

Synthesis and Solar Cells Applications of EO-PF-DTBT Polymer

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ABSTRACT: Poly{[2,7-(9,9-bis-(1-(2-(2-methoxyethoxy)ethoxy)ethyl)-fluorene)]-alt-[5,5-(4,7-di-2'-thienyl-2,1,3-benzothiadiazole)]} (EO-PF-DTBT) was synthesized by Suzuki coupling reaction. The polymer is soluble in common organic solvent, such as toluene, THF, and chloroform, and it also shows solubility in polar solvent, such as cyclopentanone. Solar cells based on EO-PF-DTBT and PC₆₁BM show maximum power conversion efficiency of 2.65% with an open circuit voltage (V_{OC}) of 0.86 V, a short circuit current density (J_{SC}) of 6.10 mA/cm², and a fill factor of 51% under AM 1.5G illumination at 100 mW/cm², which is the best results for fluorene and 4,7-di-2-thienyl-2,1,3-benzothiadiazole copolymers and PC₆₁BM blend. The 1,8-diiodooctane can work well to reduce the over-aggregated phase structure in polymer solar cells. Our results suggest that the introducing high hydrophilic side chain into conjugated polymer donor materials can tune the aggregation structure and improve the solar cells performances. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40478.

KEYWORDS: optical and photovoltaic applications; morphology; conducting polymers

Received 2 December 2013; accepted 17 January 2014

DOI: 10.1002/app.40478

INTRODUCTION

In recent years, polymer solar cells (PSCs) with bulk heterojunction (BHJ) structure are particularly attractive because of their ease of processing, large area with mechanical flexibility, and potential low-cost production.¹ So far, great efforts have been devoted to designing new polymers used as active layer in BHJ structure. The highest power conversion efficiency (PCE) of the devices based on polymer donors has reached 9–10%.² Among the variety of conjugated polymers, poly(p-phenylenevinylene) (PPV), polythiophene (PT), polybenzodithiophene (BDT), and poly(alkylfluorene) (PF) are typical p-type electron donor materials.^{3,4}

Typically, polyfluorene is a wide band gap polymer.⁵ Narrow band gap segment is incorporated in the polyfluorene backbone to tune the band gap and the energy level of polyfluorene, which make it suitable for solar cell applications. Narrow band gap polyfluorene was first synthesized by alternating copolymerization of fluorene and 4,7-dithienyl-2,1,3-benzothiadiazole (DTBT).⁶ In 2003, Andersson and coworkers report one fluorene and DTBT based polymer-poly{[2,7-(9-(2-ethylhexyl)-9-hexylfluorene)]-alt-[5,5-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)]} (PFDTBT).⁷ The solar cells based on this polymer as donor and PC₆₁BM as acceptor show PCE of 2.2%, and this is the best results of the PSCs in 2003. This polymer show moderate molecular weight with $M_n = 4800$, and the limited solubility of the polymer

arises from the large number of unsubstituted aromatic ring in the polymer backbone, which make the high molecular weight polymer insoluble.⁷ In 2002 and 2004, Cao and coworkers decreased the molar percentage of insoluble DTBT down to 35% in the polymer backbone, which make the polymer show relatively high molecular weight with $M_n = 11,000$.⁸ The solar cells based on this polymer as donor and PC₆₁BM as acceptor show PCE of 1.95%,⁹ which performance is similar with Andersson's results probably due to the declined molar percentage of main absorption units DTBT. In 2004, Cao and coworkers introduced one chain to the thiophene unit in PF-DTBT polymer to make the polymer-poly{[2,7-(9,9-bis-(dioctylfluorene)]-alt-[5,5-(4,7-di-(4-hexylthien-2-yl)-2,1,3-benzothiadiazole)]} (PF-DHTBT), which show high molecular weight about $M_n = 40,000$, but solar cell performance is not reported.¹⁰ In 2009, Yang and Hou reported two new materials based on PF-DTBT, poly{[2,7-(9,9-bis-(2-ethylhexyl)-fluorene)]-alt-[5,5-(4,7-di-2'-thienyl-2,1,3-benzothiadiazole)]} (BisEH-PFDTBT) and poly{[2,7-(9,9-bis-(3,7-dimethyl-octyl)-fluorene)]-alt-[5,5-(4,7-di-2'-thienyl-2,1,3-benzothiadiazole)]} (BisDMO-PFDTBT).¹¹ By introducing a long and branched chain to the fluorene units, these two polymers show high molecular weight about $M_n = 20,000$ with narrow PDI around 1.3 to 1.5, and the record-high PCE around 4.5% was reported for PF-DTBT with PC₇₁BM. In 2012, Hwang group reported that introducing one flat

perylene unit into the PF-DTBT backbone can enhance the π - π interaction, which will benefit the solar cells performances. The solar cells based on polymer PF-DTBT with 10% perylene units in the backbone and PC₇₁BM show PCE around 3.16%.¹²

