

Synthesis and Characterization of a Thiophene-Benzothiadiazole Copolymer

Ji-Cheng Li, Se-Jung Kim, Soo-Hyoung Lee, and Youn-Sik Lee*

Division of Chemical Engineering, Nanomaterials Processing Research Center, Chonbuk National University, Chonbuk 561-756, Korea

Kyukwan Zong

Division of Science Education, Chonbuk National University, Chonbuk 561-756, Korea

Soo-Chang Yu

Department of Chemistry, Kunsan National University, Chonbuk 573-701, Korea

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Introduction

In polymer-based photovoltaic devices, a blend of an electron-donor (*p*-type conjugated polymer) and an electron-acceptor (*n*-type polymer or [6,6]-phenyl-C₆₁-butyric acid methyl ester, PCBM) is positioned as a photoactive layer between two electrodes,^{1,2} representing the most widely used configuration of polymer-based photovoltaic devices and referred to as bulk heterojunction devices. Due to the low cost of the solution fabrication process, and the light weight, large area, and flexible panels, as well as their potential contribution to clean and renewable energy, increasing attention has been attracted by polymer-based, bulk, heterojunction, photovoltaic devices since their discovery.^{3,4}

Of the various types of polymer-based photovoltaic devices, the most efficient photovoltaic devices, with power conversion efficiency (PCE) of about 3-4%, were fabricated using a blend of poly(3-hexylthiophene) (P3HT) and PCBM as the active layer.^{5,6} Soon after the initial reports, the P3HT/PCBM-based photovoltaic devices were optimized to achieve PCEs approaching 5%.⁷⁻⁹ For further improvements in polymer-based photovoltaic devices, new *p*-type polymers with smaller band gaps, which absorb light more broadly and better match solar radiation, should be developed and HOMO/LUMO energy levels and charge mobilities of the *p*-type materials should be optimized to achieve high photovoltaic performances, as proposed by Scharber *et al.*¹⁰

It has been reported that the coupling between an elec-

tron-rich unit with an electron-deficient one in a polymer backbone can result in an effective expansion of the light absorption range of these substances. 2,1,3-Benzothiadiazole (BT) is a well-known electron-deficient molecule^{11,12} that can be conjugated with an electron-rich molecule to form oligomers or polymers with small energy band gaps. Several different polymers of this type have been synthesized for applications in light emitting diodes, solar cells,¹³ light-harvesting, and other optical or electronic functional devices.¹⁴ For example, Heeger and co-workers used a polymer composed of alternating cyclopentadithiophene and dibenzothiadiazole units in the fabrication of photovoltaic cells, achieving a PCE of 5%.¹⁵ Carbazole derivatives have received much attention as optical materials as they have a conjugated planar structure and a good hole transporting property as well as electron-donating property¹⁶ and when carbazole units are employed in the fabrication of photovoltaic devices, PCEs reaching to 3.6% have been achieved.¹⁷

We synthesized an alternating conjugated polymer (PHT₃BT), consisting of three 3-hexylthiophene (3HT) and a BT units, and measured their optical and electrochemical properties. This paper describes details on the characteristics of the polymer.

Experimental

Materials. 3-Hexylthiophene (3HT), 2,1,3-benzothiadiazole (BT), *n*-butyllithium (2.5 M in hexane), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, tributyltin chloride, tetrakis(triphenylphosphine)palladium(0), tetrahydrofuran (THF), *N*-bromosuccinimide (NBS), potassium carbonate, bromine, hydrogen bromide, toluene, and chloroform were purchased from Aldrich and used without further purification.

2-Bromo-3-hexylthiophene (1): 3HT (2.02 g, 12.0 mmol) and NBS (2.16 g, 12.0 mmol) were dissolved in chloroform (50 mL), and the resulting solution vigorously stirred at 50 °C for 5 h under nitrogen, cooled, washed with water, and the organic phase dried over anhydrous magnesium sulfate. Further purification was performed using flash silica gel column chromatography (hexane) to give a colorless oil (2.67 g, 90% yield). ¹H NMR (CDCl₃, δ/ppm): 7.15 (d, 1 H), 6.77 (d, 1 H), 2.55 (t, 2 H), 1.54 (m, 2 H), 1.29 (m, 6 H), and 0.86 (t, 3 H).

