be realized. The PCE of PSCs can be further improved by designing suitable electron donor and acceptor materials and by further optimizing the assembled solar cell structure. Given that [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) is still one of the best electron acceptors, most recent efforts have focused on the development of low band gap polymer donors. The most powerful strategy for designing a low band gap conjugated polymer is by incorporating electron-rich (donor) and electron-deficient (acceptor) units in the polymer main chains because their absorption and band gaps can be readily tuned by controlling the intramolecular charge transfer from donor to acceptor. Using this strategy, a variety of promising low-band gap materials have been developed, showing efficient photovoltaic response.^{7–15} Another alternative approach for designing low-band gap polymers is by developing conjugated polymers with pendant acceptor groups, where the electron acceptors are located at the end of the polymer side chains. Several new conjugated polymers with pendent acceptor units have been reportedly used in PSCs.^{16–19}

Among various donor materials, narrow band gap fluorene-based copolymers are important donor materials for solar cells because of their high thermal and chemical stability and processability. Many narrow band gap fluorene-based copolymers with pendent acceptor units or donor–acceptor (D–A) structures on the main chain have been reported, showing high PCE.^{20–26} However, most of the reported narrow band gap fluorene-based copolymers are based on alkylfluorene. Only a few reports are available on fluorene-based copolymers with pendent D–A structures on the C9 site side chain of fluorene for application in PSCs.²⁷ In our previous work,²⁷ we synthesized a series of random fluorene-based copolymers derived from alkylfluorene, fluorene unit with pendent D–A structures on the C9 site, and 4,7-dithienyl-2,1,3-benzothiadiazole (DBT). We then studied the effect of pendent D–A structure content on photophysical, electrochemical, and photovoltaic properties. Compared with the polyfluorene copolymers based on alkylfluorene and DBT, introducing the fluorene unit with pendent D–A structure can increase the intensity of absorption band and favor the light harvesting of the PSCs. In this article, we synthesized two polyfluorene copolymers (PF-BTh-DBT and PF-BTh) with pendent D–A structure unit on the C9 site of fluorene and/or on the polymer main chain to study further the influence of the D–A structure on polymer photovoltaic performance. The effects of D–A structure on the main and side chains on the absorption and electrochemical properties were studied, and the results indicate that the copolymer PF-BTh-DBT with D–A structure both on the main and side chains has broader

and stronger absorption and narrower band gap than the copolymer PF-BTh with only a pendent D–A structure. The bulk heterojunction (BHJ) PSCs using PF-BTh-DBT as donor and PC₇₁BM as acceptor showed a PCE of 1.6% and a high V_{oc} of 0.84 V without annealing and additives.

EXPERIMENTAL

Materials and Measurement

Elemental analysis was performed on a FlashEA1112 elemental analysis instrument (Elementar Co., Germany). ¹H- and ¹³C-NMR spectra were recorded on a Varian Inova 400 (Varian Inc., Palo Alto, California) in deuterated chloroform solution at 298 K. The thermogravimetry (TG) curve was recorded on a Netzschsta409P (NETZSCH-Gerätebau GmbH, Germany) with a heating rate of 10 °C/min at N₂ atmosphere. UV–visible absorption spectra were recorded on a UV-2550 spectrophotometer (Shimadzu Co., Japan). Electrochemical measurements of the copolymer films were performed in a 0.1 mol/L tetrabutylammonium perchlorate (TBAP)–acetonitrile (CH₃CN) solution using a glass–carbon electrode at a scan rate of 50 mV/s against a calomel reference electrode with a CHI610A electrochemical workstation (Shanghai, China).

2,7-Dibromo-9,9-bis(4-hydroxyphenyl)fluorene²⁸ (1), 4-(4-(diphenylamino)-phenyl)-7-(2-(1-bromohexylthiophene)-5-yl)-2,1,3-benzothiadiazole²⁹ (GX-Br) (2), and 4,7-bis(5-bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazole³⁰ were prepared following published procedures.

Fabrication and Characterization of Photovoltaic Cells

The BHJ PSCs were made using assembled solar cell structure glass/indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) (PEDOT) : poly(styrenesulfonic acid) (PSS) (40 nm)/copolymers : PC₇₁BM/LiF (0.6 nm)/Al (100 nm). The ITO-covered glass substrates were cleaned by detergent and acetone. PEDOT : PSS was spin-cast onto the cleaned substrate and heated for 10 min at 120 °C. The substrates were then moved into a glove box filled with N₂. The active layers were spin-coated from chloroform (CF) solutions on top of the PEDOT : PSS-coated ITO glass substrates. The substrates were transferred into a vacuum chamber where 0.6 nm LiF and 100 nm Al were thermally evaporated at a pressure less than 4×10^{-4} Pa. The active areas of all PSCs were 4.5 mm², as defined by the overlap between two electrodes measured by optical microscopy. Current density–voltage (J – V) curves were measured using a Keithley 2400 Source Meter under illumination of AM 1.5 filtered light, with an intensity of 100 mW/cm² (solar simulator Model SS-50A, Photo Emission Tech., Camarillo, California). External quantum efficiency (EQE) spectra were obtained using a Newport Merlin lock-in, with the solar cells illuminated with chopped monochromatic light through the ITO side.