Poly-ether group is widely introduced into the polyfluorene side chain to act as Li salt transporting materials in polymer light emitting electrochemical cell.^{13–15} There also are reports that poly-ether with Li salt blend can be used as electrochemical dopant to form the p-i-n junction, which can help the carrier dissociation and charge transport in MEH-PPV and PCBM BHJ solar cells.¹⁶ In 2007, Zhang et al. demonstrated that a solution-processed poly(ethylene oxide) (PEO) layer could form dipoles at the active layer/Al interface, resulting in enhanced PCE and V_{oc} .¹⁷ The hydrophilic side group is also reported to have strong tendency to form aggregation in polymer materials,¹⁸ and this will be helpful to modulate the synthesized solar cells donor materials and PCBM blend thin film morphology, which have been proved to be key factor for high performances solar cells.¹⁹

In this article, we report one new member of PF-DTBT polymers EO-PF-DTBT, which we introduce 1-(2-(2-methoxyethoxy)ethoxy)ethyl into the fluorene unit as side chain. The polymer was synthesized by polymerizing 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-(1-(2-(2-methoxyethoxy)ethoxy)ethyl)-fluorene with 4,7-bis-(5-bromo-2-thienyl)-2,1,3-benzothiadiazole. The polymer is soluble in common organic solvent, such as THF and chloroform, and it also shows solubility in polar solvent, such as cyclopentanone. The hydrophilic properties of 1-(2-(2-methoxyethoxy)ethoxy)ethyl chain and the resulted aggregation properties make this polymer show unusual behavior in organic electronic applications.

EXPERIMENTAL

Materials

All the reagents were obtained from Aldrich, Aladdin, Energy Chemical and Fluka, and used as received. 2,7-Dibromo-fluorene (1) and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di(1-(2-(2-methoxyethoxy)ethoxy)ethyl)fluorene (6) were characterized by the ¹H NMR spectra.

Characterization

¹H NMR spectrum was recorded on a Bruker Advance III 600 (600 MHz). UV-vis absorption spectra were recorded using a Shimadzu UV-1750 spectrophotometer. Photoluminescence (PL) spectra were measured on a Fluorolog-3 fluorescence spectrometer. Cyclic voltammetry (CV) measurements were performed on a LK2005A electrochemical workstation with glassy carbon working electrode, an Ag/AgCl reference electrode and a platinum column counter electrode. Surface roughness and morphology of thin films were characterized by atomic force microscopy (AFM) on an Agilent 5400. The X-ray diffraction (XRD) pattern was obtained on a Bruker D8 ADVANCE. The transmission electron microscopy (TEM) images were obtained on TEM, H-7650, Japan.

Device Fabrication

Solar cells devices were fabricated on 15 × 15 mm² prepatterned indium tin oxide (ITO) coated glass substrates with a

layered structure of ITO/PEDOT:PSS(30 nm)/EO-PF-DTBT:PC₆₁BM(~80 nm)/Ca(10 nm)/Al(100 nm). The ITO coated glass substrates were cleaned in acetone, detergent, deionized water, and isopropyl alcohol sequentially. The substrates were then oxygen plasma treated for 20 min, spin coated with PEDOT: PSS at 5000 rpm, and dried in an oven for 20 min at 160°C. The EO-PF-DTBT and PC₆₁BM were dissolved in deoxygenated anhydrous chloroform in the weight ratios of 1:2 and stirred overnight in a nitrogen filled glovebox. An active layer consisting of the blend of EO-PF-DTBT and PC₆₁BM was then spin coated on PEDOT:PSS with a thickness of 80 nm. Typical concentration of the EO-PF-DTBT/PC₆₁BM blending solution was 10 mg/mL. Subsequently, Ca (10 nm) and aluminum (100 nm) were thermally evaporated at a vacuum of $\sim 2 \times 10^{-4}$ Pa on top of the active layer as a cathode. The device area was 0.1 cm² defined by the shadow mask. Photovoltaic performance was characterized under illumination with an AM1.5 (100 mW/cm²) in a nitrogen atmosphere (<0.1 ppm H₂O and O₂), and current voltage curves was recorded by Keithley 2420. The external quantum efficiencies (EQE) of solar cells were analyzed using a certified Newport incident photon conversion efficiency (IPCE) measurement system.

