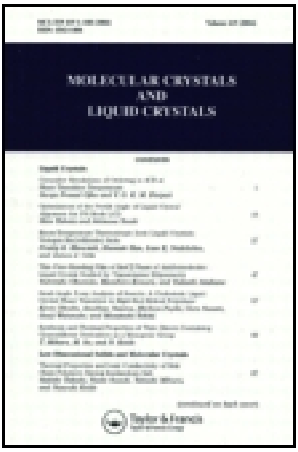


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Electro-Optical Properties of Fluorene-Based Copolymer for Organic Photovoltaic Device Application

Jang Soo Kim [a], Myungkwan Song [a], Jin Su Park [a], Mikyoung Yoon [a], Hoe Won Yoon [a], Ae Jin Kim [a], Jae Wook Lee [b], Yeong-Soon Gal [c] & Sung-Ho Jin [a]

[a] Department of Chemistry Education, Interdisciplinary Program of Advanced Information and Display Materials, and Center for Plastic Information System, Pusan National University, Busan, Korea

[b] Department of Chemistry, Dong-A University, Busan, Korea

[c] Polymer Chemistry Lab., Kyungil University, Hayang, Korea

Version of record first published: 16 May 2011

To cite this article: Jang Soo Kim, Myungkwan Song, Jin Su Park, Mikyoung Yoon, Hoe Won Yoon, Ae Jin Kim, Jae Wook Lee, Yeong-Soon Gal & Sung-Ho Jin (2011): Synthesis and Electro-Optical Properties of Fluorene-Based Copolymer for Organic Photovoltaic Device Application, Molecular Crystals and Liquid Crystals, 538:1, 223-231

To link to this article: http://dx.doi.org/10.1080/15421406.2011.564076

Mol. Cryst. Liq. Cryst., Vol. 538: pp. 223–231, 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.564076

Taylor & Francis
Taylor & Francis Group

Synthesis and Electro-Optical Properties of Fluorene-Based Copolymer for Organic Photovoltaic Device Application

JANG SOO KIM,[1] MYUNGKWAN SONG,[1] JIN SU PARK,[1] MIKYOUNG YOON,[1] HOE WON YOON,[1] AE JIN KIM,[1] JAE WOOK LEE,[2] YEONG-SOON GAL,[3] AND SUNG-HO JIN[1]

[1]Department of Chemistry Education, Interdisciplinary Program of Advanced Information and Display Materials, and Center for Plastic Information System, Pusan National University, Busan, Korea
[2]Department of Chemistry, Dong-A University, Busan, Korea
[3]Polymer Chemistry Lab., Kyungil University, Hayang, Korea

*The following soluble π-conjugated polymer was synthesized by palladium-catalyzed Suzuki polymerization: poly[(9,9-dioctylfluorene)-*alt*-(3-hexylthiophen-5-yl)-(4′-hexylthiazol-5′-yl)] poly(FO-HThHTha) derived from poly(9,9-dioctylfluorene) (PFO) and poly[(3-hexylthiophen-5-yl)-2,2′-(4′-hexylthiazol-5′-yl)] poly(HThHTa). The polymer, poly(FO-HThHTa) was soluble in common organic solvents and easily spin coated onto indium-tin oxide (ITO) coated glass substrates. Bulk heterojunction photovoltaic cells with an ITO/PEDOT/poly(FO-HThHTa): $PC_{70}BM/TiO_x/Al$ configuration were fabricated and the photovoltaic cell using poly(FO-HThHTa):$PC_{70}BM$ (1:4) showed the best photovoltaic performance compared with those using poly(FO-HThHTa):$PC_{70}BM$ (1:2 and 1:6). The optimal bulk heterojunction photovoltaic cell exhibits a power conversion efficiency (PCE) of 0.39% ($V_{oc} = 0.44$ V, $J_{sc} = 2.57$, $FF = 0.34$) with poly(FO-HThHTa): $PC_{70}BM$ (1:4) measured by using an AM 1.5 G irradiation (100 mW/cm^2) on an Oriel Xenon solar simulator (Oriel 300 W).*