Synthesis

2,7-Dibromo-9,9-bis(7-(4-(diphenylamino)phenyl)-2,1,3-benzothiadiazole-4-(2-thiophene-5-hexyloxy))phenyl fluorene (Monomer 3)²⁷. In a three-necked flask, anhydrous K₂CO₃ (0.996 g, 7 mmol) and 18-crown-6 (0.044 g, 0.168 mmol) were added to a solution of 2,7-dibromo-9,9-bis(4-hydroxyphenyl)fluorene (0.356 g, 0.7 mmol) and 4-(4-(diphenylamino)phenyl)-7-(2-(1-bromohexyl-thiophene)-5-yl)-2,1,3-benzothiadiazole (1.048 g,

1.68 mmol) in acetone (40 mL) under a N₂ atmosphere. The mixture was refluxed for 24 h, and then cooled to room temperature and extracted with dichloromethane. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel, petroleum ether/chloroform (1 : 1)) and recrystallized from ethanol to yield a red needle-like solid title product (0.993 g, 89%). M.p.: 127–129 °C. Fast atom bombardment mass spectrometry (FAB-MS): 1596. ¹H-NMR (400 MHz, CDCl₃, δ): 7.94 (d, 2H), 7.88 (dd, 4H), 7.84 (dd, 2H), 7.68 (dd, 2H), 7.57 (dd, 2H), 7.47 (s, 2H), 7.45 (dd, 2H), 7.32–7.28 (m, 8H), 7.22–7.18 (m, 12H), 7.07 (m, 4H), 7.06 (dd, 4H), 6.88 (d, 2H), 6.78 (dd, 4H), 3.92 (t, 4H), 2.90 (t, 4H), and 1.78–1.26 (m, 16H). ¹³C-NMR (100 MHz, CDCl₃, δ): 158.14, 153.89, 153.68, 152.79, 147.92, 147.41, 147.37, 137.81, 136.91, 136.27, 131.71, 130.81, 130.71, 129.82, 129.34, 129.27, 129.22, 128.97, 127.32, 127.25, 126.03, 125.25, 124.85, 123.28, 122.88, 121.78, 121.52, 114.31, 67.76, 64.33, 31.51, 30.18, 29.14, 28.81, and 25.83. Anal. calcd for C₉₃H₇₄O₂N₆S₄Br₂: C 70.01, H 4.64, N 5.27, S 8.03; found: C 70.15, H 4.82, N 5.14, S 7.96.