Synthesis

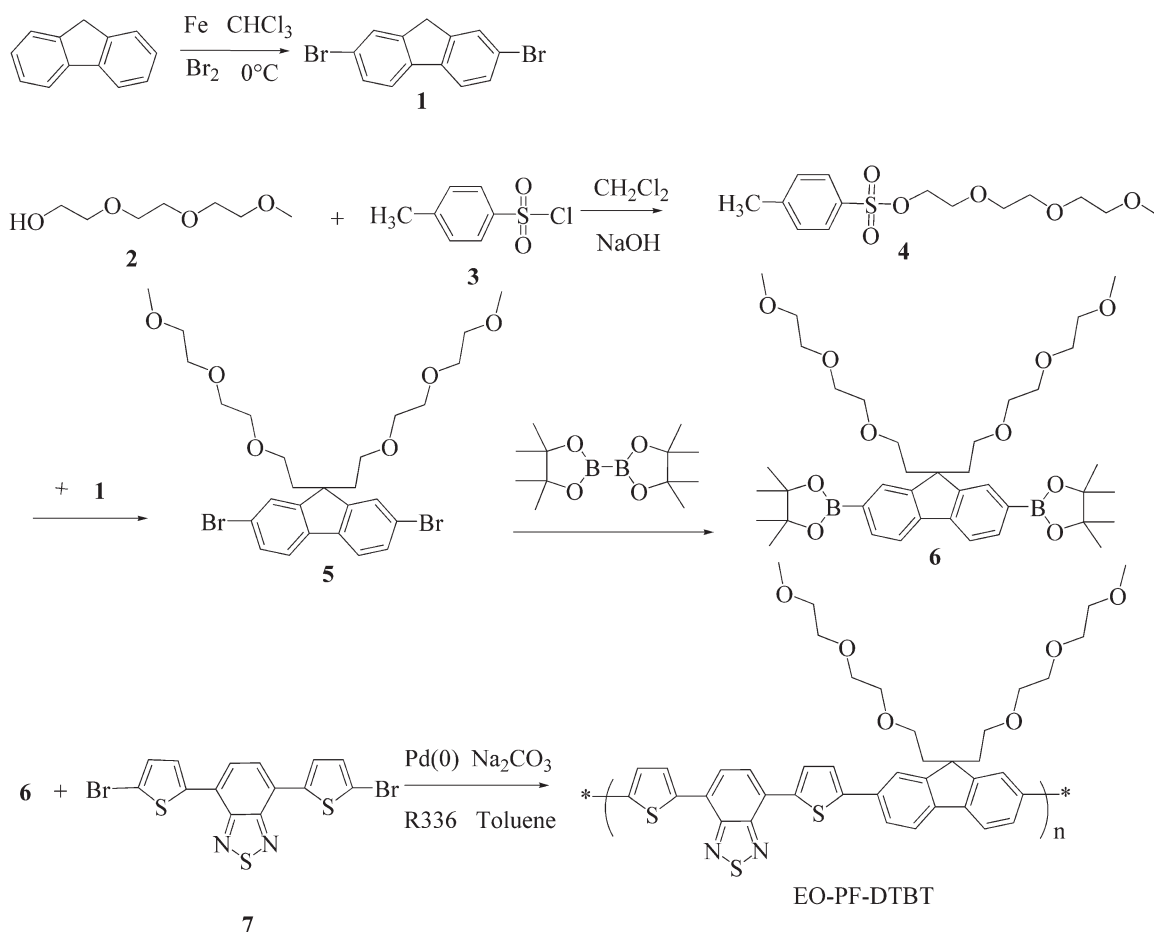
2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di(1-(2-(2-methoxyethoxy)ethoxy)ethyl)fluorene (6)^{20,21}. A mixture of 9,9-bis(2-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)-2,7-dibromo-fluorene (3.08 g, 5 mmol), KOAc (4.7 g, 48 mmol), bis(pinacolato)diborane (3.15 g, 12.4 mmol), and Pd(dppf)Cl₂ (73.1 mg, 0.1 mmol) in 40 mL of degassed 1,4-dioxane was stirred for 24 h at 80°C under argon atmosphere. After cooled to room temperature, water and ether were added to the mixture, and the separated organic layer was dried over anhydrous MgSO₄. After the removal of the solvent under reduced pressure, the crude product was recrystallized from ethanol to get white crystals.

¹H-NMR (600 MHz, CDCl₃, δ): 7.865 (s, 2H), 7.826 (dd, J = 7.8 Hz, 2H), 7.721 (dd, J = 6.0 Hz, 2H), 3.535 (m, 4H), 3.490 (m, 4H), 3.414 (m, 4H), 3.353 (s, 6H), 3.205 (m, 4H), 2.699 (m, 4H), 2.261 (m, 4H), 1.416 (s, 24H).

Polymer EO-PF-DTBT. Polymer EO-PF-DTBT was synthesized via a Suzuki coupling reaction of monomer 6 and 4,7-bis-(2-bromo-5-thienyl)-2,1,3-benzothiadiazole (DTBT). Monomer 6 (0.289 g, 0.407 mmol), DTBT (0.1832 g, 0.4 mmol), Pd(dba)₃ (7.3 mg), P(o-tol)₃ (19.5 mg), and Aliquat 336 were dissolved in a mixture of toluene and an aqueous solution of 2 mL K₂CO₃ (2M). The solution was refluxed with vigorous stirring at 90°C for 48 h in an argon atmosphere. At the end of polymerization, the polymers were end-capped with 2 mL bromobenzene. The organic mixture was then poured into methanol and the polymer precipitate was separated by filtration. The polymer was purified by Soxhlet extraction, air-dried, and followed by drying in vacuum at room temperature.