Keywords Bulk heterojunction; low-band gap polymer; organic photovoltaics

Introduction

Since the initial discovery of π-conjugated polymers in the late 1970s, diverse applications of these materials have emerged owing to their remarkable electronic and photonic properties [1]. There are many reasons for the interest in organic photovoltaics (OPVs) when comparing the technology to the silicon-based

---

Address correspondence to Sung-Ho Jin, Department of Chemistry Education, Interdisciplinary Program of Advanced Information and Display Materials, and Center for Plastic Information System, Pusan National University, Busan 609-735, Korea. E-mail: shjin@pusan.ac.kr photovoltaics (PVs) and interestingly the two very different technologies are complementary in many ways. The OPVs offer low cost, solution processing, flexible substrates, and a very high speed of processing. In the late 1990s, when the OPVs were in their infancy they showed low power conversion efficiency (PCE) and short lifetime [2]. In recent years, this has changed dramatically and both the PCE and lifetime of OPVs have improved significantly with efficiencies of around 6% and estimated operational lifetimes of 20,000 h [3]. During the last decade several research groups have reported the synthesis and use of materials which absorb light with wavelengths above 600 nm in OPVs. Among the different concepts which have been proposed in OPVs, the bulk heterojuction approach is an attractive and significant progress is being made in improving the PCE of OPVs in recent times. One of the possible ways to improve the PCE of photovoltaic cells is the implementation of new materials absorbing the part of the solar spectrum. So it is important to design and synthesis of low-band gap polymers, which improved overlap of the polymer absorption spectrum with the standard solar spectrum under AM 1.5 global [4]. Low-band gap polymers are loosely defined as a polymer with a band gap below 2.0 eV, i.e., absorbing light with wavelengths longer than 620 nm [5]. One successful approach to synthesis of low-band gap polymer is arranging the electron-donor and electron-acceptor repeating units alternatively along the polymeric backbone [6]. From this synthetic design rule, a number of low-band gap polymers have been synthesized, which have lower band gaps around 0.3–0.5 eV compared to the conventional π-conjugated polymers [7]. OPVs made of low-band gap polymers have been reported previously [8].

In the present article, we report the synthesis and characterization of a new π-conjugated polymer with electron-donating fluorene and electron-withdrawing thiophene-thiazole units and its characterization of photovoltaic properties of bulk heterojunction photovoltaic cells.

Experimental

3-Hexylthiophene, copper cyanide, N-bromosuccinimide (NBS), O,O′-diethyl dithiophosphate, 2-octanone, palladium(II) acetate, tricyclohexylphosphine, and tetraethylammonium hydroxide, were purchased from Aldrich Chemical Co. Solvents were dried and purified by fractional distillation over sodium/benzophenone and handled in moisture free atmosphere. ^{1}H-NMR spectra were recorded in $CDCl_3$ on a Varian Mercury 300 and chemical shifts were recorded in ppm. The absorption and photoluminescence (PL) spectra were measured using a Jasco V-570 UV-visible spectrometer and a Hitachi F-4500 fluorescence spectrophotometer, respectively. The molecular weight and polydispersity of polymer were determined with gel permeation chromatography (GPC) analysis relative to polystyrene calibration (Agilent 1100 series GPC, Plgel 5 µm MIXED-C, refractive index detector) in THF solution. The thermal analysis were carried out on a Mettler Toledo TGA/SDTA 851^e, DSC 822^e analyzer under an N_2 atmosphere at a heating rate of 10°C/min. Cyclic voltammetry (CV) was carried out with a Bioanalytical Systems CV-50 W voltammetric analyzer at a potential scan rate of 50–100 mV/s in a 0.1 M solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in anhydrous acetonitrile. Each polymer film was coated onto a Pt disc electrode (0.2 cm^2) by dipping the electrode into the polymer solution.