2,5-Dibromo-3-hexylthiophene (2): 3HT (1.95 g, 11.6 mmol) and NBS (4.49 g, 24.7 mmol) were dissolved in chloroform/glacial acetic acid (1/1, v/v) (70 mL) and the resulting solution vigorously stirred during reflux for 5 h under nitrogen, cooled, washed with water, and the organic phase dried over anhydrous magnesium sulfate. Further purification as above produced a colorless oil (3.51 g, 93% yield). ¹H NMR (CDCl₃, δ/ppm): 6.52 (s, 1H), 2.57 (t, 2H), 1.59 (m, 2H), 1.29 (m,

*Corresponding Author. E-mail: yosklear@chonbuk.ac.kr

6H), and 0.96 (t, 3H).

2,5-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-3-hexylthiophene (3): *n*-Butyllithium (3.8 mL of a 2.5 M solution in hexane, 9.5 mmol) was slowly added to a solution of 2,5-dibromo-3-hexylthiophene (1.30 g, 4.0 mmol) in THF (30 mL) at -78 °C, stirred for 2 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.4 mL, 11.6 mmol) was promptly injected into the solution, which was then stirred for 1 h at -78 °C and allowed to stand overnight at room temperature under nitrogen. Next, the mixture was poured into ice-water, extracted with dichloromethane, dried over anhydrous magnesium sulfate, concentrated, and purified by flash silica gel column chromatography (ethyl acetate/hexane, 1/10, v/v) to give a colorless viscous oil (0.84 g, 50% yield). ¹H NMR (CDCl₃, δ/ppm): 7.49 (s, 1H), 2.85 (t, 2H), 1.57 (m, 2H), 1.34 ~1.28 (m, 30H), and 0.87 (t, 3H).

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane)-4-hexylthiophene (4): *n*-Butyllithium (4.0 mL of a 2.5 M solution in hexane, 10 mmol) was slowly added to a solution of 3HT (1.68 g, 10 mmol) in THF (40 mL) at -78 °C, stirred for 2 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.2 mL, 10.6 mmol) was promptly injected into the solution, stirred for 1 h at -78 °C, and allowed to stand overnight at room temperature under nitrogen. The mixture was poured into ice-water, extracted with dichloromethane, dried over anhydrous magnesium sulfate, concentrated, and purified by flash silica gel column chromatography (ethyl acetate/hexane, 1/10, v/v), to give a colorless viscous oil (2.62 g, 89% yield). ¹H NMR (CDCl₃, δ/ppm): 7.47 (s, 1H), 7.21 (s, 1H), 2.62 (t, 2H), 1.62-1.49 (m, 2H), 1.34 (s, 12H), 1.28-1.18 (m, 6H), and 0.89-0.86 (t, 3H).

4,7-Dibromo-2,1,3-benzothiadiazole (5): Bromine (6.40 g, 40 mmol) was slowly added to a mixture of BT (2.72 g, 20 mmol) and 40 mL of 47% aqueous HBr was refluxed for 2 h, yielding a needle-like precipitate, which was isolated by hot filtration. The supernatant was cooled to room temperature, forming a needle-like precipitate, which was also isolated by filtration, combined with the first precipitate, washed with water, and recrystallized from ethyl acetate to give compound **5** as white needle-shaped crystals (4.82 g, 82% yield). ¹H NMR (CDCl₃, 400 MHz, δ/ppm): 7.71 (s, 2H).

4,7-Bis(4-hexylthiophene-2-yl)benzo[c][1,2,5]thiadiazole (6): Compounds **5** (0.59 g, 2 mmol) and **1** (1.76 g, 6 mmol), and Pd(PPh₃)₄ (138 mg, 6 mol %) were dissolved in toluene (40 mL), followed by the addition of aqueous potassium carbonate (2.0 M, 40 mL), and the reaction mixture vigorously stirred at 90 °C for 24 h under nitrogen, cooled, extracted with toluene, washed with water, and the organic phase dried over anhydrous magnesium sulfate. Further purification was performed using flash silica gel column chromatography (chloroform/hexane, 1/4, v/v) to give a bright orange solid (0.78 g, 83% yield). ¹H NMR (CDCl₃, δ/ppm): 7.97 (d, 2H), 7.83 (s, 2H), 7.04 (s, 2H), 2.69 (t, 4H), 1.70 (m, 4H), 1.35 (m, 12H), and 0.90 (t, 6H).