¹H NMR (600MHz,CDCl₃) δ : 8.18, 7.97, 7.73, 7.78, 7.53, 3.51, 3.45, 3.30, 2.92, 2.55.

$M_n = 5900$, $M_w/M_n = 1.41$



Scheme 1. Synthetic routes to EO-PF-DTBT.

RESULTS AND DISCUSSION

Synthesis and Characterization

Poly{[2,7-(9,9-bis-(1-(2-(2-methoxyethoxy)ethoxy)ethyl)-fluorene)]-alt-[5,5-(4,7-di-2'-thienyl)-2,1,3-benzothiadiazole]} (EO-PF-DTBT) was synthesized by polymerizing 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-(1-(2-(2-methoxyethoxy)ethoxy)ethyl)-fluorene with 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole by Suzuki coupling reaction. The synthetic routes to the polymer are shown in Scheme 1. The polymer is soluble in common organic solvent, such as toluene, THF, and chloroform,

and it also shows solubility in polar solvent, such as cyclopentanone. The polymer was characterized by ^1H NMR, and the chemical shift from 3.5 to 2.5 is assigned to the polar 1-(2-(2-methoxyethoxy)ethoxy)ethyl side group. The peaks at ca 7.52, 7.79, and 7.81 are assigned to the six hydrogen atoms in the DTBT units. The molar ratio of substituted fluorene to DTBT in the copolymer estimated by ^1H NMR peak areas are 45 : 55, which is in agreement with the feed ratio (50 : 50) of the monomers. The soluble part of the polymer shows a number-average molecular weight of 5900 and polydispersity

Table I. Basic Properties and Solar Cells Performance Based on EO-PF-DTBT : PC_{61}BM Blends and Other Reported High-Performance PF-DTBT Copolymers

| Materials | Uv-vis Peak (nm) | E_g | $M_n \times 10^3$ | Acceptor/Cathode | D/A ratio | V_{oc} | J_{sc} | FF | PCE (%) | Refs. |
|------------------|------------------|-------|-------------------|-----------------------------------|-----------|----------|----------|----|---------|-----------|
| EO-PF-DTBT | 397,566 | 1.89 | 5.9 | PC_{61}BM Ca/Al | 1 : 2 | 0.89 | 4.41 | 53 | 2.09 | This work |
| EO-PF-DTBT + DIO | 397,566 | 1.89 | 5.9 | PC_{61}BM Ca/Al | 1 : 2 | 0.86 | 6.10 | 51 | 2.65 | This work |
| PFDTBT | 545 | - | 4.8 | PC_{61}BM LiF/Al | 1 : 4 | 1.04 | 4.66 | 46 | 2.2 | 7 |
| PFO-DTBT35 | 388,551 | 2.01 | 11 | PC_{61}BM Ba/Al | 1 : 2 | 0.95 | 4.59 | 35 | 1.95 | 9 |
| BisEH-PFDTBT | - | - | 21 | PC_{71}BM Ca/Al | 1 : 3 | 0.95 | 8.4 | 44 | 3.5 | 11 |
| BisDMO-PFDTBT | - | - | 20 | PC_{71}BM Ca/Al | 1 : 3 | 0.97 | 9.1 | 51 | 4.5 | 11 |
| PFDTBT_10Per | 390,558 | 1.92 | 12 | PC_{71}BM LiF/Al | 1 : 5 | 0.74 | 7.19 | 40 | 2.16 | 12 |
| PFDTBT_10Per | 390,558 | 1.92 | 12 | PC_{71}BM TiOx/Al | 1 : 5 | 0.81 | 9.61 | 41 | 3.16 | 12 |

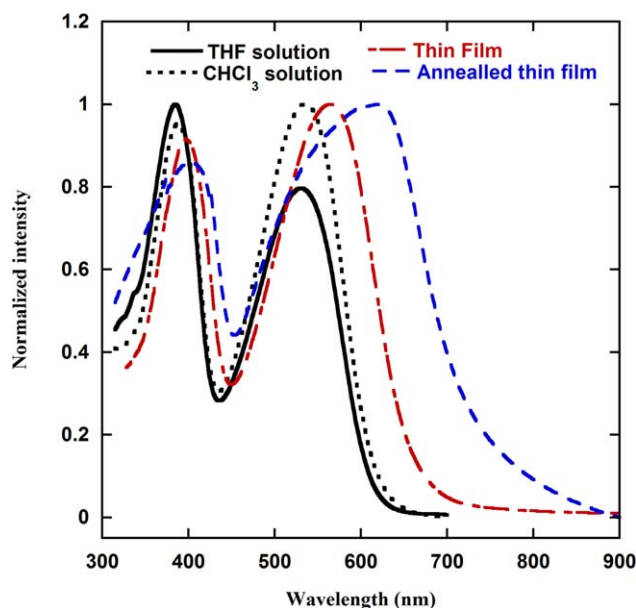


Figure 1. UV-vis absorption spectra of EO-PF-DTBT in THF solution, CHCl_3 solution, and thin solid film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of 1.41, which is relatively low molecular weight in PF-DTBT polymer family (Table I) probably due to high molecular weight section is insoluble.