Synthesis of 2-Bromo-3-hexylthiophene

N-Bromosuccinimide (5.8 g, 3.27 mmol) and DMF (10 mL) were placed in a three neck round bottom flask (100 mL). 3-Hexylthiophene (5 g, 29.7 mmol) was added flask under N_2 atmosphere. The solution was stirred overnight at room temperature. The solution was extracted with ethyl acetate and water (2–3 times) and dried with anhydrous $MgSO_4$. Flash column chromatography using hexane as an eluent to give 2-bromo-3-hexylthiophene (3.48 g, 47%).

^{1}H-NMR ($CDCl_3$, δ ppm): 7.19 (d, 1H, aromatic protons on thiophene), 6.89 (d, 1H, aromatic protons on thiophene), 2.5–2.6 (t, CH_2), 1.59 (m, CH_2), 1.32 (m, 3CH_2), 0.85 (m, CH_3).

Synthesis of 2-Cyano-3-hexylthiophene

2-Bromo-3-hexylthiophene (4 g, 16.2 mmol) and copper cyanide (8.11 g, 90.6 mmol) were stirred in DMF (30 mL) in a three neck round bottom flask (100 mL) under N_2 atmosphere. The reaction mixture was stirred 24 h at 130°C. The reaction mixture was extracted with toluene and water (2–3 times). The obtained organic phase was dried with anhydrous $MgSO_4$ and the product was obtained by column chromatography (eluent: hexane:ethyl acetate = 8:2) to give 2-cyano-3-hexylthiophene (2.43 g, 77%).

^{1}H-NMR ($CDCl_3$, δ ppm): 7.48 (d, 1H, aromatic protons on thiophene), 6.99 (d, 1H, aromatic protons on thiophene), 2.7–2.8 (t, CH_2), 1.62 (m, CH_2), 1.25 (m, 3CH_2), 0.82 (m, CH_3).

Synthesis of 2-Thioamino-3-hexylthiophene

2-Cyano-3-hexylthiophene (1 g, 5.17 mmol), THF and water (10:1) (15 mL) were stirred in a three neck round bottom flask (100 mL) under N_2 atmosphere. Then O,O′-diethyl dithiophosphate (4 mL, 25.8 mmol) was added into the flask. After reaction was carried out at 70°C for 20 h, the cooled reaction mixture was quenched with water and then extracted 2–3 times with ethyl acetate and water. The obtained organic phase was dried with anhydrous $MgSO_4$ and the product was purified using column chromatography using hexane and ethyl acetate (8:2) as an eluent to give 2-thioamino-3-hexylthiophene (1 g, 85%).

^{1}H-NMR ($CDCl_3$, δ ppm): 7.27 (d, 1H, aromatic protons on thiophene), 6.9 (d, 1H, aromatic protons on thiophene), 2.8–2.9 (m, CH_2), 2.0 (s, NH_2), 1.6 (m, CH_2), 1.3 (m, 3CH_2), 0.82 (m, CH_3).

Synthesis of 2-Thiazole (3′-hexyl)-3-hexylthiophene

1-Bromo-2-octanone (1.36 g, 6.59 mmol) was added to a DMF solution of the obtained 2-thioamino-3-hexylthiophene (0.5 g, 2.19 mmol). After reaction was carried out at 130°C for about 1.5 h, the reaction mixture was quenched with water and extraction with ethyl acetate, water (2–3 times) and brine. The obtained organic phase was dried with anhydrous $MgSO_4$ and the product was purified by column chromatography using hexane and dichloromethane (3:2) as an eluent to give 2-thiazole (3′-hexyl)-3-hexylthiophene (0.65 g, 89%).

^{1}H-NMR ($CDCl_3$, δ ppm): 7.25 (d, 1H, aromatic protons on thiophene), 6.95 (d, 1H, aromatic protons on thiophene), 6.82 (d, 1H, aromatic protons on thiazole), 2.8 (t, CH_2, hexyl group of thiazole), 2.89 (t, CH_2, hexyl group of thiophene), 1.65 (m, $2CH_2$, hexyl group of thiophene and thioazole), 1.35 (m, $6CH_2$, hexyl group of thiophene and thiazole), 0.9 (m, $2CH_3$, hexyl group of thiophene and thiazole).

