

A Low-Band-Gap Polyfluorene Derivative for Use in Polymer Solar Cells

Joerg Wlosnewski¹, Phimwipha Piyakulawat¹, Anusit Keawprajak¹,
Chaiyuth Saekung² and Udom Asawapirom^{1*}

¹ National Nanotechnology Center, 111 Thailand Science Park, Phahonyothin Rd., Klong 1, Klong Luang, Pathumthani 12120, Thailand.

² Institute of Solar Energy Technology Development, 111 Thailand Science Park, Phahonyothin Rd., Klong 1, Klong Luang, Pathumthani 12120, Thailand.

*E-mail: udom@nanotec.or.th

Abstract

The novel soluble conjugated copolymer (PFTBzTT) derived from 4,7-dithienyl-2,1,3-benzothiadiazole, 9,9'-dioctylfluorene and 2,2'-bisthiophene was polymerized by a palladium catalyzed Suzuki type cross-coupling reaction. The copolymer obtained showed light absorption from 300 to 600 nm and photoluminescence from about 600 to 850 nm. The polymer-based solar cells could be prepared via solution deposition techniques (spin coating). The cells showed power conversion efficiency of 0.78 % when using PFTBzTT as donor and PCBM as acceptor with a ratio of 1 to 3 (w/w).

Keywords: polymer solar cell, low-band-gap, polyfluorene, benzothiadiazole

1. Introduction

The development of organic semi-conductors from small molecules and polymers has gained increasing attention in recent years. They have the potential to become the basis of cheap flexible electronic devices. Two main applications are polymer light-emitting diodes (PLEDs)^[1] and polymer photovoltaic cells (PPVCs).^[2,3] One configuration of PPVCs is the bulk heterojunction type device which is composed of a blend of an electron-donating material (p-type) such as polymers with a π -conjugation throughout the main chain, and an electron-accepting material (n-type), such as (6,6)-phenyl C₆₁-butyric acid methyl ester (PCBM).^[4] Due to the increased contact area the power conversion efficiency could be increased. Changing the ratio between the polymer, working as donor, and PCBM as acceptor can change

processibility and efficiency of the resulting PPVC. It is desired that the absorption spectra of these polymers should match that of the solar-terrestrial radiation (600-1000 nm) to maximize photon harvesting. Polyfluorenes (PFs) possess high hole mobilities and high stability against chemical doping. However, PFs show absorption maxima below 500 nm, due to the large band gaps which can be reduced by copolymerization with such as sulfur-containing heterocyclic materials.^[5] The low energy level of the highest occupied molecular orbital (HOMO) of polymer can increase the open-circuit voltage (V_{OC}) of its copolymers.^[6]

In this paper the synthesis of a low band gap copolymer based on fluorene is described. The optical and electrical properties of the polymer were investigated with ultraviolet-visible (UV-Vis) spectro-

scopy, photoluminescence spectroscopy (PL) and cyclic voltammetry (CV), respectively. In addition bulk-hetero-junction solar cells with different ratios of polymer to PCBM were fabricated and investigated to increase the power conversion efficiency (PCE).

2. Experimental

2.1 Materials

9,9-Dioctylfluorene-2,7-bis(trimethyl borate) (**5**) was obtained commercially. 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (**3**) and 2,2'-dibromo-5,5'-bisthiophene (**4**) were prepared during this work. Poly(3,4-ethylenedioxy-thiophene): polystyrene sul-fonate (PEDOT:PSS) was received from Aldrich. Aluminum (99.99%) for the cathode was from Kurt J. Lesker. All other chemicals were obtained

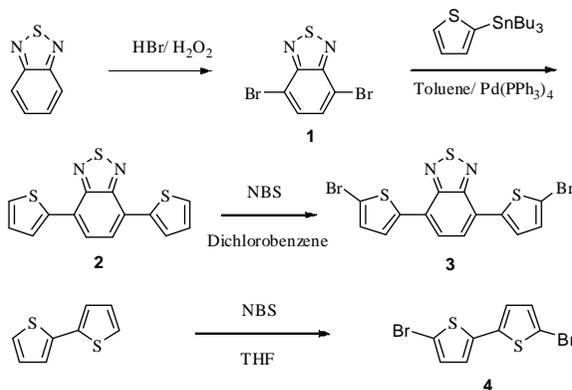
commercially at the highest grade available. All solvents were used as puris p.a. quality.