UV-Vis Absorption Properties

The normalized UV-vis absorption spectra of EO-PF-DTBT in THF solution, CHCl_3 solution, solid film, and annealed thin film are shown in Figure 1. The absorption spectrum of EO-PF-DTBT in solution shows two broad peaks at 384 and 531 nm.

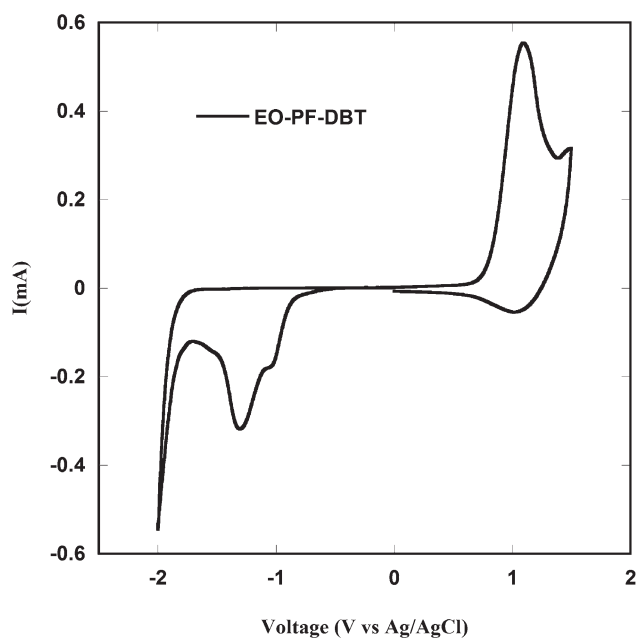


Figure 2. Cyclic voltammogram of EO-PF-DTBT coated on a platinum working electrode in a 0.1M LiClO_4 solution in acetonitrile (Scan rate is 50 mV/s).

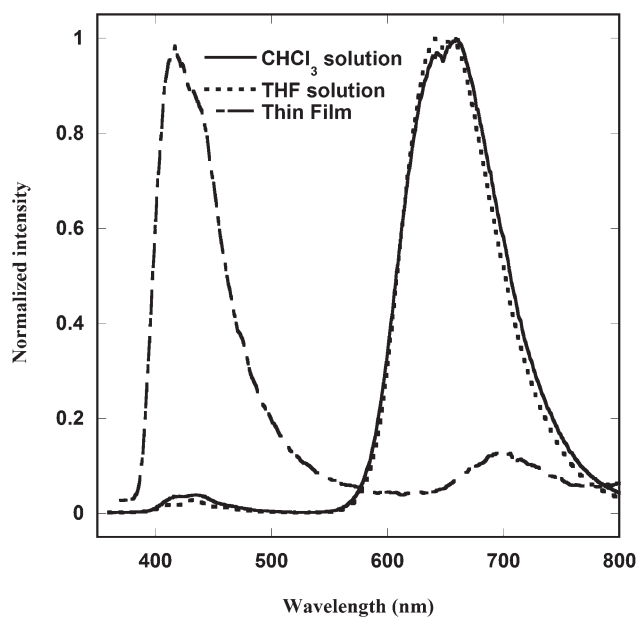


Figure 3. PL spectra of EO-PF-DTBT in THF solution, CHCl_3 solution, and thin solid film (excitation: 350 nm).

In thin film, the maximum absorption wavelengths are at 397 and 566 nm and the optical band gap obtained from UV-vis absorption onset is 1.89 eV (655 nm). The DTBT unit absorption peak redshifts about 10 nm as compared with the PF-DTDT polymer without poly ether side chain (Table I). The thin films show a similar but red-shifted absorption spectrum when compared with the solution. The absorption maxima of thin film are red-shifted by 13 nm (λ_{max1}) and 35 nm (λ_{max2}) when compared with solutions. This behavior can be attributed to strong polymer interchain interaction and the hydrophilic

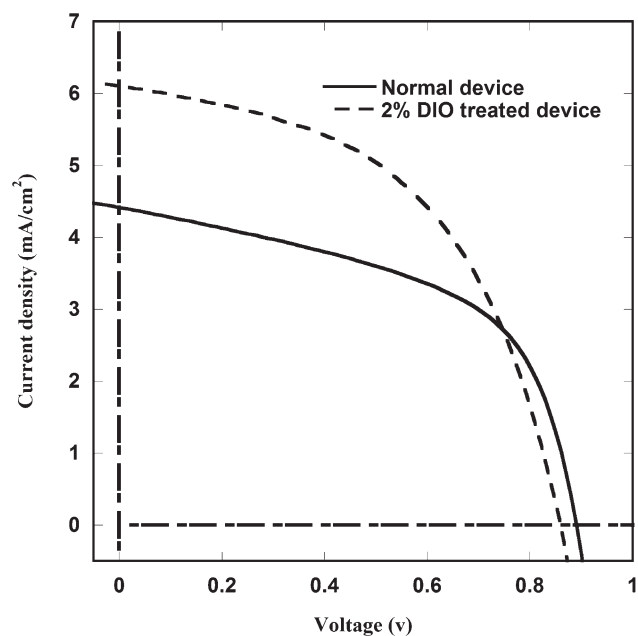


Figure 4. Current density-voltage (J - V) curves of EO-PF-DTBT with or without DIO treatment.