Synthesis of 5-Bromo-2-thiazole (2′-bromo-3′-hexyl)-3-hexylthiophene

NBS (0.58 g, 3.27 mmol) was added to a DMF (40 mL) solution of 2-thiazole (3′-hexyl)-3-hexylthiophene (0.5 g, 1.49 mmol) in a three neck round bottom flask (100 mL) under N_2 atmosphere. After reaction was carried out at 40°C for overnight, the reaction mixture was extracted with ethyl acetate and water (2–3 times) and obtained organic phase was dried with anhydrous $MgSO_4$. Column chromatography using hexane and dichloromethane (5/1) as an eluent gave the product (0.6 g, 83%).

^{1}H-NMR ($CDCl_3$, δ ppm): 6.88 (d, 1H, aromatic protons on thiophene), 2.75 (m, $2CH_2$, hexyl group of thiophene and thiazole), 1.63 (m, $2CH_2$, hexyl group of thiophene and thiazole), 1.35 (m, $6CH_2$, hexyl group of thiophene and thioazole), 0.9 (m, $2CH_3$, hexyl group of thiophene and thiazole).

Synthesis of Poly[(9,9-dioctylfluorene)-alt-*(3-hexylthiophen-5-yl)-2,2′-(4′-hexylthiazol-5′-yl)] poly(FO-HThHTha)*

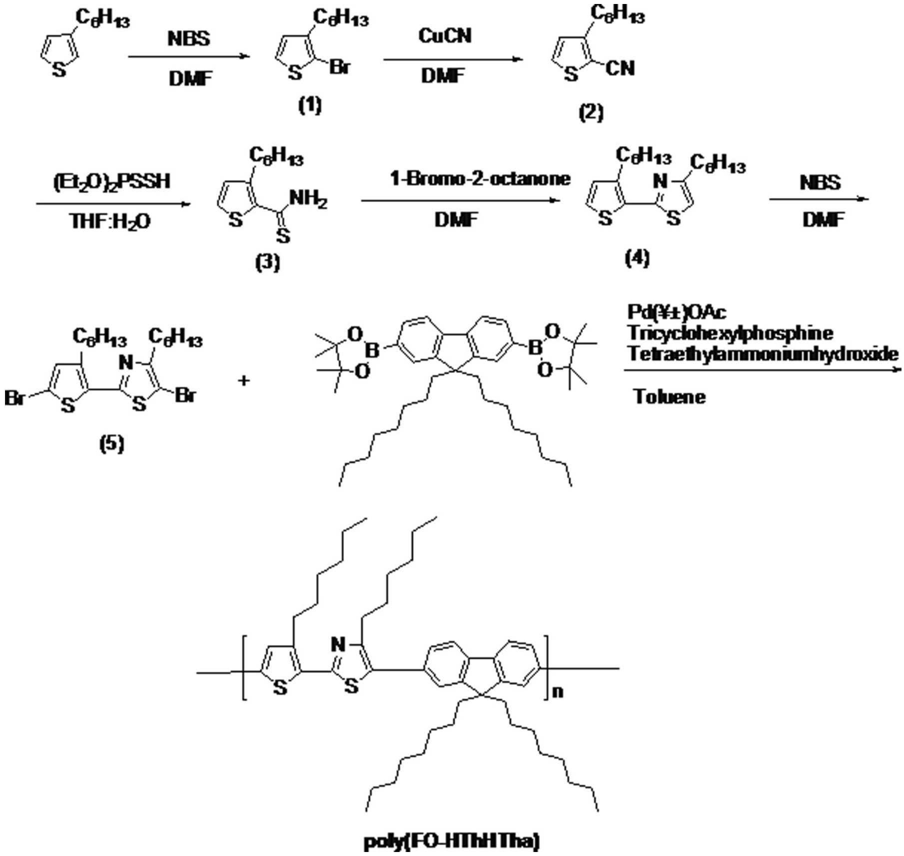
5-Bromo-2-(5-bromo-3-hexylthiophen-2-yl)-4-hexylthiazole (0.13 g) and 2,7-bis (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (0.169 g) were dissolved in anhydrous toluene (2 mL) with stirring under N_2 atmosphere. After addition of palladium(II) acetate (8.5 mg) and tricyclohexyl phosphine (2.5 mg), the reaction mixture was stirred at 90°C for 5 min under N_2 condition. Tetraethylammonium hydroxide (0.37 mL) was added and then stirred at 90°C for 1 h. After the reaction was completed, the reaction solution was dark brown solid. The obtained polymer (0.14 g) was concentrated and reprecipitated into excess amount of methanol (250 mL).

