Fine-Tuning of Fluorinated Thieno[3,4-b]thiophene Copolymer for Efficient Polymer Solar Cells

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ABSTRACT: Novel low band gap fluorinated copolymers have been synthesized and characterized. The performance of inverted polymer solar cells made by these fluorinated copolymers blended with fullerene derivatives was also investigated. The studies of the effect of fluorine units on the electronic properties and the thin film morphologies of fluorinated copolymers demonstrated that an optimal window of 20–40% fluorine units coupled with thieno[3,4-b]-thiopehene exists for a maximum hole mobility that correlated well with a dispersed interconnected morphology of the fluorinated copolymer, thus enhancing the performance of polymer solar cells. More fluorine units coupled with



thieno[3,4-b]thiopehene adversely affected the phase morphology to coarsen that in turn reduced polymer solar cells performance. Nevertheless, the polymer solar cell performance of the highest fluorinated content polymer was twice as much as the nonfluorinated copolymer. These results indicate that the electronic properties as well as the thin film morphologies, not only in nanoscale but also in microscale, of electroactive and photoactive polymers are collectively very important for organic photovoltaic devices.

INTRODUCTION

Despite the envisioned advantages and recent technology advances, so far bulk heterojunction (BHJ) polymer solar cells (PSCs) based on conjugated polymers (electron donors, D) blended with fullerene derivatives (electron acceptors, A) are still inferior to inorganic counterparts in terms of power conversion efficiency (PCE) and stability.¹⁻³ PSCs with PCE over 15% are necessary for widespread application.^{4,5} There are many factors limiting the PCE of PSCs.^{6–8} Among them, the optical and electronic properties of the BHJ composite are the most dominating factor in the overall PSCs' performance because the fundamental processes such as light harvesting, charge generation, and charge transport occur in the BHJ active layer. Toward high PCE (high short-circuit current, Jsc, and large open-circuit voltage, Voc), low band gap conjugated polymers with a deep HOMO (highest occupied molecular orbital) energy level are required.^{9–12} In addition, thin film morphology of BHJ composite plays a very important role in achieving high J_{sc} and large fill factor (FF), thus enhancing the PCE of PSCs.¹³⁻¹⁶

The use of D–A structures has become an efficient strategy to obtain low band gap polymers with deep HOMO levels and modulated electronic properties. For instance, 2,1,3-benzothiadiazole^{17,18} and 4,7-dithien-2-yl-2,1,3-benzothiadiazole^{19,20} have been copolymerized with fluorenes,^{21,22} cabazoles,^{23,24} dibenzosiloles,²⁵ dithienosloles,^{26–28} and ladder oligo-p-phenylenes^{26–28} to create novel low band gap polymers. The PSCs made by these low band gap polymers mixed with fullerene derivatives have demonstrated PCEs over 7%.^{29–31} Recently, low band gap conjugated polymers based on alternating ester substituted thieno[3,4-b]thiophene and benzodithiophene units have shown great potential for application in PSCs.³² However, the V_{oc} from the PSCs fabricated by these polymers blended with fullerene derivatives is small.

Taking all recent results and all the current studies on the electronic properties of polymer and film morphologies of BHJ active layer correlated with the molecular structures of polymers into account, we are very interested in the fluorinated copolymers based on thieno[3,4-b]thiopehene unit,^{11,12,33,34} in particular, the influence of the fluorine unit on the electronic properties of the copolymer, and thin film morphologies of BHJ active layer and their correlation with light harvest and conversion in PSCs.

In order to investigate the correlation between the fluorine unit in fluorinated copolymers and the performance of PSCs fabricated by fluorinated copolymers, a series of fluorinated copolymers based on thieno[3,4-b]thiopehene coupled with different fluorine units (Fx), PTB7-Fx (x = 0, 20, 40, 60, 80),

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Scheme 1. Synthetic Routes for Polymers PTB7-Fx



were designed, synthesized, and characterized. The performance of PSCs made of these fluorinated copolymers blended with fullerene derivatives was also investigated.