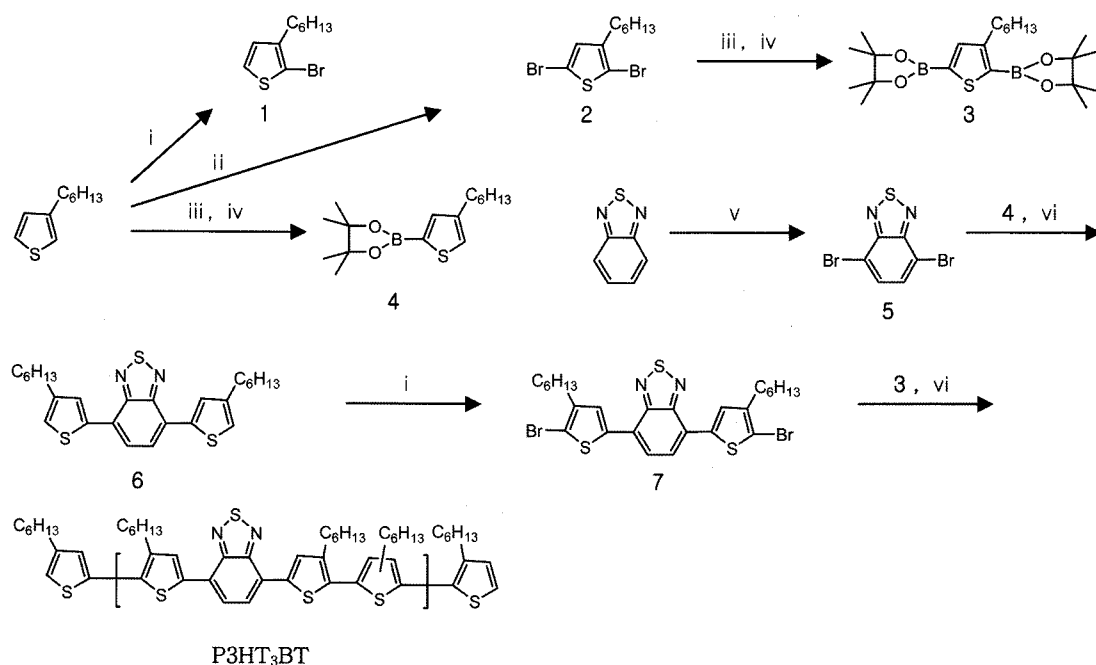
4,7-Bis(5-bromo-4-hexylthiophene-2-yl)benzo[c][1,2,5]thiadiazole (7): Compound **6** (0.45 g, 0.96 mmol) and NBS (0.35 g, 2 mmol) were dissolved in chloroform (30 mL), vigorously stirred at 50 °C for 5 h under nitrogen, cooled, extracted with chloroform, washed with water, and the organic phase dried over magnesium sulfate. Further purification was performed using flash silica gel column chromatography (chloroform/hexane, 1/4, v/v) to give an orange solid (0.51 g, 85% yield). ¹H NMR (CDCl₃, δ/ppm): 7.97 (d, 2H), 7.83 (s, 2H), 2.66 (t, 4H), 1.66 (m, 4H), 1.35 (m, 12H), and 0.91 (t, 6H).

P3HT₃BT: Compounds **7** (0.625 g, 1.0 mmol) and **3** (0.420 g, 1.0 mmol), and Pd(PPh₃)₄ (69 mg, 6 mol%) were dissolved in toluene (30 mL), followed by the addition of aqueous potassium carbonate (2 M, 30 mL), stirred at 90 °C for 48 h under nitrogen, and, for end-capping, compound **1** was added and allowed to react for 6 h, followed by the addition of compound **4** and a further 6 h of reaction time. After cooling, the reaction mixture was poured slowly into methanol, the resulting precipitate collected by filtration, dissolved in chloroform, poured into methanol, and the resulting precipitate recovered to obtain P3HT₃BT (0.48 g, 66% yield).

Measurements. The ¹H NMR spectra were recorded using a JEOL FT-NMR (400 MHz) spectrometer, the UV-visible spectra obtained using a Shimadzu UV-2550 spectrophotometer, and cyclic voltammetry (CV) measurements performed on a Bioanalytical System 100B, using a solution of tetrabutylammonium tetrafluoroborate (*n*Bu₄NBF₄) (0.10 M) in chloroform in an argon atmosphere at a scan rate of 50 mV/s at room temperature. A platinum wire and Ag/Ag⁺ were used as a counterelectrode and a reference electrode, respectively. Photoluminescence (PL) emission spectra of films or solutions in chloroform were obtained, using a photoncounting spectrometer (ISS Inc.). The number- and weight-average molecular weights (*M_n* and *M_w*) of P3HT₃BT were determined by gel permeation chromatography (GPC) in chloroform on a PL-GPC110 with a RI detector using polystyrene standards.