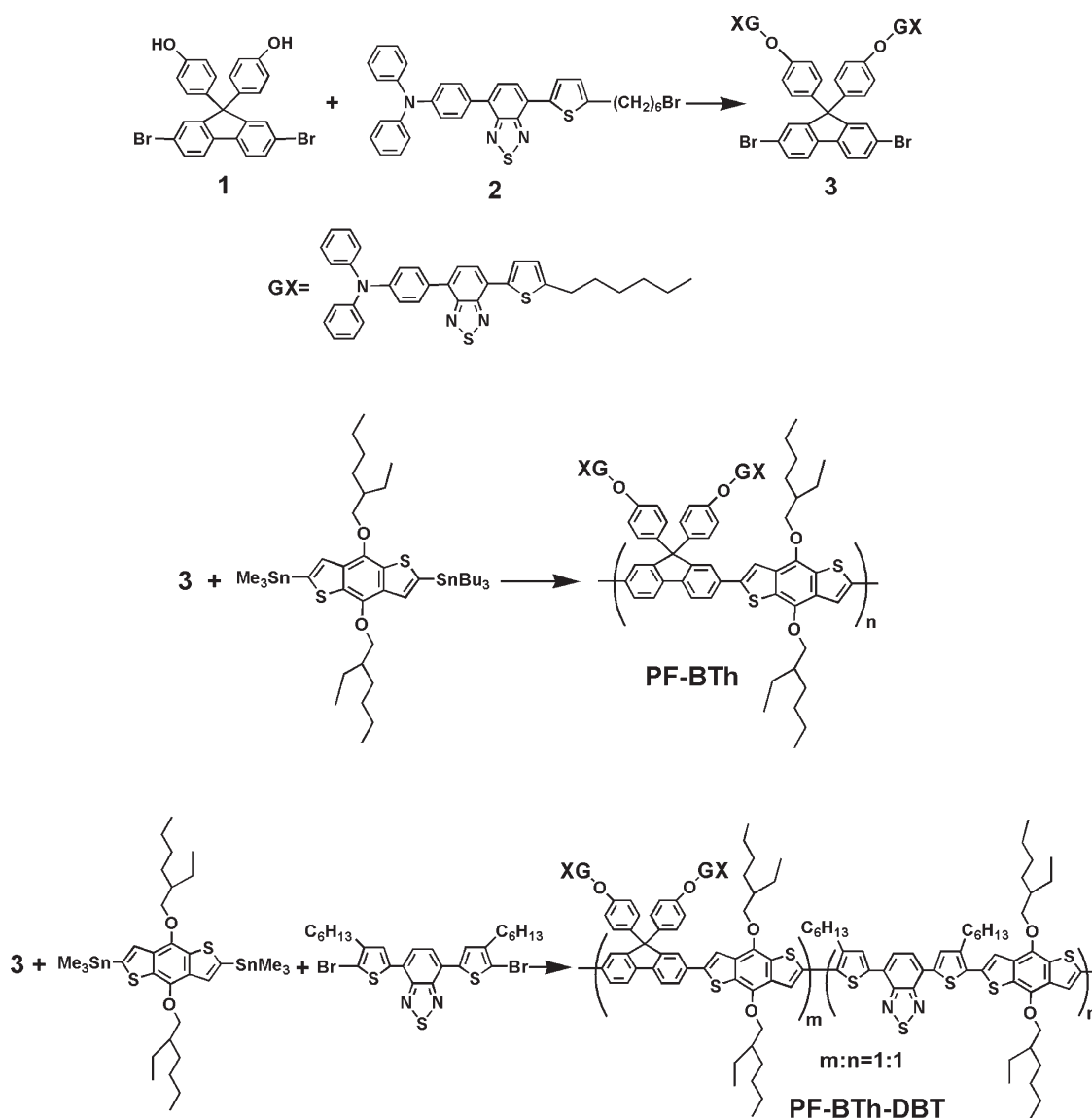
9,9-Bis(7-(4-(diphenylamino)phenyl)-2,1,3-benzothiadiazole-4-(2-thiophene-5-hexyloxy))phenylfluorene-co-4,8-bis(2-ethyl-hexyloxy)benzo[1,2-b;4,5-b']di-thiophene copolymer (PF-BTh). Synthesis of the copolymer was carried out using palladium-catalyzed Stille couplings. Under a nitrogen atmosphere, monomer 3 (0.399 g, 0.25 mmol), 2,6-bis(trimethyltin)-4,8-bis(2-ethyl-hexyloxy)benzo[1,2-b;4,5-b']dithiophene (0.193 g, 0.25 mmol), toluene (5 mL), and Pd(PPh₃)₄ (28.9 mg) were sequentially added to a 50 mL three-necked flask. The reaction mixture was warmed to 90 °C and stirred for 48 h. A small amount of bromobenzene and 4-(hexyl-2-thienyl)stannane were added respectively to end-cap the polymer chain. The reaction mixture was cooled to room temperature and poured into methanol. The resulting solid was filtered and extracted with acetone for 24 h to remove oligomers and catalyst residues and obtained a black-brown solid (yield, 67%). ¹H-NMR (400 MHz, CDCl₃, δ): 7.87–7.89 (m, 2H), 7.83–7.84 (d, 4H), 7.76–7.78 (d, 4H), 7.62 (s, 4H), 7.19 (s, 8H), 7.06 (s, 4H), 6.83 (s, 4H), 4.20 (s, 4H), 3.92 (s, 4H), 2.90–2.93 (m, 4H), 1.27–1.86 (m, 34H), 1.05 (s, 6H), 0.93 (s, 6H).

9,9-Bis(7-(4-(diphenylamino)phenyl)-2,1,3-benzothiadiazole-4-(2-thiophene-5-hexyloxy))phenylfluorene-co-4,8-bis(2-ethyl-hexyloxy)benzo[1,2-b;4,5-b']dithiophene-co-4,7-bis(4-hexyl-2-thienyl)-2,1,3-benzothiadiazole copolymer (PF-BTh-DBT). With the similar synthetic method as PF-BTh with 4,7-bis(5-bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazole (0.0785 g, 0.125 mmol) (2) and monomer 3 (0.1995 g, 0.125 mmol), instead of monomer 3 (0.25 mmol), afford a reddish purple solid. (Yield, 85%). ¹H-NMR (400 MHz, CDCl₃, δ): 8.06 (s, 2H), 7.84–7.88 (m, 10H), 7.76–7.78 (d, 6H), 7.61 (s, 6H), 7.18 (s, 12H), 7.05 (s, 4H), 6.84 (s, 8H), 4.21 (s, 8H), 3.92 (s, 4H), 2.87 (s, 8H), 1.26–1.76 (m, 34H), 1.07 (s, 12H), 0.93 (s, 12H).