EXPERIMENTAL PROCEDURES

Polymer Characterization. The ¹³C NMR and ¹H NMR measurements were performed on the Bruker AVANCE Digital 300 MHz NMR workstation. Mass spectrometry (MS) data was obtained from the Bruker Esquire HCT PLUS with atmospheric pressure chemical ionization resource (APCI). Molecular weights of the polymers were determined by the Waters 2410 gel permeation chromatograph (GPC) with a refractive index detector in tetrahydrofuran (THF) using a calibration curve of polystyrene standards. The elemental analysis was performed on the Vario EL elemental analysis instrument (ELEMENTAR Co.).

Cyclic Voltammetry. Cyclic voltammetry (CV) measurements were carried out on the CHI800 electrochemical workstation equipped with a graphite working electrode, a saturated calomel electrode as the reference electrode, and a Pt sheet counter electrode. The measurements were done in anhydrous acetonitrile (CH₃CN) with tetrabutylammonium hexafluorophosphate ((C₄H₉)₄N(PF₆), 0.1 M) as the supporting electrolyte under an argon atmosphere at a scan rate of 50 mV/s. The potential of saturated calomel reference electrode was internally calibrated using the ferrocene/ferrocenium redox couple (Fc/Fc⁺) (0.1 eV measured under the same condition), which is assumed to have an absolute energy level of -4.8 eV.

UV–Vis Absorption Spectra. The PTB7-Fx (x = 00, 20, 40, 60, 80) solid films were cast from 1,2-dichlorobenzene (DCB) solution. UV–vis absorption spectra of PTB7-Fx thin films were measured using the HP 8453 spectrophotometer.

Mobility Measurement. Hole-only devices were fabricated to determine the hole mobility using the space charge limited current (SCLC) method.^{35,36} The mobility was determined by fitting the dark current observed from the hole-only diode according to the model of a single carrier SCLC. The structure of hole-only diode is ITO/PEDOT:PSS/PTB7- $Fx/MoO_3/Ag$, where ITO is indium tin oxide and PEDOT:PSS is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate). Approximately 30 nm thick PEDOT:PSS was casted on the cleaned ITO-glass substrate, followed by thermal annealing at 150 °C for 20 min under ambient conditions. The substrates were then

transferred into a nitrogen filled glovebox. The polymer thin films with a thickness of 120 nm were deposited from dichlorobenzene (DCB) solution by spin-casting. Subsequently, the thin films were transferred into a thermal evaporator. About a 10 nm thick MoO_3 layer and Ag (~5 nm) coated with an Al (~100 nm) layer were deposited in sequence. The effective area of the diode was measured to be 0.045 cm².

Device Fabrication. PSCs with an inverted device structure were fabricated. Patterned ITO-glass substrates were used as the cathode in the inverted PSCs. The ITO coated glass substrates were cleaned by ultrasonic washing in detergent, deionized water, acetone, and isopropyl alcohol and then dried in an oven overnight. After an oxygen plasma treatment, an ~40 nm thick ZnO thin layer was spin-coated on the ITO surface from the ZnO precursor, followed with thermal annealing at 200 °C for 30 min under ambient conditions. The substrates were then transferred into a nitrogen filled glovebox. The BHJ composite layer, PTB7-Fx:PC₇₁BM (1:1.5 by weight), was casted on the ZnO layer from DCB solution with 3% (v/v) 1,8-diiodooctane (DIO). The thickness of the BHJ composite layer is about 120 nm. Subsequently, ~10 nm thick MoO₃, Ag (\sim 5 nm thick), and Al (\sim 100 nm thick) layers were thermally deposited in sequence in vacuum. The effective area of the devices was measured to be 0.045 cm².

Device Characterization. PSCs were measured under an AM1.5G calibrated solar simulator (Newport model 91160-1000) with a light intensity of 100 mW/cm². The light intensity was calibrated by a standard silicon solar cell. The current density–voltage (J-V) characteristics were recorded with a Keithley 240 source meter.

TEM Measurement. Transmission electron microscopy (TEM) experiments were carried out with a JEOL TEM using an accelerating voltage of 120 kV.