Fabrication and Measurement of Bulk Heterojunction Photovoltaic Cells

Each glass substrate was coated with a transparent ITO electrode (110 nm thick, 10–20 Ω/sq sheet resistance). The ITO-coated glass substrates were ultrasonically cleaned with detergent, deionized water, acetone, and isopropyl alcohol. Bulk heterojunction photovoltaic cells was fabricated by spin-coating a 40 nm thick layers of PEDOT:PSS (CLEVIOS P VP AI 4083) on a ultrasonically cleaned 110 nm thick ITO coated patterned glass substrate, followed by baking on a hot plate at 150°C for 30 min. For the fabrication of the active layer composed of interconnected networks of electron donor, poly(FO-HThHTha) (10 mg/mL) and electron acceptor, $PC_{70}BM$ (15 mg/mL) were dissolved in 1,2-dichlorobenzene and chloroform (1:1 wt%), respectively, followed by shaking at room temperature for 12 h. The poly(FO-HThHTha) and $PC_{70}BM$ blend was then prepared by mixing the two solutions and subsequent shaking for 12 h was performed to obtain a homogeneously mixed blend system. The weight ratio of the active layer as an electron donor, poly (FO-HThHTha) to electron acceptor, $PC_{70}BM$ was 1:2, 1:4 and 1:6, respectively. The TiO_x precursor solution (1 wt%) was spin cast (4000 rpm) onto the active layer with thickness around 10 nm and heated at 80°C for 10 min in air. During this process the precursor converts to TiO_x by hydrolysis. Subsequently the devices were pumped down in vacuum (5×10^{-6} torr) and then Al electrodes with thickness around 100 nm were deposited. The top metal electrode area, determining active area of the devices, was evaluated to be 4 mm^2. Photovoltaic performance was measured using a A.M. 1.5 G solar simulator (Oriel 300 W) at 100 mW/cm^2 light illumination after adjusting the light intensity using Oriel power meter (model No. 70260 which is calibrated using laboratory standards that are traceable to the National Institute of Standards and Technologies USA). Current density-voltage (J-V) curves were recorded using a standard source measurement unit (Keithley 236). All fabrication steps and characterization measurements were performed in an ambient environment without a protective atmosphere. Thickness of the thin films was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of ±1 nm.

Results and Discussion

Scheme 1 shows the synthetic routes for the monomer and the polymer *via* Suzuki polymerization method. 2-Bromo-3-hexylthiophene, 2-cyano-3-hexylthiophene [9],



Scheme 1. Synthetic routes for poly(FO-HThHTha).

2-thioamino-3-hexylthiophene, 2-thiazole (3′-hexyl)-3-hexylthiophene [10], and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene [11] were synthesized according to literature procedures. The monomer, 5-bromo-2-thiazole (2′-bromo-3′-hexyl)-3-hexylthiophene was successfully prepared by the bromination of 2-thiazole (3′-hexyl)-3-hexylthiophene using NBS/DMF. Polymerization was carried out with an excess of palladium(II) acetate in dried toluene under N_2 atmosphere for 1 h. The polymer, poly[(9,9-dioctylfluorene)-*alt*-(3-hexylthiophen-5-yl)-2,2′-(4′-hexylthiazol-5′-yl)] poly(FO-HThHTha) was found to be completely soluble in various organic solvents such as acetone, chloroform, 1,2-dichloroform, and THF, etc. The good solubility of poly(FO-HThHTha) is a very important requirement for device fabrication. To improve device performance, poly(FO-HThHTha) was further purified by soxhlet extraction with different solvents including methanol, acetone and finally chloroform to remove the unreacted monomers, impurities and oligomers. By carrying out these processes, the highly purified poly(FO-HThHTha) was obtained. Table 1 summarizes the polymerization results, molecular weight, polydispersity, and thermal characteristics of poly(FO-HThHTha). The weight-average molecular weight (M_w) and the polydispersity (PDI) of the poly(FO-HThHTha) was 48,100, 2.45, respectively. The glass transition temperature of poly(FO-HThHTha) was 58°C as determined by DSC. The TGA thermogram of the poly(FO-HThHTha) revealed a 5% weight loss at 415°C under a N_2 atmosphere.