Results and Discussion

Synthesis. The synthesis of P3HT₃BT is outlined in Scheme I. The *M_n* of P3HT₃BT was estimated to be 8,400 g/mol through the comparison of the proton NMR peak integrals of the polymer with that of 4-dinitrobenzaldehyde, which was added to the NMR sample as an internal reference, as its aldehyde proton peak was located in a region not interfered with by proton peaks originating from the polymer. The *M_n* and *M_w* of P3HT₃BT were estimated to be 9,100 and 15,200 by GPC, respectively. This result is in good agreement with the NMR data even though the GPC measurement may not give a very accurate *M_n* value of P3HT₃BT since the conjugated polymer and polystyrene



Scheme I. Synthetic route to P3HT₃BT: (i) NBS, CHCl₃, 50 °C; (ii) NBS, CHCl₃, CH₃CO₂H, 50 °C; (iii) *n*-BuLi, THF, -78 °C; (iv) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, -78 °C; (v) Br₂, HBr, reflux; (vi) Pd(PPh₃)₄, toluene, K₂CO₃.

standards are chemically quite different.

Optical Properties. The UV-visible absorption and PL emission spectra of P3HT₃BT in chloroform showed that P3HT₃BT absorbed light in a spectral range from UV to near 600 nm, with two absorption peaks at 326 and 495 nm. A PL emission peak of P3HT₃BT in solution was observed at 577 nm but, in solid, the corresponding peak was observed at 647 nm. UV-visible and PL emission spectra of conjugated polymers in solid state usually exhibit slight bathochromic shifts, as compared to those of their solution samples, due to closer intermolecular interactions in solid.¹⁸ However, the UV-visible spectrum of P3HT₃BT in solid did not exhibit any significant bathochromic shift, but its PL emission spectrum did exhibit a very significant shift, when compared to the solution sample. This observation appeared to result from the very small Stoke's shift in the solution sample of P3HT₃BT, which is not yet fully understood.

The PL spectra were collected from solid blends of PHT₃BT/PCBM in various weight ratios and showed that the PL intensity of the conjugated polymer decreased with increasing weight ratio of PCBM to the polymers from 1:0 to 1:4, even though the film thickness may be slightly different from each other (Figure 2). This observation indicated that the photo-excited electrons of the conjugated polymer more efficiently transferred to PCBM with increasing PCBM content in the blend films, resulting in a more efficient quenching of the PL emissions of the polymer.

Electrochemical Properties. In order to examine the electrochemical properties of P3HT₃BT, the CV experiment was carried out in a three-electrode cell, set up with 0.10 M

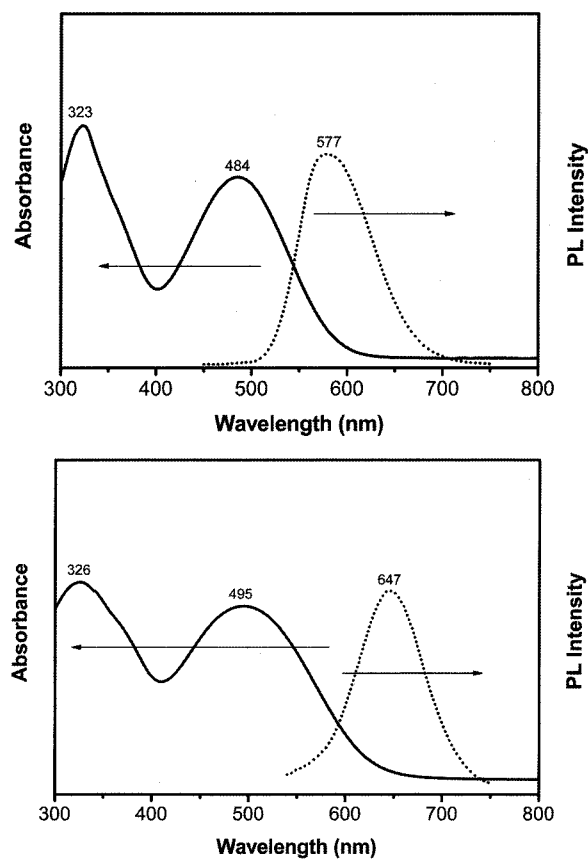


Figure 1. UV-visible absorption spectra (solid line) and PL emission spectra (dotted line) of P3HT₃BT: (top,) chloroform solution and (bottom) film.