2.2 Syntheses of the monomers

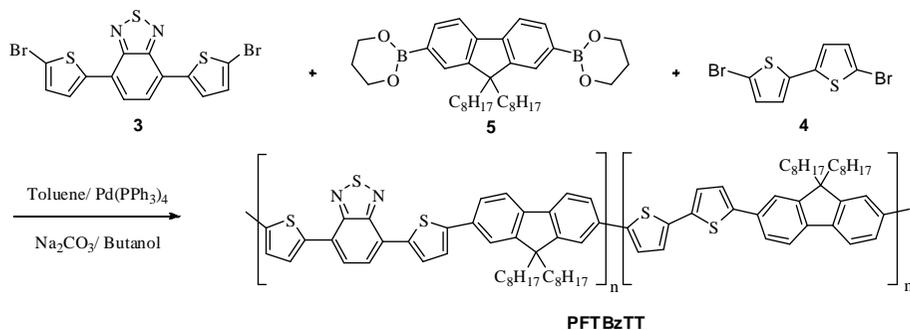
(Scheme 1)

4,7-dibromo-2,1,3-benzothiadiazole (**1**)

A solution of 2,1,3-benzothiadiazole (1.10 g, 8.08 mmol) in HBr (48%) (10 ml) was heated under reflux and H₂O₂ (30%) (6 ml) was added drop-wise within 30 min. The mixture was stirred while refluxing over night, then allowed to cool down and diluted with acetone. The solid arising was liquefied using a heat gun and ultrasonic. The mixture was poured into water (150 ml) to form a precipitate which was recrystallized in methanol, filtered, washed with methanol/water (1:1 v/v) and dried at high vacuum. Yield: 753 mg (35%) of **1**. ¹H-NMR δ (CDCl₃): 7.71 (s, 1H).



Scheme 1: Synthesis of 4,7-Bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (**3**) and 2,2'-dibromo-5,5'-bisthiophene (**4**)



Scheme 2: Synthesis of PFTBzTT

4,7-Dithienyl-2,1,3-benzothiadiazole (2)

A Stille coupling was used to synthesize **2**. A solution of 2,7-dibromo-2,1,3-benzothiadiazole **1** (1.00 g, 3.33 mmol), 2-(tributylstannyl)-thiophene (2.085 g, 6.66 mmol) and tetrakis (triphenylphosphino) palladium Pd(PPh₃)₄ (170 mg, 0.147 mmol) in 20 ml toluene was refluxed under a nitrogen atmosphere over night. After cooling down 20 ml of aqueous HCl (2M) was added. The product was extracted with chloroform, filtered through silica gel, dried over Na₂SO₄, and the solvent was removed. The remaining residue was recrystallized from ethanol. The compound **2** was obtained as a yellow solid. Yield: 860 mg (86%). ¹H-NMR δ (CDCl₃): 8.10 (d, 1H), 7.87 (s, 2H), 7.44 (d, 1H), 7.20 (t, 1H). ¹³C-NMR δ (CDCl₃): 153.0, 139.5, 128.0, 127.5, 126.8, 125.8.

4,7-Bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (3)

A mixture of 4,7-dithienyl-2,1,3-benzothiadiazole **2** (0.991 g, 3.3 mmol) and n-bromo-succinimide (NBS, 1.24 g, 6.6 mmol) in dichlorobenzene was heated to 55 °C for 3 h to give a red precipitate. The precipitate was filtered off, washed with water/ethanol (1:1 v/v) and recrystallized from dichlorobenzene to give the required compound **3**. Yield: 2.2 g (67%). ¹H-NMR δ (CDCl₃): 7.79 (d, 2H), 7.77 (s, 2H), 7.14 (d, 2H). ¹³C-NMR δ (CDCl₃): 152.3, 140.8, 130.9, 127.5, 125.6, 125.2.

2,2'-Dibromo-5,5'-bisthiophene (4)

2,2'-Bisthiophene was dissolved in THF. NBS was added and the mixture stirred under reflux for 5h. The solvent was evaporated and hexane was added. Filtration gave a clear brown solution which was dried over Na₂SO₄ and filtered. The hexane was removed to give the product **4**. Yield: 1.73 g (88%). ¹H-NMR δ (CDCl₃): 6.94 (d, 1H), 6.83 (d, 1H). ¹³C-NMR δ (CDCl₃): 137.8, 130.7, 124.1, 111.5.