RESULTS AND DISCUSSION

Synthesis and Thermal Properties

Scheme 1 shows the synthetic routes to the monomer and copolymers. Monomer 3 was synthesized from 2,7-dibromo-9,9-



Scheme 1. Synthetic routes of the monomer and copolymers.

bis(4-hydroxyphenyl)fluorene and 4-(4-(diphenylamino)phenyl)-7-(2-(1-bromohexylthiophene)-5-yl)-2,1,3-benzothiadiazole (GX-Br) (2) using Williamson reaction in a high yield of 89%, in which a thiophene-benzothiadiazole-triphenylamine (Th-BT-TPA) unit was attached to 2,7-dibromofluorene with alkyl phenyl spacers. The copolymers can be obtained from 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene, copolymerized with monomer 3 and/or 4,7-bis(5-bromo-4-hexyl-2-thienyl)-2,1,3-benzothiadiazole by Stille reaction, respectively. At the end of polymerization, 4-(hexyl-2-thienyl)stannane and bromobenzene were added to remove the bromine and tributyl stannane end groups, respectively. The molecular weights of the copolymers are relatively low because monomer 3 has a large steric hindrance. The polydispersity indexes (M_w/M_n) of the copolymers range from 2.0 to 2.6 (Table I), which is consistent with the polycondensation reaction results. The two copolymers have good solubility in

common organic solvents such as chloroform, tetrahydrofuran, and toluene. The thermal stability of the copolymers was investigated by thermogravimetric analysis (TGA), and the corresponding results are summarized in Figure 1 and Table I. As shown in Figure 1, the TGA curves reveal degradation temperatures (T_d) of 5% weight loss of 313°C for PF-BTh and 320°C for PF-BTh-DBT. Therefore, the copolymers have excellent thermal stability.

Table I. Molecular Weights, Weight Distribution Coefficient (PDI), and Thermal Properties of the Copolymers

Copolymers	M_n (kg/mol)	M_w (kg/mol)	PDI	T_d (5% loss) (°C)
PF-BTh	16.4	33.0	2.0	313
PF-BTh-DBT	17.9	46.9	2.6	320

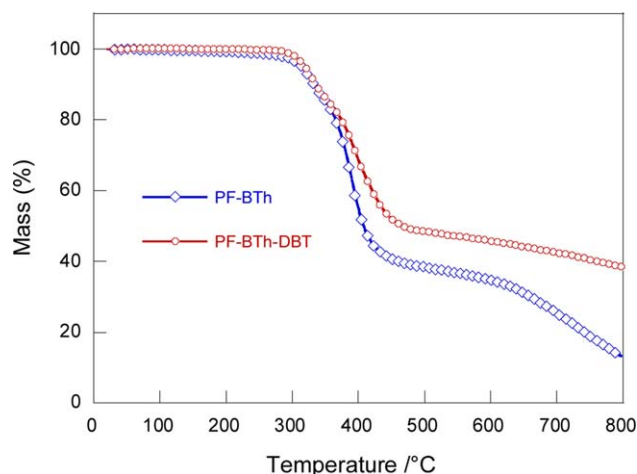


Figure 1. TG curves of copolymers at scan rate of 20 °C/min under nitrogen atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Photophysical and Electrochemical Properties

The UV-vis absorption spectra of copolymers in dilute chloroform solution (concentration 10^{-5} mol/L) and in thin film are depicted in Figure 2. The absorption spectrum of the monomer 3 is also depicted in Figure 2 to compare the absorption spectra of the copolymers. The absorption spectrum of the fluorene monomer with D-A chromophores on the C9 site in dilute solution shows two absorption peaks at 322 and 468 nm, which can be assigned to the $\pi-\pi^*$ absorption of the molecule and the intramolecular charge transfer from the electron-donating unit (triphenylamine) to the electron-accepting unit (benzothiadiazole). The copolymer PF-BTh displays a similar absorption spectrum in the solution as that of monomer 3 [Figure 2(a)]. Except for the two absorption peaks at 317 and 449 nm, the copolymer PF-BTh-DBT has a weak absorption band at 500 nm to 650 nm, which can be attributed to the intramolecular charge transfer from the electron-donating units (fluorene and 4,8-bis-(2-ethylhexyloxy)benzo[1,2-b;4,5-b']dithiophene) to the electron-accepting units (DBT) on the polymer main chain. The molar absorption coefficient of PF-BTh for the visible absorption band at the peak of 463 nm calculated from Beer's law equation is 2.77×10^4 mol/(L cm), and the molar absorption coefficient of PF-BTh-DBT is 6.16×10^4 mol/(L cm) at the peak of 449 nm. The absorption peaks of the copolymers in the film are consistent with that in CHCl_3 solution, and the absorption band of copolymer PF-BTh-DBT at 550 nm to 700 nm is stronger than that in CHCl_3 solution, demonstrating that a strong interaction among the copolymers in the film. The absorption edge of the PF-BTh and PF-BTh-DBT films are at 561 and 709 nm, respectively,