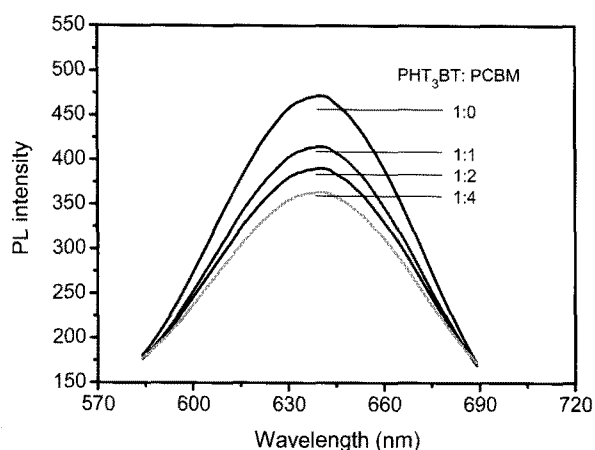


Figure 2. PL spectra of P3HT₃BT/PCBM thin films in different weight ratios.

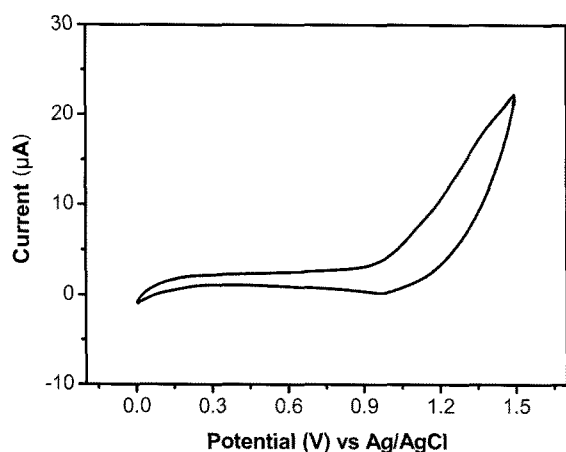


Figure 3. CV curve of P3HT₃BT in chloroform containing 0.10 M Bu₄NBF₄.

n-Bu₄NBF₄ as a supporting electrolyte in chloroform (Figure 3). In the anodic scan, the onset of oxidation potential ($E_{ox, onset}$) of P3HT₃BT occurred at 0.98 V. The CV curves remained essentially unchanged over 10 oxidation-reduction cycles, indicating that P3HT₃BT was electrochemically stable under these experimental conditions.

The highest occupied molecular orbital (HOMO) energy level of P3HT₃BT was estimated to be -5.69 eV, according to the empirical formula, $HOMO = -(E_{ox, onset} + 4.71)$ eV.¹⁹ This result suggested that the polymer was air-stable, and could be easily handled under atmospheric conditions, because the HOMO energy was below -5.2 eV.²⁰ The optical energy band gap (E_g) of P3HT₃BT, estimated from the UV-visible absorption spectrum (in solution) was 1.98 eV, which was very close to that of P3HT (~2.0 eV).²¹⁻²³ Based on the correlation between the HOMO energy level and E_g , the lowest unoccupied molecular orbital (LUMO) energy level of P3HT₃BT was calculated to be -3.71 eV. The lower energy band edge of the UV-visible absorption ($\lambda_{ab, onset}$), $E_{ox, onset}$, E_g , and HOMO/LUMO energy of P3HT₃BT are listed in Table I.

Table I. Summary of the Optical and Electrochemical Data of P3HT₃BT

	$\lambda_{Ab, onset}$ Film (nm)	$\lambda_{PL, max}$ Film (nm)	$E_{ox, onset}$ (V)	E_g^a (eV)	HOMO (eV)	LUMO (eV)
P3HT ₃ BT	625	647	0.98	1.98	-5.69	-3.71

$$^a E_g \text{ (eV)} = 1,240 / \lambda_{ab, onset}$$

The difference in the LUMO energy levels between P3HT₃BT and PCBM was close to 0.6 eV, which suggested that the electron transfer from the excited conjugated polymer to PCBM may be sufficiently efficient for efficient electron transfer, since the energy difference in the LUMOs should be at least equal to or slightly larger than the exciton binding energy (~0.4-0.5 eV).²⁰ The comparison of the energy band of P3HT₃BT with that of PCBM indicated that the polymer could be used as an electron-donor material in photovoltaic devices.