2.3 Preparation of the copolymer (Scheme 2)

PFTBzTT was synthesized via Suzuki cross-coupling as given in scheme 2. 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (**3**) (188 mg, 0.41 mmol), 2,2'-Dibromo-5,5'-bisthiophene (**4**) (133 mg, 0.41 mmol), 9,9-dioctylfluorene-2,7-bis(trimethylborate) (**5**) (458 mg, 0.82 mmol) and tetrakis (triphenylphosphino) palladium (Pd(PPh₃)₄) (52 mg) were dissolved in a mixed solvent of 15 ml THF and 15 ml toluene under argon atmosphere. 5 ml Na₂CO₃ solution (0.2 g/ml) and 5 ml n-butanol were added. The reaction mixture was stirred and heated at 80 °C for 3 days under protection from light. The suspension was allowed to cool down before aqueous (2M) HCl was added to stop the reaction. The polymer was extracted with chloroform. The organic phase was treated with an EDTA solution, NaHCO₃ solution and washed with water, respectively. The chloroform fraction was dried over Na₂SO₄, filtered and removed by a rotary evaporator. The polymer was solvated in CHCl₃ and precipitated into a mixture of methanol/(2M) HCl (10:1 v/v). The precipitate was purified by Soxhlet extraction with methanol, acetone and chloroform, respectively. The chloroform phase was recovered, concentrated and crystallized in methanol/(2M) HCl (10:1 v/v). The red precipitate was filtered off and dried at high vacuum. Yield: 248 mg (50%). ¹H-NMR δ (C₂D₂Cl₃): 8.13 (s, 2H), 7.90 (s, 2H), 7.66 (m, 8H), 7.57 (m, 4H), 7.47 (s, 2H), 7.30 (s, 2H), 7.21 (s, 2H), 2.05 (s, 8H), 1.25-1.11 (m, 48), 0.79 (m, 12H). ¹³C-NMR δ (CDCl₃): 152.8, 152.1, 146.6, 144.2, 140.7, 140.4, 138.6, 136.6, 133.1, 129.0, 127.3, 126.0, 125.5, 124.8, 124.2, 123.8, 120.2, 55.5, 40.2, 31.8, 30.0, 29.7, 29.2, 24.0, 22.6, 14.0.

2.4 Fabrication of solar cell devices

The polymer photovoltaic cells were fabricated using indium doped tin oxide (ITO) coated on glass (Semiconductor wafer, Inc. 15 Ω/sq) as an anode. The ITO-

coated glass substrates were first cleaned thoroughly with detergent, de-ionized water, methanol, acetone and isopropyl alcohol for 15 min in an ultrasonic bath and subsequently dried with N_2 . Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) as the hole-injection layer was deposited by spin coating at 2000 rpm and dried at 120 °C for 30 min in vacuum. For the bulk-heterojunction layer, PFTBzTT was first blended with PCBM and dissolved in chlorobenzene (CB) (ratio 1:1, 1:2, and 1:3; 20 mg/mL). The blend solution was stirred for at least 24 hours at 40 °C. The composite material was spin coated onto the PEDOT:PSS layer at 1500 rpm. Then the films were thermally annealed at 150 °C for 40 min under argon atmosphere. Finally, aluminum as a cathode was deposited via thermal evaporation to a thickness of approximately 200 nm. An outline of the solar cell is presented in figure 1.

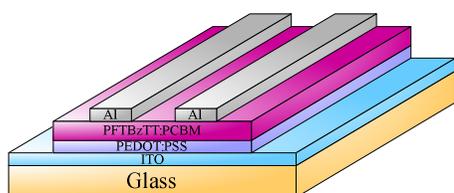


Figure 1 Device structure of bulk-heterojunction photovoltaic cells was ITO/PEDOT:PSS/PFTBzTT:PCBM/Al.