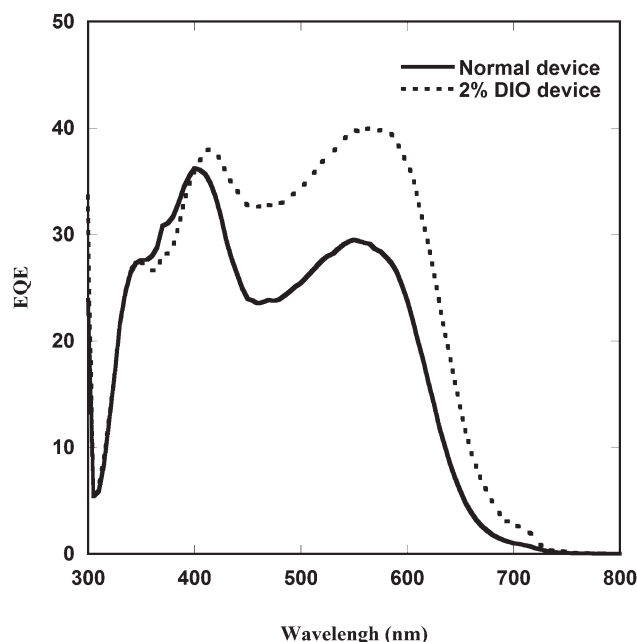


Figure 5. EQE curve of devices with or without DIO treatment (EO-PF-DTBT : PC₆₁BM = 1 : 2).

1-(2-(2-methoxyethoxy)ethoxy)ethyl chain induced aggregation in the solid state. The UV-vis absorption spectra of EO-PF-DTBT annealed thin film show obvious redshift as compared with pristine film. This might come from increased aggregations after annealing. As far as we know, this is the most obvious aggregation induced UV-vis absorption red-shifts in PF-DTBT family.^{22,23}

Electrochemical Properties

The electrochemical properties of EO-PF-DTBT were investigated by CV methods. Figure 2 shows the cyclic voltammograms of EO-PF-DTBT film on a glassy carbon working electrode with 0.1M LiClO₄/CH₃CN as the electrolyte and Ag/AgCl as the reference electrode. The onset potentials of p-doping and n-doping are

0.82 and -0.88 V, respectively. The HOMO and LUMO levels are calculated according to the empirical formula $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.4)$ (eV) and $E_{\text{LUMO}} = -(E_{\text{re}} + 4.4)$ (eV). The calculated HOMO and LUMO level of EO-PF-DTBT are -5.22 and -3.52 eV, respectively. The energy band gap of EO-PF-DTBT calculated from HOMO and LUMO levels is 1.70 eV, which is consistent with the optical bandgap (1.89 eV) estimated from absorption onset in thin solid film.¹³

PL Properties

The normalized PL spectra of the polymer EO-PF-DTBT in THF solution, CHCl₃ solution (concentration ca. 0.002 mg/mL) and thin solid film are shown in Figure 3. In solution, the PL peaks are around 420 and 650 nm, which is attributed to polyfluorene and DTBT, respectively. In solid state, the PL peaks are around 417 and 698 nm, which show obvious emission from polyfluorene parts. It is very unusual that polyfluorene PL emission is not quenched in solid states for one narrow band gap alternating polyfluorene. In thin solid films, polyfluorene PL emission is completely quenched, and PL emission consists exclusively of DTBT emission at DTBT concentrations as low as 1% in PF-DTBT polymer system.⁸ The difference between PF-DTBT and EO-PF-DTBT is the side chain, so the poly-ether side chain plays some important role in this phenomenon. The hydrophilic poly ether is introduced as PF-DTBT side chain, which might induce strong aggregation, and this could twist the polymer backbone to make the interchain and intrachain energy transfer from PF segment to DTBT units difficult. So in the solid state EO-PF-DTBT PL spectrum there are emissions from both PF and DTBT. However, the mechanism of this unusual phenomenon needs further study.