Conclusions

The P3HT₃BT copolymer was successfully synthesized via a multi-step procedure. The polymer absorbed light in a spectral range from UV region to near 600 nm. The energy band gap was estimated to be 1.98 eV and the polymer exhibited reversible oxidation-reduction cycles under the experimental conditions. In solid films, the PL emissions of the polymer were quenched in the presence of PCBM. Our current experimental data indicated that the polymer blends with PCBM can be employed in the fabrication of bulk heterojunction photovoltaic devices.

References

- (1) C. Winder and N. S. Sariciftci, *J. Mater. Chem.*, **14**, 1077 (2004).
- (2) M. C. Scharber, D. Mühlbacher, M. Koppe, P. Denk, C. Waldauf, A. J. Heeger, and C. J. Brabec, *Adv. Mater.*, **18**, 789 (2006).
- (3) G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, *Science*, **270**, 1789 (1995).
- (4) J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friends, S. C. Moratti, and A. B. Holmes, *Nature*, **376**, 498 (1995).
- (5) S. E. Shaheen, C. J. Brabec, N. S. Sariciftci, F. Padinger, T. Fromherz, and J. C. Hummelen, *Appl. Phys. Lett.*, **78**, 841 (2001).
- (6) F. Padinger, R. Rittberger, and N. S. Sariciftci, *Adv. Funct. Mater.*, **13**, 85 (2003).
- (7) M. Reyes-Reyes, K. Kim, and D. L. Carroll, *Appl. Phys. Lett.*, **87**, 83506 (2005).
- (8) W. Ma, C. Yang, X. Gong, K. Lee, and A. J. Heeger, *Adv. Funct. Mater.*, **15**, 1617 (2005).
- (9) J. Y. Kim, S. H. Kim, H.-H. Lee, K. Lee, W. Ma, X. Gong, and A. J. Heeger, *Adv. Mater.*, **18**, 572 (2006).

- (10) P.-L. T. Boudreault, A. Michaud, and M. Leclerc, *Macromol. Rapid Commun.*, **28**, 2176 (2007).
- (11) M. Akhtaruzzaman, M. Tomura, J. Nishida, and Y. Yamashita, *J. Am. Chem. Soc.*, **117**, 6791 (1995).
- (12) H. A. M. V. Mullekom, J. A. J. M. Vekemans, and E. W. Meijer, *Chem. Eur. J.*, **4**, 1235 (1998).
- (13) M. Velusamy, K. R. J. Thomas, J. T. Lin, Y. Hsu, and K. Ho, *Org. Lett.*, **7**, 1899 (2005).
- (14) Q.-G. He, C. He, Y.-X. Sun, H.-X. Wu, Y.-F. Li, and F.-L. Bai, *Thin Solid Films*, **516**, 5935 (2008).
- (15) J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger, and G. C. Bazan, *Nat. Mater.*, **6**, 497 (2007).
- (16) K. R. Yoon, N. M. Byun, and H. S. Lee, *Synth. Met.*, **157**, 603 (2007).
- (17) N. Blouin, A. Michaud, and M. Leclerc, *Adv. Mater.*, **19**, 2295 (2007).
- (18) D. Moses, A. Dogariu, and A. J. Heeger, *Phys. Rev. B*, **61**, 9373 (2000).
- (19) Y. Zhu, A. R. Rabindranath, T. Beyerlein, and B. Tieke, *Macromolecules*, **40**, 6981 (2007).
- (20) B. C. Thompson, Y.-G. Kim, T. D. McCarley, and J. R. Reynolds, *J. Am. Chem. Soc.*, **128**, 12714 (2006).
- (21) J. H. Hou, Z. A. Tan, Y. Yan, Y. J. He, C. H. Yang, and Y. F. Li, *J. Am. Chem. Soc.*, **128**, 4911 (2006).
- (22) J. Cremer, P. Bäuerle, M. M. Wienk, and R. A. J. Janssen, *Chem. Mater.*, **18**, 5832 (2006).
- (23) C. J. Shi, Y. Yao, Y. Yang, and Q. B. Pei, *J. Am. Chem. Soc.*, **128**, 8980 (2006).