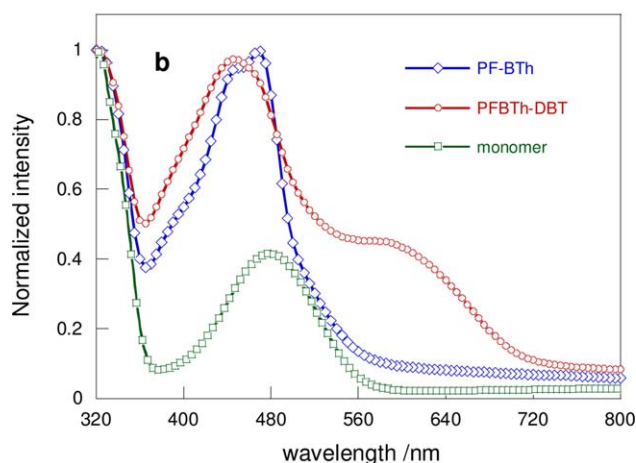
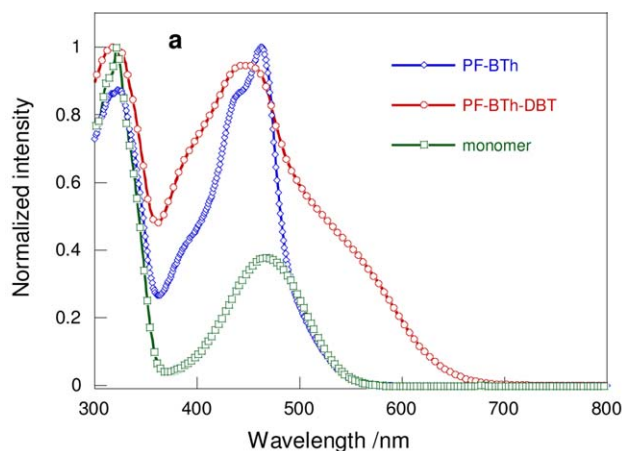


Figure 2. UV-vis absorption spectra in CHCl_3 of 10^{-5} mol/L (a) and in film (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

corresponding to the energy gap of 2.21 and 1.75 eV, respectively. The absorption spectrum of the copolymer with D-A structure both on the polymer main and side chains is broader and stronger than that of the copolymer with only a pendent D-A structure, demonstrating that the introduction of D-A chromophores in the polymer side and main chains can further tune the absorption and band gap of the polymer.

Cyclic voltammetry was used to investigate the electrochemical redox behaviors of the copolymers and to determine their highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. The results of the electrochemical measurements and calculated energy levels of the copolymers are listed in Table II. The oxidation potentials

Table II. Optical and Electrochemical Properties of the Copolymers

Copolymers	ϵ ($\times 10^4$ mol/L cm)	λ_{film} (nm)	Optical band gap ^a (eV)	V_{ox} (V)	E_{HOMO} (eV)	E_{LUMO}^b (eV)
PF-BTh	2.77	320, 470	2.21	1.05	-5.45	-3.24
PF-BTh-DBT	6.16	320, 445	1.80	0.95	-5.35	-3.55

^a Estimated from the onset wavelength of optical absorption in the film.

^b Calculated from the HOMO level and optical band gap.

derived from the onsets of electrochemical p-doping, namely, the HOMO levels, were calculated according to an empirical formula ($E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.4)$ (eV)).³¹ The LUMO levels were estimated from the optical band gap and the HOMO levels. The oxidation onset of PF-BTh was exhibited at 1.05 V, and that of PF-BTh-DBT was at 0.95 V. The n-doping processes were unrecorded after many trials. The copolymers exhibit relatively low HOMO energy levels (-5.45 eV for PF-BTh and -5.35 eV for PF-BTh-DBT), which are beneficial for obtaining high V_{oc} . The LUMO levels are located at -3.24 eV for PF-BTh and -3.29 eV for PF-BTh-DBT, which is consistent with the LUMO energy level of an ideal donor for the acceptor of PCBM ([6,6]-phenyl- C_{71} -butyric acid methyl ester, $E_{\text{LUMO}} = -4.3$ eV). The HOMO energy levels of the copolymers are determined by the conjugated main chains and the pendant acceptor units have less effects on the HOMO energy levels of the copolymers.^{32–37} The HOMO energy level of PF-BTh-DBT is higher than that of PF-BTh because PF-BTh-DBT has lower oxidation onset due to the electron acceptor benzothiadiazole unit in the main chain, which is consistent with the results reported