Photovoltaic Performance

The solar cells devices were fabricated with device structure ITO/PEDOT : PSS/EO-PF-DTBT : PC₆₁BM/Ca/Al. The weight ratio of EO-PF-DTBT to PC₆₁BM is 1 : 2. The *J-V* curves of the device with or without 2% weight 1,8-diiodooctane (DIO) treatment are shown in Figure 4, and the photovoltaic performances are listed in Table I. The maximum PCE of 2.65% was

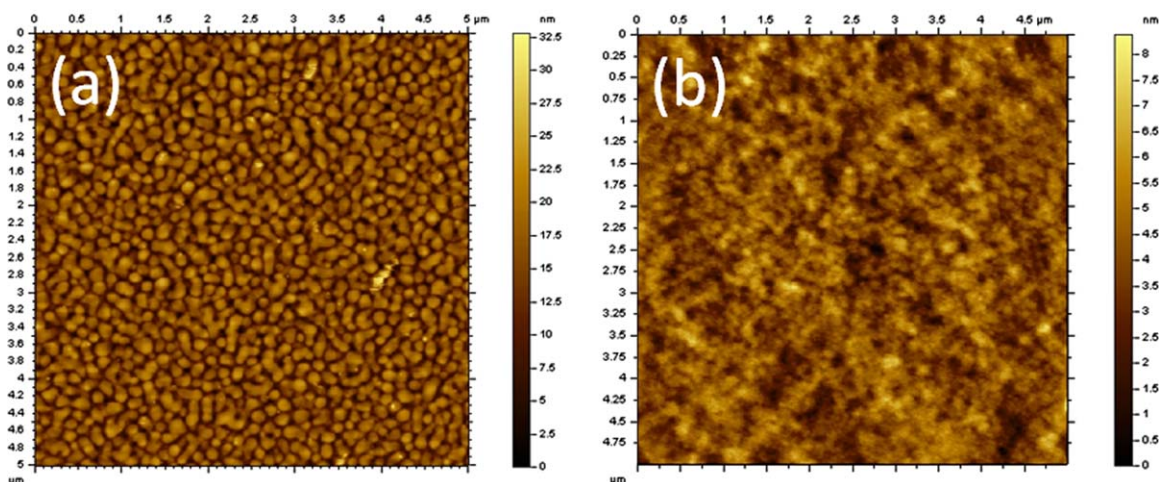


Figure 6. AFM images of (a) EO-PF-DTBT : PC₆₁BM = 1 : 2 blend film and (b) DIO treated film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

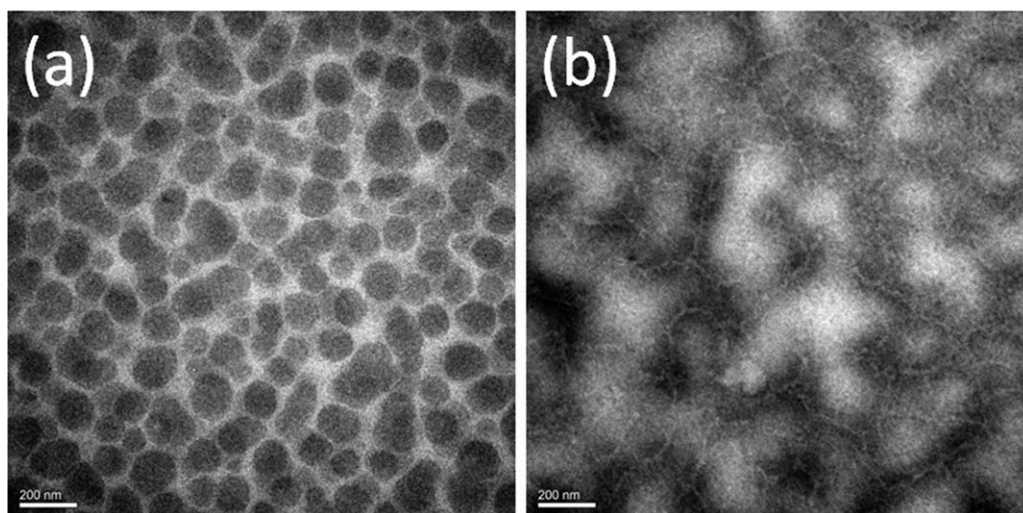


Figure 7. TEM images of EO-PF-DTBT : PCBM (1 : 2) composite thin film (a) without and (b) with DIO treatment.

obtained with an open circuit voltage (V_{OC}) of 0.86 V, a short circuit current density (J_{SC}) of 6.10 mA/cm², and a fill factor (FF) of 51% under AM 1.5G illumination at 100 mW/cm² for the DIO treated devices. The EO-PF-DTBT based device performance is the best in PF-DTBT materials and PC₆₁BM based solar cells,^{7,9} which is a little lower than PC₇₁BM based device.^{11,12} This is common in PSCs for the different energy level of PC₇₁BM and PC₆₁BM and the relative high and wide absorption of PC₇₁BM, which also contribute to the solar cell performances. The EO-PF-DTBT based device without DIO treatment shows around 0.1 V lower Voc, similar J_{sc} and a little higher FF as compared with PF-DTBT family materials, which make the final PCE is almost the same.⁷ (Table I) The DIO treated devices show increased J_{sc} (6.10 mA/cm²), then EO-PF-DTBT based device shows higher PCE than the reported PF-DTBT with hydrophobic alkyl chain, which might come from the hydrophilic poly ether side chain can help to modulate the blend film morphology⁷ (Table I). We further measured the EQE curve to investigate the response range of the devices (Figure 5). The J_{SC} calculated from the EQE is 5.91 and 4.23 mA/cm², which are in good agreement with tested J_{SC} 6.10 and 4.41 mA/cm² of the device with or without DIO treatment. As a comparison, the basic properties and solar cells performance based on EO-PF-DTBT : PC₆₁BM blends and other reported high-performance fluorene and 4,7-di-2-thienyl-2,1,3-benzothiazole copolymers (PF-DTBT)^{7,9,11,12} are listed in Table I. The AFM images of EO-PF-DTBT and PC₆₁BM blend film with or without DIO treatment are shown in Figure 6. It is found that the surface of EO-PF-DTBT : PCBM (1 : 2) composite thin film is not very smooth [Figure 6(a)], and its root-mean-square (RMS) of roughness is about 4.21 nm. This is the evidences of the extraordinarily strong interchain interaction of EO-PF-DTBT in the solid state film. The AFM images of DIO treated EO-PF-DTBT and PC₆₁BM blending film is show in Figure 6(b), which show relative smooth surface and the RMS value is only 1.02 nm. This can help to forming more polymer and PC₆₁BM interface. Typically in polymer solar cell research, the DIO is used to induce aggregation in polymer phase, which will

