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Processing temperature control of a diketopyrrolopyrrole-*alt*-thieno [2,3-*b*]thiophene polymer for high-mobility thin-film transistors and polymer solar cells with high open-circuit voltages



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A R T I C L E I N F O

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ABSTRACT

We synthesized a planar pDPPTTi-OD polymer based on diketopyrrolopyrrole (DPP) and thieno [2,3-*b*] thiophene (TTi) and investigated the electrical properties of the pDPPTTi-OD polymer. pDPPTTi-OD films displayed a low optical bandgap of 1.57 eV, and HOMO and LUMO levels of -5.40 and -3.74 eV, respectively. The 150°C-annealed pDPPTTi-OD films showed a high hole mobility of 0.16 cm²V⁻¹s⁻¹ in organic thin-film transistor (OTFT) devices. The photovoltaic properties of polymer solar cells (PSCs) incorporating the pDPPTTi-OD were also measured. A pDPPTTi-OD:PC₇₁BM blend film was spin-coated at 25, 70 and 90 °C. High-temperature processing significantly improved the power conversion efficiency of PSCs by effectively reducing the PC₇₁BM domain sizes, which improved the miscibility between pDPPTTi-OD and PC₇₁BM. This work demonstrated that the TTi moiety is a useful donor building block for high-performance D–A type polymers in OTFTs and PSCs, and that processing temperatures should be controlled to fully realize the materials' beneficial intrinsic properties.

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1. Introduction

Conjugated polymers have been developed for use in highperformance polymer solar cells (PSCs). The photovoltaic properties of such PSCs have great potential in low-cost, light-weight flexible applications such as future energy sources [1,2]. Intensive synthetic efforts to synthesize donor (D)-acceptor (A)-type polymers have significantly improved power conversion efficiencies (PCEs) [2–5]. The connection of electron-rich donor moieties with electron-deficient acceptor moieties can lower an optical bandgap and optimally position the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels for broader absorption of sunlight, efficient charge separation and a

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http://dx.doi.org/10.1016/j.polymer.2016.10.024 0032-3861/© 2016 Elsevier Ltd. All rights reserved. high open-circuit voltage (V_{oc}). While oligothiophenes or benzo [1,2-b:4,5-b']dithiophenes have frequently been used as donors, diketopyrrolopyrroles (DPPs) [3,6–8] and benzothiadiazole (BTs) [4,9] have been used as acceptors. Although BT-based D-A-type polymers currently outperform DPP-based polymers, the latter are particularly advantageous in terms of absorbing low-energy photons. Hence, they are good candidates for visibly transparent solar cells and tandem solar cells [10–13]. A limiting photovoltaic parameter in most DPP-based photovoltaic devices is the low $V_{\rm oc}$ value (typically < 0.7 V) [6.14–17]. This is mainly because DPPs as acceptor moieties were often connected alternately with thieno [3,2-*b*]thiophenes or dialkoxybenzo [1,2-*b*:4,5-*b*']dithiophenes, which provided planar polymer backbones. These structured polymers displayed low bandgaps of 1.2-1.31 eV, high-lying HOMO levels ranging from -5.10 to -5.16 eV with high carrier mobilities over 1 cm² V⁻¹s⁻¹ [6,7,14,18,19]. To approach a predicted high-PCE zone, DPPs were polymerized with phenyl (a weak donor) linkages.

This connection resulted in tuning the bandgap and HOMO level of the DPP-based polymers positively for high photovoltaic properties [19–22]. However, the phenyl linkage may disfavor efficient charge transport because of increased dihedral angles along the polymer backbone [23,24].

In searching for new and appropriate donor moieties that would provide both high backbone planarity and deep-lying HOMO levels, the thieno [2,3-*b*]thiophene (TTi) moiety is an interesting donor candidate and it has been rarely used in the synthesis of D–A-type polymers. The literature indicates that the TTi moiety is a less electronically communicating moiety compared with thieno [3,2-*b*] thiophene, which can keep the HOMO levels of DPP polymers low [25,26]. Moreover, the linkage of DPPs with TTi units in the polymer backbone would provide planarity, which could in turn provide good charge transport behavior in organic thin-film transistors (OTFTs) [17,18].

Herein we report the synthesis and electrical properties of an alternating polymer of poly (2,5-bis(2-octyldodecyl)-3-(5-(thieno [2,3-*b*]thiophen-2-yl)thiophen-2-yl)-6-(thiophen-2-yl)pyrrolo [3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione) (pDPPTTi-OD) based on TTi and DPP units. The synthesized pDPPTTi-OD polymer had a low optical bandgap of 1.57 eV and a HOMO level of -5.40 eV. A good hole mobility of 0.16 cm² V⁻¹s⁻¹ was measured for the OTFT device and a PCE of 2.9% was achieved via control of the processing temperature.

2. Experimental section

2.1. Materials

Thieno [2,3-*b*]thiophene (TTi), 1.6 M *n*-butyllithium (*n*-BuLi) in hexane, *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA), 1.0 M trimethyltin chloride solution in tetrahydrofuran (THF), tetrakis (triphenylphosphine)palladium (0) (Pd(PPh₃)₄) were purchased from Sigma-Aldrich, Acros, and TCI. 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo [3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (M2) was synthesized as reported previously [18]. Common organic solvents were purchased from Daejung, J. T. Baker, and Sigma-Aldrich. THF was dried over sodium and benzophenone prior to use. All other reagents were used as received without further purification.