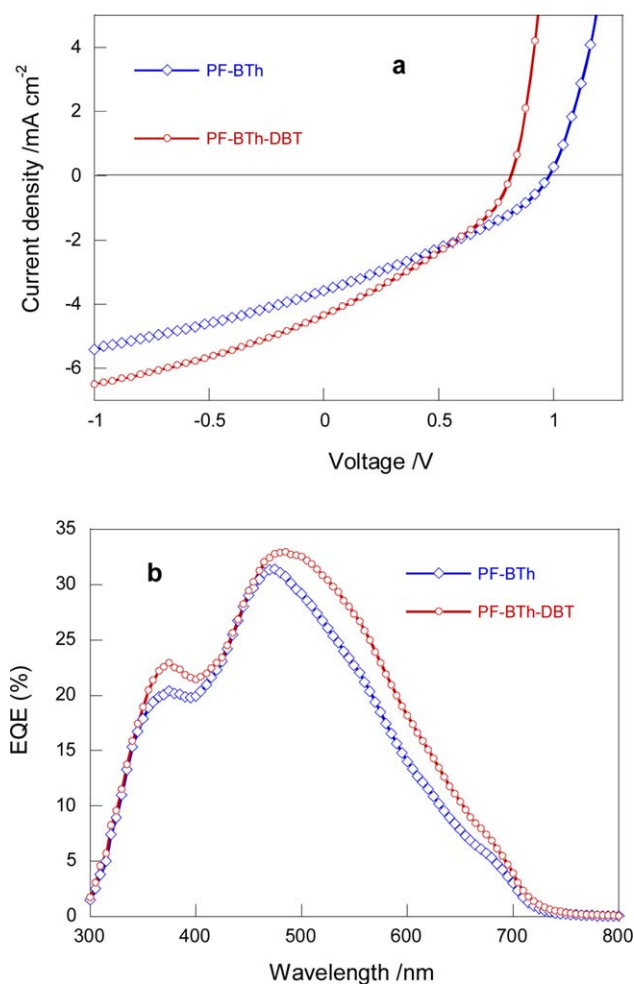


Figure 3. (a) J - V characteristics; (b) EQE spectra of assembled solar cells with a structure of ITO/PEDOT : PSS/copolymer : PC₇₁BM (1 : 3)/LiF/Al under the illumination of an AM 1.5 G solar simulator (100 mW/cm²). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Assembled Solar Cell Performances of the Copolymers

Copolymers	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	PCE (%)
PF-BTh	3.84	0.98	0.37	1.40
PF-BTh-DBT	4.80	0.84	0.39	1.60

in the literature.^{32–37} The LUMO energy level of PF-BTh-DBT is lower than that of PF-BTh which may be the effects of D-A units both on the main chain and side chains.

Photovoltaic Properties

BHJ solar cells with a typical configuration of ITO/PEDOT : PSS/copolymers : PC₇₁BM (1 : 3)/LiF/Al were fabricated and tested under simulated AM1.5G illumination (100 mW/cm²). Figure 3 shows the current density (J)-voltage (V) curves and EQE spectra of copolymers/PC₇₁BM BHJ solar cells without annealing and other solvent additives. The corresponding values are summarized in Table III. As shown in Figure 3(a) and Table III, the assembled solar cells fabricated with PF-BTh/PC₇₁BM exhibit a PCE of 1.4% with short circuit current density (J_{sc}) = 3.84 mA/cm², fill factor (FF) = 0.37, and open circuit voltage (V_{oc}) = 0.98 V. Those fabricated with PF-BTh-DBT/PC₇₁BM exhibit a PCE of 1.6% with J_{sc} = 4.8 mA/cm², FF = 0.39, and V_{oc} = 0.84 V, respectively. To show the photo response of assembled solar cells at different wavelengths, corresponding EQEs of the solar cells were measured under illumination of monochromatic light. For all of the blends, broad photo responses were observed from 300 nm to 700 nm. The maximum EQEs of the solar cells based on PF-BTh-DBT/PC₇₁BM is 32.9% at 485 nm. PF-BTh-DBT with D-A structure both on the main and side chains has higher J_{sc} and EQE in accordance to its broader and stronger absorption. The V_{oc} of the PSCs is correlated with the difference of the LUMO of the electron acceptor and the HOMO of the electron donor; theoretically, lower polymer HOMOs produce higher V_{oc} values.³⁸ The V_{oc} of PF-BTh-DBT is slightly lower than that of PF-BTh, which is consistent with its higher HOMO level. The assembled solar cell based on the copolymer PF-BTh-DBT has relatively low J_{sc} which is consistent with the weak absorption of the copolymer PF-BTh-DBT in the 500–700 nm and has low FF due to the relatively low molecular weight of the copolymer, which leads to the relatively low PCE. The absorption spectrum of the resulting copolymers with D-A structure both on the polymer side and main chains could be easily modulated by adjusting the donors and acceptors on the main chain and the side chains. The optimization of the assembled solar cell structure and the structural design of the copolymers are in progress.