increase interface area of the active materials. The EO-PF-DTBT polymer shows very strong aggregation capability [Figure 6(a)], which is not very common in PSCs donor materials. The TEM images of EO-PF-DTBT : PCBM (1 : 2) composite thin film without and with DIO treatment are shown in Figure 7(a,b), respectively. In the Figure7(a), the dark spherical regions with domain size around 100–200 nm are attributed to molecular aggregation of EO-PF-DTBT, which is consistent well with the AFM results [Figure 6(a)]. For the TEM of DIO treated EO-PF-DTBT : PCBM (1 : 2) film [Figure 7(b)], there is not any obvious aggregation, which is also consistent with the AFM smooth surface [Figure 6(b)]. The XRD pattern of EO-PF-DTBT : PCBM (1 : 2) composite thin film is shown in Figure 8, and there is not any diffraction peak observed, which means

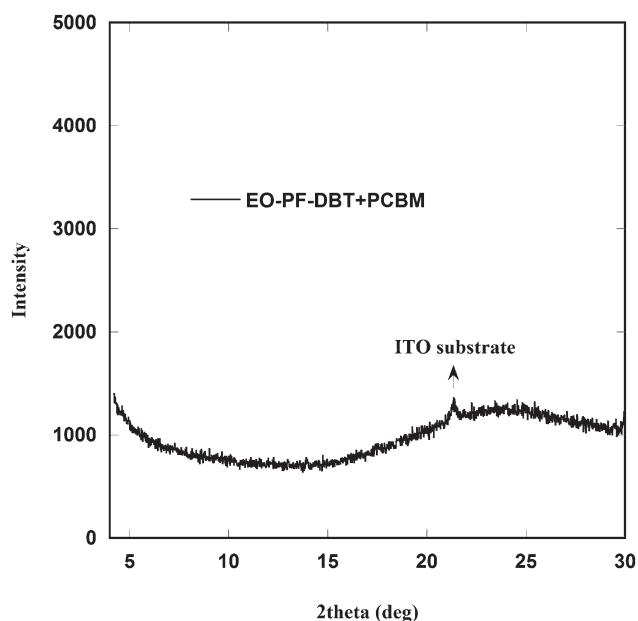


Figure 8. XRD pattern of EO-PF-DTBT : PCBM (1 : 2) composite thin film.

there is not any ordered structure in the aggregation. Our results suggest that DIO works well to reduce the over-aggregated phase structure in PSCs active layer. Further work to utilize the unique solubility of the polymer in polar solvent such as cyclopentanone to optimize the device performance is underway.

CONCLUSIONS

Poly{[2,7-(9,9-bis-(1-(2-(2-methoxyethoxy)ethoxy)ethyl)-fluorene)]-alt-[5,5-(4,7-di-2'-thienyl-2,1,3-benzothiadiazole)]} (EO-PF-DTBT) was synthesized by Suzuki coupling of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-di-(1-(2-(2-methoxyethoxy)ethoxy)ethyl)-fluorene with 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole. The polymer is soluble in common organic solvent, such as toluene, THF, chloroform, and cyclopentanone. Solar cells based on EO-PF-DTBT and PC₆₁BM show maximum PCE of 2.65%, which is the best results for PF-DTBT copolymers and PC₆₁BM blend. The DIO can work well to reduce the over-aggregated phase structure in PSCs. Our results suggest that introducing high hydrophilic side chain in solar cells donor materials PF-DTBT can tune the aggregation structure.

ACKNOWLEDGMENTS

The authors are deeply grateful to the National Natural Science Foundation of China (Project no. 21274134, 51173199, 61107090), New Century Excellent Talents in University (NCET-11-0473), Shandong Provincial Natural Science Foundation (ZR2011BZ007), and Qingdao Municipal Science and Technology Program (13-1-4-200-jch, 11-2-4-22-hz) for financial support.

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