Figure 1 shows the normalized UV-visible and photoluminescence (PL) spectra of the poly(FO-HThHTha) in thin film state. The absorption spectrum of the poly(FO-HThHTha) has broad peaks at 423 nm in solution state and at 424 nm in thin film state. The absorption band in thin film state was slightly red-shift compared to the solution state because of the interchain interactions between the polymer chains. From the onset of the absorption spectrum, the band gap of poly(FO-HThHTha) was calculated to be 2.4 eV. The PL spectrum of the poly(FO-HThHTha) has at 527 nm in solution state and at 579 nm in thin film state. These results indicate that more efficient energy transfer from the wide-band gap of fluorene segment to the low-band gap thiophene-thiazole segment has occurred in the poly(FO-HThHTha), due to the completely disappearance of PL emission from the fluorene unit. The transfer of the exciton energy from fluorene segment to the thiophene-thiazole segment occurs mainly along the poly(FO-HThHTha) chain and/or intermolecular energy transfer occurs in poly(FO-HThHTha).

We carried out redox measurements using cyclic voltammetry (CV). The HOMO energy level of poly(FO-HThHTha) for the standard ferrocene/ferrocenium

Table 1. Polymerization results, thermal and electro-optical properties of poly(FO-HThHTha)

	M_w[a] ($\times 10^4$)	PDI[a]	DSC[b] (°C)	TGA[c] (°C)	Abs (nm) solution	Abs (nm) film[d]	PL (nm) solution	PL (nm) film[d]	E_g[e] (eV)
Polymer	4.81	2.45	58	415	423	424	527	579	2.45

[a] M_w and PDI of the polymers were determined by GPC using polystyrene standard.
[b] Determined by DSC at a heating rate of 10°C/min under N_2 atmosphere.
[c] TGA was measured at temperature of 5% weight loss for the polymer.
[d] Measured in the thin film onto the quartz substrate.
[e] Band gap estimated from the onset wavelength of the optical absorption.

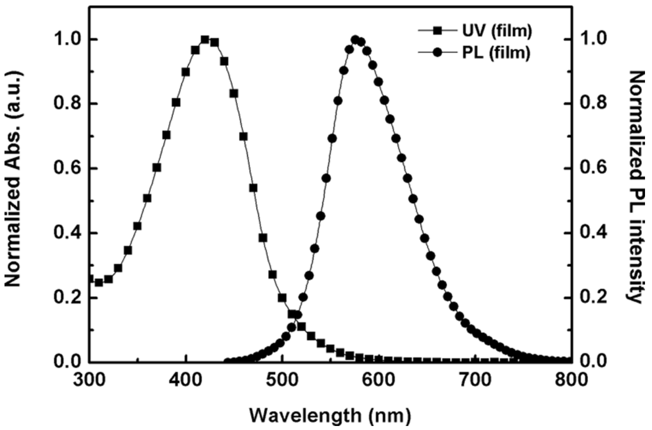


Figure 1. UV-visible absorption and PL spectra of poly(FO-HThHTha).