CONCLUSIONS

Two novel narrow band gap polyfluorene copolymers with D-A structure on the polymer side and/or main chains were synthesized through Pd-catalyzed Stille coupling reactions. The copolymer PF-BTh-DBT with D-A structure both on the polymer side and main chains has broader and stronger absorption and narrower band gap and better assembled solar cell performance than copolymer PF-BTh with D-A structure only on the polymer side chain. The PCE achieved in the assembled solar cell

configuration ITO/PEDT/PF-BTh-DBT : PC₇₁BM (1 : 3)/LiF/Al was 1.6%, with an open-circuit voltage of 0.84 V without annealing and additives. Further optimization of the molecule promises highly efficient harvesting because of the intramolecular charge transfer in the main and side chains.

ACKNOWLEDGMENTS

This research was supported by the Natural Science Foundation of China (No 50803021) and Exhibition Base of Production, Study & Research on New Polymer Materials and Postgraduate Students' Innovation Training of Guangdong Higher Education Institutes (cgzhzd1007) and Combination Project of Guangdong Province & the Ministry Education of China (2011B090400423).

REFERENCES

- Zhen, H. Y.; Li, K.; Huang, Z. Y.; Tang, Z.; Wu, R. M.; Li, G. L.; Liu, X.; Zhang, F. L. *Appl. Phys. Lett.* **2012**, *100*, 213901.
- Yu, G.; Gao, J.; Hummelen, J. C.; Wudl, F.; Heeger, A. J. *Science* **1995**, *270*, 1789.
- Park, S. H.; Roy, A.; Beaupre, S.; Cho, S.; Coates, N.; Moon, J. S.; Moses, D.; Leclerc, M.; Lee, K.; Heeger, A. J. *Nat. Photonics* **2009**, *3*, 297.
- Stalder, R.; Grand, C.; Subbiah, J.; So, F.; Reynolds, J. R. *Polym. Chem.* **2012**, *3*, 89.
- Zhou, E.; Cong, J.; Hashimoto, K.; Tajima, K. *Macromolecules* **2013**, *46*, 763.
- He, Z.; Zhong, C.; Su, S.; Xu, M.; Wu, H.; Cao, Y. *Nat. Photonics* **2012**, *6*, 591.
- Ding, P.; Chu, C. C.; Zou, Y.; Xiao, D.; Pan, C.; Hsu, C. S. *J. Appl. Polym. Sci.* **2012**, *123*, 99.
- Wang, H.; Cheng, P.; Liu, Y.; Chen, J.; Zhan, X.; Hu, W.; Shuai, Z.; Li, Y.; Zhu, D. *J. Mater. Chem.* **2012**, *22*, 3432.
- Wu, J. S.; Cheng, Y. J.; Dubosc, M.; Hsieh, C. H.; Chang, C. Y.; Hsu, C. S. *Chem. Commun.* **2010**, *46*, 3259.
- Wang, M.; Li, C.; Lv, A.; Wang, Z.; Bo, Z.; Zhang, F. *Polymer* **2012**, *53*, 324.
- Liu, H.; Qu, B.; Chen, J.; Cong, Z.; An, Z.; Gao, C. X.; Xiao, L.; Chen, Z.; Gong, Q. *J. Appl. Polym. Sci.* **2013**, *128*, 3250.
- Bronstein, H.; Frost, J. M.; Hadipour, A.; Kim, Y.; Nielsen, C. B.; Ashraf, R. S.; Rand, B. P.; Watkins, S.; McCulloch, I. *Chem. Mater.* **2013**, *25*, 277.
- Burkhart, B.; Khlyabich, P. P.; Thompson, B. C. *ACS Macro Lett.* **2012**, *1*, 660.
- Piyakulawat, P.; Keawprajak, A.; Jirakitmongkon, K.; Hanusch, M.; Wlosnewski, J.; Asawapirom, U. *Solar Energy Mater. Solar Cells* **2011**, *95*, 2167.