2.5 Characterization and Measurement

1H and ^{13}C NMR spectra were recorded on a Bruker AV 300 spectrometer and Bruker ARX 400-spectrometer with deuterated solvent at 298K, unless specified otherwise. The UV-Vis absorption spectra were taken using a Perkin Elmer/Lambda 650 UV-Vis spectrometer whereas fluorescence spectra were recorded on a Perkin Elmer LS55 spectrometer. Cyclic voltammetry (CV) was performed on an Autolab/Potentiostat galvanostat, on films which were drop cast on a platinum working electrode. After coating, the films

were dried in a vacuum oven for 10 min. The measurements were carried out in an anhydrous acetonitrile solution containing 0.1M of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) at a scan rate of 50 $mV s^{-1}$ against a platinum wire as a counter electrode and Ag/AgCl as a reference electrode. An internal ferrocene/ferrocenium standard was used. The HOMO and LUMO energy levels were determined from the oxidation and reduction onset (of the second scan from CV data) at the position where the current starts to differ from the baseline.

The current density–voltage (J–V) characteristics of the bulk-heterojunction solar cells were measured under illumination at 100 mW/cm^2 by using an AM 1.5 solar simulator at ambient conditions. The solar cells were illuminated through the side of the ITO-coated glass plate.

3. Results and Discussions

3.1 Synthesis and chemical characterization

HBr and H_2O_2 were used for bromination of 2,1,3-benzothiadiazole to gain **1**. Conversion of **1** to **2** was done by Stille coupling with 2-(tributylstannyl)-thiophene and $Pd(PPh_3)_4$ as catalyst. **3** was gained by bromination of **2** with NBS in chlorobenzene. Bromination of 2,2'-Bisthiophene with NBS led to **4**. Reaction schemes of the monomers **3** and **4** are given in scheme 1. The copolymer PFTBzTT was synthesized via Suzuki cross-coupling of **3**, **4** and **5** under typical reaction conditions with a yield of 50%. The synthesis route of PFTBzTT is summarized in scheme 2.

3.2 Optical properties

The UV-Vis absorption and photoluminescence (PL) spectra of PFTBzTT in $CHCl_3$ solution and solid film are presented in figure 2. The UV-Vis spectra display two maxima of absorption.

The absorption peaks at ca. 430 nm are attributed to the fluorene/dithiophene

segment, and the additional long wavelength absorption bands at about 530 nm are attributed to the fluorene/dithiophene-benzothiadiazole segment^[7]. The long wavelength absorption in solid film was red shifted about 15 nm compared to the corresponding spectra in CHCl₃ solution. Optical band-gap as 1.96 eV was estimated from the absorption onset (634 nm). The PL spectra of the polymer revealed the emission peak at ca. 675 nm with a low energy PL shoulder at ca. 855 nm, which corresponds to the red region, and exhibited a strong red PL.

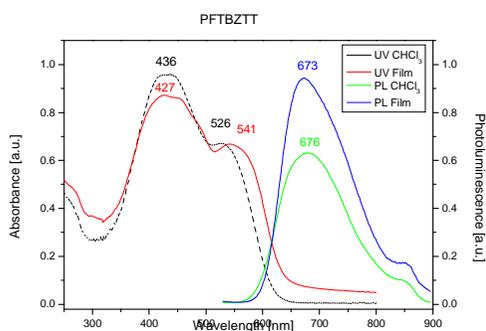


Figure 2 UV-Vis and PL spectra of PFTBzTT in solid state as film and in chloroform solution

3.3 Electrochemical characteristics

The electrochemical behavior of the copolymer (as films on Pt electrode) was investigated by cyclic voltammetry (CV). The copolymer showed two oxidation peaks with onset at 1.18 and 1.48 V, respectively. We were unable to record reduction peak after several attempts. The energies of the HOMO level $E_{\text{HOMO}} = -5.56$ eV was estimated according to an empirical equation ($E_{\text{HOMO}} = -e(E_{\text{ox}} + 4.38)$ eV) M.^[8]. The LUMO level can be estimated from its HOMO level and optical energy gaps with $E_{\text{LUMO}} = -3.60$ eV.

3.4 Solar cell characteristics

The J-V characteristics of the devices produced were measured under AM 1.5 illumination with a calibrated solar simulator with an intensity of 100 mW/cm². The results are presented in Figure 3.