AFM Phase Images. Tapping-mode atomic force microscopy (AFM) images were obtained by using a NanoScope NS3A system (Digital Instrument) to observe the surface morphologies of PTB7-Fx:PC₇₁BM thin films.

RESULTS AND DISCUSSION

The synthetical routes of PTB7-F*x* are described in Scheme 1. 2,6-Bis(trimethyltin-4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene (427 mg, 0.55 mmol) and Pd(PPh₃)₄ (25.4 mg, 0.022 mmol) were added into 2-ethylhexyl-4,6-dibromo-3-

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fluoro-thieno[3,4-b]thiophene-2-carboxylate (261 mg, 0.55 mmol), which was in a 250 mL three-neck round-bottom flask. The flask was subjected to three successive cycles of vacuum followed by refilling with argon. Then, anhydrous dimethylformamide (DMF, 5 mL) and anhydrous toluene (20 mL) were added via a syringe. The polymerization was carried out at 120 °C for 12 h under argon protection. The raw product was precipitated into methanol and collected by filtration. The precipitate was redissolved in chloroform and filtered to remove the metal catalyst. The final products were obtained by precipitate in isopropanol and dried in vacuum for 12 h. The yield of PTB7 is 230 mg. GPC: M_w : 41000. PD: 2.01.

PTB7-Fx (x = 20, 40, 60, and 80) was prepared in a procedure similar to that for PTB7, but used fluorinated 2-ethylhexyl-4,6-dibromo-3-fluoro-thieno[3,4-b]thiophene-2-carboxylate to replace 2-ethylhexyl-4,6-dibromo-3-fluoro-thieno-[3,4-b]thiophene-2-carboxylate. All the fluorinated copolymers possess similar molecular weight.

Figure 1 shows the CV curves of the polymers, PTB7-F00, PTB7-F20, PTB7-F40, PTB7-F60, and PTB7-F80. The



Figure 1. Cyclic voltammetry curves of the polymers PTB7-F00, PTB7-F20, PTB7-F40, PTB7-F60, and PTB7-F80.

HOMO energy levels were calculated by $E_{\text{HOMO}} = -(E^{\text{ox}} + 4.8 \text{ eV})$,³⁷ where E^{ox} is the oxidization potential of polymers. All these copolymers possess similar values of HOMO energy levels, indicating excess fluorine units have no contribution in lowering the HOMO energy levels of these copolymers.

As shown in Figure 2, all PTB7-F*x* thin films show very similar absorption spectra, indicating that no significant change in their optical properties is made after introduction of different fluorine units into thieno[3,4-b]thiopehene. The optical band gap of the copolymers obtained from their absorption edges (E_g^{opt}) is ~1.6 eV. The LUMO (lowest unoccupied molecular orbital) energy levels of these copolymers were estimated from the HOMO energy levels and E_g^{opt} . All these copolymers possesses similar values of LUMO energy levels. The HOMO and LUMO energy levels of these copolymers indicate that the energy gaps of low band gap fluorinated copolymer are not significantly tuned by excess fluorine units coupled with thieno[3,4-b]thiopehene.

The electronic properties, in particular, the hole mobilities, $\mu_{\rm h\nu}$ of these copolymers are estimated from the space-charge limited current (SCLC) method.^{35,36} Hole-only devices are



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Figure 2. Normalized absorption spectra of PTB7-Fx copolymers in solid thin films.