- Zhang, Z.; Peng, B.; Liu, B.; Pan, C.; Li, Y.; He, Y.; Zhou, K.; Zou, Y. *Polym. Chem.* **2010**, *1*, 1441.
- Zhang, Z. G.; Fan, H.; Min, J.; Zhang, S.; Zhang, J.; Zhang, M.; Guo, X.; Zhan, X.; Li, Y. *Polym. Chem.* **2011**, *2*, 1678.
- Duan, C.; Cai, W.; Huang, F.; Zhang, J.; Wang, M.; Yang, T.; Zhong, C.; Gong, X.; Cao, Y. *Macromolecules* **2010**, *43*, 5262.
- Gupta, A.; Watkins, S. E.; Scully, A. D.; Singh, T. B.; Wilson, G. J.; Rozanski, L. J.; Evans, R. A. *Synth. Met.* **2011**, *161*, 856.
- Sharma, G. D.; Mikroyannidis, J. A.; Singh, S. P. *Org. Electron.* **2012**, *13*, 252.
- Liu, J.; Choi, H.; Kim, J. Y.; Bailey, C.; Durstock, M.; Dai, L. *Adv. Mater.* **2012**, *24*, 538.
- Baran, D.; Pasker, F. M.; Le Blanc, S.; Schnakenburg, G.; Ameri, T.; Hoger, S.; Brabec, C. J. *J. Polym. Sci. Part A: Polym. Chem.* **2013**, *51*, 987.
- Yamamoto, N. A. D.; Lavery, L. L.; Nowacki, B. F.; Grova, I. R.; Whiting, G. L.; Krusor, B.; de Azevedo, E. R.; Akcelrud, L.; Arias, A. C.; Roman, L. S. *J. Phys. Chem.* **2012**, *116*, 18641.
- Kaya, E.; Apaydin, D. H.; Yildiz, D. E.; Toppare, L.; Cirpan, A. *Solar Energy Mater. Solar Cells* **2012**, *99*, 321.
- Zhang, Z. G.; Zhang, K. L.; Liu, G.; Zhu, C. X.; Neoh, K. G.; Kang, E. T. *Macromolecules* **2009**, *42*, 3104.
- Mori, D.; Benten, H.; Ohkita, H.; Ito, S.; Miyake, K. *ACS Appl. Mater. Interfaces* **2012**, *4*, 3325.
- Wen, S.; Pei, J.; Zhou, Y.; Li, P.; Xue, L.; Li, Y.; Xu, B.; Tian, W. *Macromolecules* **2009**, *42*, 4977.
- Hou, Q.; Xu, X.; Guo, T.; Zeng, X.; Luo, S.; Yang, L. *Eur. Polym. J.* **2010**, *46*, 2365.
- Chou, C. H.; Shu, C. F. *Macromolecules* **2002**, *35*, 9673.
- Liu, J.; Chen, L.; Shao, S. Y.; Xie, Z. Y.; Cheng, Y. X.; Geng, Y. H. *J. Mater. Chem.* **2008**, *18*, 319.
- Kitamura, C.; Tanaka, S.; Yamashita, Y. *Chem. Mater.* **1996**, *8*, 570.
- deLeeuw, D. M.; Simenon, M. M. J.; Brown, A. R.; Einerhand, R. E. F. *Synth. Met.* **1997**, *87*, 53.
- Duan, C.; Hu, X.; Chen, K.-S.; Yip, H.-L.; Li, W.; Huang, F.; Jen, A. K.-Y.; Cao, Y. *Solar Energy Mater. Solar Cells* **2012**, *97*, 50.
- Li, S.; He, Z.; Zhong, A.; Yu, J.; Wu, H.; Zhou, Y.; Chen, S.; Zhong, C.; Qin, J.; Li, Z. *Polymer* **2011**, *52*, 5302.
- Cheng, Y.-J.; Hung, L.-C.; Cao, F.-Y.; Kao, W.-S.; Chang, C.-Y.; Hsu, C.-S. *J. Polym. Sci. Part A: Polym. Chem.* **2011**, *49*, 1791.
- Jo, J. W.; Kim, S. S.; Jo, W. H. *Org. Electron.* **2012**, *13*, 1322.
- El-Shehawey, A. A.; Abdo, N. I.; El-Barbary, A. A.; Lee, J.-S. *Eur. J. Org. Chem.* **2011**, 4841.
- Chen, C.-H.; Hsieh, C.-H.; Dubosc, M.; Cheng, Y.-J.; Hsu, C.-S. *Macromolecules* **2010**, *43*, 697.
- Brabec, C. J.; Cravino, A.; Meissner, D.; Sariciftci, N. S.; Fromherz, T.; Rispen, M. T. *Adv. Funct. Mater.* **2001**, *11*, 374.