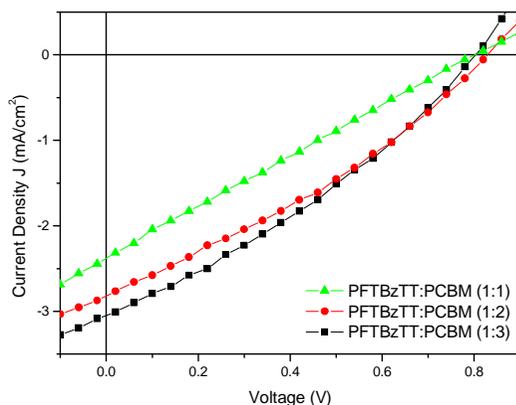


Figure 3 J-V characteristics of PFTBzTT:PCBM bulk-heterojunction solar cells annealed at 150 °C for 40 min under argon atmosphere (PFTBzTT:PCBM ratio 1:1, 1:2, 1:3).

The performances of photovoltaic (PV) devices with various PCBM ratios are given in table 1. The best performance with a short-circuit current density $J_{\text{sc}} = 3.05$ mA/cm², a fill factor $\text{FF} = 0.32$, an open-circuit voltage $V_{\text{oc}} = 0.80$ and a resulting power conversion efficiency PCE of 0.78%, was found for a cell annealed at 150°C and a ratio of PFTBzTT:PCBM (1:3, w/w).

Table 1 Summary of performance for PV devices with various PFTBzTT:PCBM ratio annealed at 150 °C

Device ratio	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	PCE (%)
1:1	0.80	2.38	0.25	0.48
1:2	0.83	2.81	0.32	0.74
1:3	0.80	3.05	0.32	0.78

4. Conclusion

The synthesis of low band gap copolymer PFTBzTT based on fluorene

was accomplished by Suzuki coupling reaction. The soluble red solid copolymer shows a UV-absorption maximum at about 430 nm and a photoluminescence maximum at 675 nm on solid state. The optical studies revealed a band-gap of 1.96 eV. The photovoltaic devices with a PFTBzTT:PCBM ratio of 1:3 (w/w) showed the highest power conversion efficiency (PCE) with 0.78 %.

5. Acknowledgement

This work was supported by the National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA).

6. References

- [1] Buergi L., Turbiez M., Pfeiffer R., Bienewald F., Kirner H. J., Winnewisser C., High-mobility Ambipolar Near-infrared Light-emitting Polymer Field-effect Transistors, *Adv. Mater.*, Vol. 20, pp. 2217-2224, 2008.
- [2] Mammo W., Admassie S., Gadisa A., Zhang F., Inganaes O., Andersson M. R., New Low Band Gap Alternating Polyfluorene Copolymer-based Photovoltaic Cells, *Sol. Energy Mater. Sol. Cells*, Vol. 91, pp. 1010-1018, 2007.
- [3] Kim J. Y., Lee K., Coates N. E., Moses D., Nguyen T. Q., Dante M., Heeger A. J., Efficient Tandem Polymer Solar Cells Fabrication by All-Solution Processing, *Science*, Vol. 317, pp. 222-225, 2007.
- [4] Ma W., Yang C., Gong X., Lee K., Heeger A. J., Thermally Stable, Efficient Polymer Solar Cells with Nanoscale Control of the Interpenetrating Network Morphology, *Adv. Funct. Mater.*, Vol. 15, pp. 1617-1622, 2005.
- [5] Asawapirom U., Guentner R., Foster M., Farrell T., Scherf U., Dialkylfluorene-oligo thiophene and Dialkylfluorene-dithienylvinylene Alternating Copolymers, *Synthesis-stuttgart*, Vol. 9, pp. 1136-1142, 2002.
- [6] Suzuki H., Yokoo A., Notomi M., Organic Emissive Materials and Devices for Photonic Communication, *Polym. Adv. Technol*, Vol. 15, pp. 75-80, 2004.
- [7] Sun M., Wang L., Du B., Xiong Y., Liu R., Cao Y., Narrow Band-gap Oligomer for Solution-processed Heterojunction Organic Solar Cells, *Synthetic Metals*, Vol. 158, pp. 125-129, 2008.
- [8] Sun M., Li W., Zhu X., Du B., Liu R., Yang W., Gao Y., Near-infrared Response Photovoltaic Device Based on Novel Narrow Band Gap Small Molecule and PCBM Fabricated by Solution Processing, *Sol. Energy Mater. Sol. Cells*, Vol. 91, Band 18, pp. 1681-1687, 2007.