fabricated to measure the hole mobility. The architecture of hole-only device is ITO/PEDOT:PSS/PTB7-Fx/MoO₃/Ag. The mobility is determined by fitting the dark current according to the model of a single carrier SCLC, which is described by $J = 9/8\varepsilon_0 \varepsilon_r \mu_h (V^2)/(d^3)$, where J is the current, μ_h is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage $(V_{\rm bi})$ from the applied voltage (V_{appl}) , $V = V_{appl} - V_{bi}$. The hole-mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves. The $J^{1/2}$ ~ V curves of the hole-only device made by PTB7-Fx are shown in Figure 3. At the same conditions, the PTB7-F00 thin film possesses a $\mu_{\rm h}$ of ~1.9 × 10⁻⁴ cm²/(V s). The PTB7-F20 thin film, however, possesses a $\mu_{\rm h}$ of 9.0 \times 10⁻⁴ cm²/(V s), the highest $\mu_{\rm h}$ among these fluorinated copolymers, which is 4 times larger than that of PTB7-F00. The PTB7-F40, PTB7-F60, and PTB7-F80 thin films possess the hole mobilities of $6.2 \times$ $10^{-4} \text{ cm}^2/(\text{V s})$, $5.1 \times 10^{-4} \text{ cm}^2/(\text{V s})$, and $2.3 \times 10^{-4} \text{ cm}^2/(\text{V s})$ s), respectively. Decreased $\mu_{\rm h}$ are observed from copolymer with more fluorine units coupled with thieno[3,4-b]thiopehene. The PTB7-F80 thin film possesses the lowest $\mu_{\rm h}$ among these fluorinated copolymers. These results demonstrate that the $\mu_{\rm b}$ of fluorinated copolymers is evidently influenced by the amount of fluorine units coupled with thieno[3,4-b]thiopehene. The performance of inverted PSCs fabricated by PTB7-Fx blended with (6,6)-phenyl-C71-butyric acid methyl ester (PC₇₁BM) is investigated. The device structure of inverted PSCs is ITO/ ZnO/PTB7-Fx:PC₇₁BM/MoO₃/Ag. Figure 4 shows the typical I-V characteristics of inverted PSCs fabricated by PTB7-Fx:PC₇₁BM (1:1.5 by weight). The PSCs performance parameters are summarized in Table 1. The inverted PSCs made by PTB7-F00:PC₇₁BM, a copolymer without any fluorine unit, shows a J_{sc} of 4.9 mA/cm², a V_{oc} of 0.54 V, and an FF of 65.4%, with a corresponding PCE of 1.70%, which is lower than that observed from the conventional PSCs made by PTB7-F00:PC71BM.34 The inverted PSCs made of PTB7-F20:PC₇₁BM, a copolymer with 20% of fluorine unit, shows a $J_{\rm sc}$ of 14.55 mA/cm², a $V_{\rm oc}$ of 0.60 V, an FF of 67%, and a corresponding PCE of 5.85%. Gradually decreased J_{sct} FF, and PCE are observed from inverted PSCs made of fluorinated copolymers which have more fluorine units coupled with thieno[3,4-b]thiophene unit. However, even for the highest

polymer	$E_{\rm HOMO}^{\rm CV}~({\rm eV})$	$E_{\rm g}^{\rm opt}$ (eV)	$E_{\rm LUMO}^{\rm opt} ({\rm eV})^a$	$J_{\rm sc}~({\rm mA/cm^2})$	$V_{\rm oc}$ (V)	FF (%)	PCE (%)
PTB7-F00	-5.02	1.61	-3.41	4.9	0.54	65.4	1.70
PTB7-F20	-5.09	1.61	-3.48	14.5	0.60	67.5	5.85
PTB7-F40	-5.08	1.62	-3.46	13.3	0.60	66.4	5.28
PTB7-F60	-5.00	1.58	-3.43	11.6	0.60	63.9	4.46
PTB7-F80	-5.10	1.65	-3.45	9.8	0.60	62.6	3.75
${}^{a}E_{\text{LUMO}}^{\text{opt}} = E_{\text{HOMO}}$	$_{\rm O}^{\rm CV} + E_{\rm g}^{\rm opt}$.						

Table 1. LUMO and HOMO Energy Levels of Polymers and PSCs Performance



Figure 3. Current–voltage characteristics of hole-only device with the architecture of ITO/PEDOT/PTB7-Fx/MoO₃/Ag.



Figure 4. Current–voltage characteristics of polymer solar cells under AM1.5 condition with a light intensity of 100 mW/cm².

fluorination, PTB7-F80, the PCE of 3.75% is twice the PCE of PTB7-F00 (1.70%). These findings are consistent with the $\mu_{\rm h}$ among these fluorinated copolymers.