2.2. Synthesis

Synthesis of 2,5-bis(trimethylstannyl)thieno [2,3-*b*]thiophene: thieno [2,3-b]thiophene (0.950 g, 6.775 mmol) was added to a 250 mL round-bottomed flask. Anhydrous THF (60 mL) was added to the 250 mL round-bottomed flask, which was then stirred at -78 °C using a dry ice/acetone bath. 1.6 M *n*-BuLi solution in hexane (1.585 mL, 16.936 mmol) dropped dropwise and TMEDA (1.9680 g, 16.936 mmol) was added. The dry ice/acetone bath was removed and the reaction flask was warmed up to room temperature slowly and stirred for 2 h. The reaction flask was cooled again to -78 °C and trimethyltin chloride solution in THF (3.3071 g, 16.936 mmol) was added dropwise. This reaction mixture was warmed up to room temperature and stirred for 4 h. After reaction completion, 50 mL of H₂O was added to the reaction mixture, which was extracted with 200 mL of CHCl₃ three times. The combined organic layer was dried with anhydrous MgSO₄. The chloroform fraction was collected and recrystallized in methanol. White crystal products were formed and then filtered to yield 1.37 g of M1 (43.5%). ¹H NMR (CDCl₃, 400 MHz) δ (ppm) 7.24 (s, 2H), 0.41 (s, 18H).

Synthesis of poly (2,5-bis(2-octyldodecyl)-3-(5-(thieno [2,3-*b*] thiophen-2-yl)-6-(thiophen-2-yl)pyrrolo [3,4-*c*]

pyrrole-1,4(2H,5H)-dione) (pDPPTTi-OD): To a 100 mL flame-dried reaction flask with a magnetic bar, M1 (0.6564 g, 0.6440 mmol), M2 (0.30 g, 0.6440 mmol), 10 mL of anhydrous toluene, and 1 mL of anhydrous DMF were added. The reaction mixture was degassed by freeze-pump-thaw three cyclings. Tetrakis (triphenylphosphine) palladium (0) (Pd(PPh₃)₄) (0.0223 g, 0.0193 mmol) was then added to the reaction mixture, which was stirred at 110 °C for 20 h under an argon atmosphere. The reaction mixture was poured into a methanol/H₂O (4/1 v/v%) solution. The precipitated polymer was redissolved in chloroform and reprecipitated in MeOH. The collected polymer was further purified by Soxhlet extraction using methanol, acetone, hexane, and chloroform. The chloroform fraction was collected, reprecipitated in methanol, and then filtered. The polymer was dried under vacuum to yield 0.38 g (60%). ¹H NMR $(CDCl_3, 400 \text{ MHz}) \delta$ (ppm) 9.32–8.69 (s, 2H), 7.63–6.48 (m, 4H), 4.37-3.22 (m, 4H), 2.28-0.59 (m, 78H); GPC M_w = 22,500 g/mol, PDI = 2.31. (¹H NMR and GPC data of pDPPTTi-OD polymer are shown in the supplementary information.)

2.3. Material characterization

¹H NMR spectra were recorded on a Bruker advance 400 spectrometer (400 MHz). The molecular weights of the polymers were measured by gel permeation chromatography (GPC, Waters) at 80 °C using o-dichlorobenzene as an eluent and polystyrene as a standard. UV-visible absorption spectra were obtained on a Perkin Elmer Lambda 9 UV-VIS spectrophotometer. Differential scanning calorimetry (DSC) was taken on a Perkin-Elmer Pyris 1 DSC instrument at a rate of 10 °C/min between 30 and 300 °C under nitrogen. Thermogravimetric analysis was conducted on a TA TGA 2100 thermogravimetric analyzer under nitrogen at a scan rate of 10 °C/min. Cyclic voltammetry (CV) was taken on a CH instruments electrochemical analyzer, and a degassed acetonitrile solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆, Sigma-Aldrich) as the electrolyte was used. The potential sweep rate was 50 mVs⁻¹. A Pt wire electrode coated with a thin film of pDPPTTi-OD polymer was used as the working electrode, another Pt wire was used as the counter electrode, Ag/Ag⁺ was the reference electrode, and ferrocene was used as the internal standard for potential calibration (-4.8 eV). The crystalline structures of the ambipolar polymer films were characterized by grazing incidence X-ray diffraction (GIXD) experiments at the Pohang Light Source II (9A beamline, X-ray wavelength 0.1115 nm, X-ray incidence angle 0.13°) in Korea. The morphology of polymer:PC₇₁BM blend films examined by transmission electron microscopy (TEM) (Philips CM-30, 200 kV) and the film surface was probed by tapping mode atomic force microscopy (AFM) (D3100 Nanoscope V, Veeco).