(−4.8 eV) was −5.5 eV. The LUMO energy level was −3.1 eV, which was calculated from the value of HOMO energy and the optical band gap. The energy band diagrams of poly(FO-HThHTha), $PC_{70}BM$ and TiO_x are shown in Figure 2. Photogeneration of charge in most of π-conjugated polymers is not very efficient because there is always the recombination of two charge carriers involved. However, from these energy band diagrams, we predict that the required transfer of charges can be realized at the interface between poly(FO-HThHTha) as an electron donor and $PC_{70}BM$ as an electron acceptor due to the higher LUMO energy levels of poly(FO-HThHTha) and their lower HOMO energy level of $PC_{70}BM$.

Bulk heterojunction photovoltaic cells were fabricated using the poly(FO-HThHTha) as an electron donor and $PC_{70}BM$ as an electron acceptor. The photovoltaic cell structure was ITO/PEDOT:PSS (40 nm)/poly(FO-HThHTha):$PC_{70}BM$ (80 nm)/TiO_x (10 nm)/Al (120 nm) using a different ratio of electron donor to electron acceptor materials at a fixed photoactive layer thickness of 80 nm. We used TiO_x layer for electron transfer from active layer to Al. The energy level of TiO_x matches well with the energy level of Al. Many research groups obtained their best

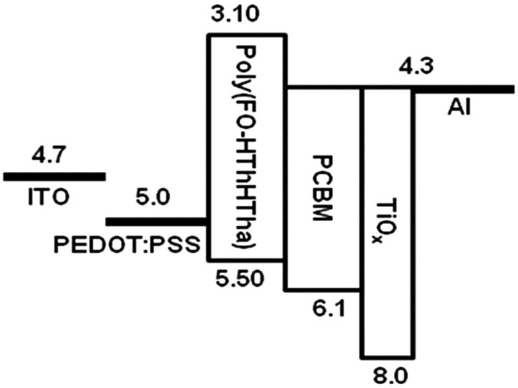


Figure 2. Energy band diagram of poly(FO-HThHTha), $PC_{70}BM$ and TiO_x.

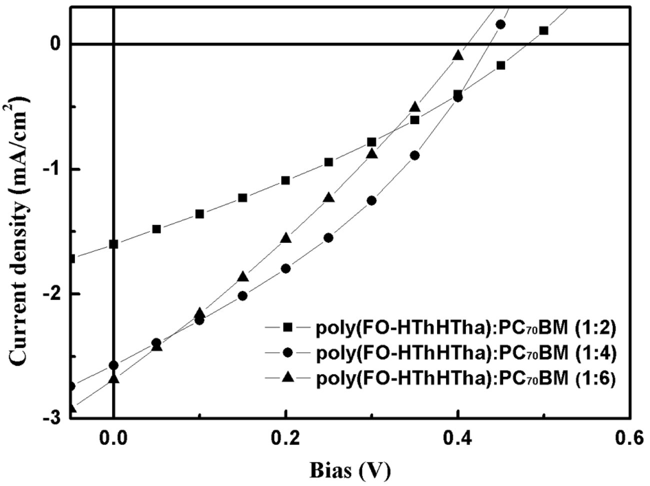


Figure 3. Current density-voltage (J-V) characteristics of the poly(FO-HThHTha):PC$_{70}$BM blend of photovoltaic cells.

photovoltaic performance by optimization of different ratio of electron donor to electron acceptor. The charge balance depends on overall active layer thickness and an appropriate amount of PC$_{70}$BM in the blended active layer. Here, we study the effect of active layer compositions on photovoltaic performance using 1,2-dichlorobenzene and chloroform cosolvent system. The current density-voltage (J-V) characteristics of bulk heterojunction photovoltaic cells fabricated with 1:2, 1:4 and 1:6 ratios of poly(FO-HThHTha) to PC$_{70}$BM under AM 1.5 G illumination are shown in Figure 3 and these photovoltaic performance are summarized in Table 2. The open-circuit voltage (V_{oc}) of bulk heterojunction photovoltaic cell is closely related to the energy difference between the HOMO energy level of the electron donor and the LUMO energy level of the electron acceptor. The V_{oc} of the bulk heterojunction photovoltaic cell are almost identical, but a higher short-circuit current density (J_{sc}) were observed with increment of the amount of PC$_{70}$BM in the blended active layer. The bulk heterojunction photovoltaic cell fabricated with 1:4 ratio of poly(FO-HThHTha) to PC$_{70}$BM with TiO$_x$ exhibited higher photovoltaic performance when compared with the poly(FO-HThHTha) to PC$_{70}$BM with TiO$_x$ giving a V_{oc} of 0.44 V, a J_{sc} of 2.57 mA/cm^2, a FF of 34% and a PCE of 0.39% as