In order to further understand the correlation between PSCs performance and molecular structures of fluorinated copolymers, TEM and AFM are employed to investigate the thin film morphologies. Figure 5 shows the interpenetrating network morphologies of the BHJ active layer. Small isolated, segregated, polymer-rich (black area) domains (~50 nm) indicative of immiscible phase behavior are observed from the PTB7-F00:PC₇₁BM composite films (Figure 5a). This kind of morphology is not favorable for charge transport. However, large polymer-rich domains (~100 nm) and a seemingly continuous interpenetrating network are observed from PTB7-F20:PC₇₁BM composite films (Figure 5b). The PTB7-F40:PC₇₁BM and PTB7-F60:PC₇₁BM composites films show similar morphologies (Figure 5c and 5d). Nevertheless, partially segregated polymer-rich domains present in these films thus would break the interpenetrating network. Larger and coarse segregated domains are observed from the PTB7-F80:PC₇₁BM composite films (Figure 5e). These TEM images indicate that the thin film morphologies for PTB7-F*x*:PC₇₁BM were influenced by the amount of fluorine units in the fluorinated copolymers. Increasing the coupled fluorinate units over 20– 40% into thieno[3,4-b]thiopehene to form fluorinated copolymers will not enhance the formation of finely dispersed and potentially interconnected domain and phase separation.

AFM phase images of the BHJ active layers are also studied to further confirm the film morphologies observed from TEM images. Figure 6 shows the AFM phase images of BHJ active layer. All the films form similarly nanometer-scale fibrillar domains (nanofibril domains); however, the shape and connectivity of the nanofibril domains are dependent on the fluorine unit. Partial isolated nanofibril domains are observed from the PTB7-F00:PC₇₁BM composite films (Figure 6a). These coarse domains will not benefit the charge transport. Only fewer isolated domains are observed from the PTB7-F20:PC₇₁BM composite films. The PTB7-F40:PC₇₁BM (Figure 6c) and PTB7-F60:PC71BM (Figure 6d) composite films show similar morphologies with PTB7-F20:PC71BM films, although continuous domain walls are also observed from the PTB7-F40:PC71BM composite films. However, larger phase separation is observed from the PTB7-F80:PC71BM composite film (Figure 6e), which results in larger nanofibril domains than those from other composite films. These large nanofibril domains will induce a high energy barrier for interfibrillar hopping,35 resulting in a low carrier mobility among the fluorinated copolymers. As a result, the PSCs made of fluorinated copolymers with more fluorinate units coupled with thieno[3,4-b]thiopehene showed a decreased PCE.

CONCLUSIONS

In conclusion, new low band gap fluorinae-thienothiophene copolymer are designed and synthesized. Inverted polymer solar cells are fabricated by these copolymers. The studies of the effect of fluorine units on the electronic properties and the thin film morphologies of fluorinated copolymers demonstrate that an optimal window of 20–40% fluorine units coupled with thieno[3,4-b]thiopehene exist for maximum hole mobility that correlates well with a dispersed interconnected morphology of the fluorinated polymer, thus enhanced polymer solar cell performance. An efficiency of 5.85% is observed from PSCs made of copolymers with 20% fluorine units. More fluorine units coupled with thieno[3,4-b]thiopehene adversely affects the phase morphology to coarsen that in turn reduce the device



Figure 5. TEM bright field images of PBT7-Fx:PC₇₁BM films: (a) PTB7-F00:PC₇₁BM, (b) PTB7-F20:PC₇₁BM, (c) PTB7-F40:PC₇₁BM, (d) PTB7-F60:PC₇₁BM, and (e) PTB7-F80:PC₇₁BM.



Figure 6. AFM phase images of the PTB7-Fx:PC₇₁BM: (a) PTB7-F00:PC₇₁BM, (b) PTB7-F20:PC₇₁BM, (c) PTB7-F40:PC₇₁BM, (d) PTB7-F60:PC₇₁BM, and (e) PTB7-F80:PC₇₁BM.

performance. These results indicate that the electronic properties as well as the thin film morphologies, not only in nanoscale but also in microscale, of electroactive and photoactive polymers are collectively very important for organic photovoltaic devices.

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Notes

The authors declare no competing financial interest.

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