Table 2. Photovoltaic performance of poly(FO-HThHTha):PC$_{70}$BM

Device	Ratio	V_{oc} (V)^a	J_{sc} (mA/cm^2)^b	FF (%)^c	PCE (%)^d
1	1:2	0.48	1.60	31.25	0.24
2	1:4	0.44	2.57	34.49	0.39
3	1:6	0.41	2.68	28.21	0.31

[a] V_{oc}: open-circuit voltage.
[b] J_{sc}: short-circuit current density.
[c] FF: fill factor.
[d] PCE: power conversion efficiency.

opposed to 0.31% for the poly(FO-HThHTha):$PC_{70}BM$ (1:6) bulk heterojunction photovoltaic cell.

Conclusions

We have synthesized a new class of high molecular weight poly(FO-HThHTha) by Suzuki polymerization. Poly(FO-HThHTha) exhibited a high glass transition temperature and can be easily spin casted onto the ITO substrates. Bulk heterojunction photovoltaic cells with an ITO/PEDOT:PSS/poly(FO-HThHTha):$PC_{70}BM/TiO_x$/Al configuration were fabricated with poly(FO-HThHTha) as an electron donor and $PC_{70}BM$ as an electron acceptor. The bulk heterojunction photovoltaic cells were fabricated with 1:2, 1:4 and 1:6 ratios of poly(FO-HThHTha) to $PC_{70}BM$. The maximum PCE of 0.39% (under an AM 1.5 simulated solar light at 100 mW/cm^2) (J_{sc}: 2.57 mA/cm^2, V_{oc}: 0.44 V, FF: 34%) was achieved with poly (FO-HThHTha):$PC_{70}BM$ (1:4 wt%).

Acknowledgment

This work was supported by the New & Renewable Energy program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant (No. 20103020010050) funded by the Ministry of Knowledge Economy, Republic of Korea.

References

[1] Nalwa, H. S. (1996). *Handbook of Organic Conductive Molecules and Polymers*, J. Wiley & Sons: New York.
[2] Sun, S. S., & Sariciftci, N. S. (2005). *Organic Photvoltaics—Mechanisms. Mater. Devices*, CRC Press: Boca Raton, FL, ISBN 0-8247-5963-X.
[3] Ma, W., Yang, C., Gong, X., Lee, K., & Heeger, A. J. (2005). *Adv. Funct. Mater.*, *15*, 1617.
[4] Winder, C., & Sariciftci, N. S. (2004). *J. Mater. Chem.*, *14*, 1077.
[5] Eva, B., & Frederik, C. K. (2007). *Sol. Energy Mater. Sol. Cells*, *91*, 954.
[6] Park, J. S., Ryu, T. I., Song, M. K., Yoon, K. J., Lee, M. J., Shin, I. A., Lee, G. D., Lee, J. W., Gal, Y. S., & Jin, S. H. (2008). *J. Polym. Sci. Part A: Polym. Chem.*, *46*, 6175.
[7] Akoudad, A., & Roncali, J. (1998). *Chem. Commun.*, 2081.
[8] Zhang, F., Person, E., Wang, X., Mammo, W., Andersson, M. R., & Inganäs, O. (2005). *Adv. Funct. Mater.*, *15*, 745.
[9] Dohi, T., & Kita, Y. (2009). *Tetrahedron*, *65*, 10797.
[10] Lee, B. L., Han, K. M., Lee, E. K., Kang, I. N., Kim, D. H., & Lee, S. Y. (2009). *Synthetic Metals*, *159*, 132.
[11] Ranger, M., Rondeau, D., & Leclerc, M. (1997). *Macromolecules*, *30*, 7686.