2.4. OTFT fabrication and characterization

To examine electrical property of pDPPTTi-OD polymer films, bottom-gate top-contact OTFT devices were fabricated. Heavily doped n-type Silicon (Si) wafers having a thermally grown 300 nm thick silicon oxide (SiO₂) layer were employed as the substrate, where the doped Si wafer part acted as a OTFT gate and the 300 nm SiO₂ layer worked as a gate insulator. The SiO₂ surface was cleaned in piranha solution for 30 min at 100 °C and washed with distilled water. A SiO₂ layer was then modified using octadecyltrichlorosilane (ODTS, Gelest, Inc) to be hydrophobic. A 90 nm thick layer of the ambipolar semiconducting polymer was formed by spin-coating a 1.0 wt% chloroform solution onto the ODTS-treated Si substrates. The spin-coated polymer films were dried in a vacuum chamber (10^{-5} Torr) for 1 d, and heated for 1 h at 150 °C. The 50 nm thick Au source/drain electrodes were evaporated under high vacuum (2×10^{-6} Torr) through a shadow mask onto the

polymer film, with the channel length and width of 100 and 800 μ m, respectively. Transistor current–voltage characteristics were recorded on Keithley 2400 and 236 source/measure units at room temperature under vacuum conditions (10⁻⁵ Torr) in dark condition.

2.5. Organic solar cell fabrication and characterization

Patterned ITO-coated glass substrates (15 $\Omega/sq.$, 2.5 \times 2.5 cm²) were cleaned ultrasonically in isopropyl alcohol, acetone, and isopropyl alcohol sequentially for each 10 min. The ITO glass substrates were then cleaned by UV/ozone treatment for 20 min. A (3,4-ethylenedioxythiophene):poly (styrenesulfonate) polv (PEDOT:PSS, Clevios™ P VP AI 4083, Heraeus) solution diluted with methanol (1/1, v/v) was spincoated on the clean ITO substrate and further dried at 80 °C for 10 min, forming 30 nm thick PEDOT:PSS layer. Photoactive layers were formed on top of the PEDOT:PSS layer by spincoating a chlorobenzene/1,8-diiodooctane solution (97/3, v/ v) containing pDPPTTi-OD and [6,6]-phenyl-C71-butyric acid methyl ester (PC71BM) at a ratio of 1:1.5 (wt/wt) (total concentration = 24 mg/mL; the thickness of the photoactive layer was ~100 nm. Finally, a 100 nm thick Al layer was thermally evaporated through a shadow mask at a pressure of less than 2×10^{-6} Torr with a deposition rate of ~5 Å/s. The active area of each cell was 0.20 cm². Current density versus voltage characteristics of PSC cells were recorded on a Keithley model 2400 source measuring unit. A class-A solar simulator with a 1000 W Xenon lamp (Yamashita denso) equipped with a KG-5 filter served as a light source. Its light intensity was adjusted to AM 1.5 G 1 sun light intensity (100 mW/cm²) using a NREL-calibrated mono Si solar cell. External quantum efficiency (EQE) was measured as a function of wavelength from 300 to 1000 nm on incident photon-to-current conversion equipment (PV measurement Inc.). Light intensity was calibrated by using a silicon photodiode G425 which is NISTcalibrated as a standard.

3. Results and discussion

A new pDPPTTi-OD polymer was synthesized using Stille coupling of 2,5-bis(trimethylstannyl)thieno [2,3-*b*]thiophene with 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo [3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione in toluene/DMF (10/1, v/v) solution using Pd(PPh₃)₄ as a catalyst (Scheme 1). The weight-average molecular weight of pDPPTTi-OD, as determined by gel permeation chromatography (GPC) using *o*-dichlorobenzene as an eluent and polystyrene as a standard, was $M_w = 22,500 \text{ g mol}^{-1}$ with a poly-dispersity index of 2.31. The thermal stability of the synthesized pDPPTTi-OD polymer was characterized by thermogravimetric analysis (TGA). The pDPPTTi-OD was thermally stable with 5% degradation at 390 °C (Fig. 1a). Differential scanning calorimetry (DSC) established that there were no notable thermal transitions up to 260 °C (Fig. 1b).

The optical characteristics of the pDPPTTi-OD polymer were investigated by UV-visible absorption spectroscopy. Fig. 2a shows the absorption spectra of the polymer in chloroform solution and in the spin-coated film state. The spectrum of the polymer in solution had a broad absorption band ranging from 320 to 770 nm. Absorption peaks observed at 360, 438, 655 and 706 nm were attributed to $\pi - \pi^*$ and $\sigma - \pi^*$ transitions, including a HOMO-to-LUMO transition [27,28]. A well-developed vibronic peak was observed at 706 nm even for the dilute solution, which implied that the pDPPTTi-OD assumed a planar structure similar to other planar polymers [29–31]: the vibronic peak was more intense in the solid state. The UV-visible absorptions of the polymer film were slightly red-shifted, indicating that good intermolecular interactions occurred in the solid state. An optical bandgap of 1.57 eV was calculated using the absorption edge of the polymer film at 792 nm (Table 1). This optical bandgap is larger than that of poly (2,5-bis(2octyldodecyl)-3-(5-(thieno [3,2-b]thiophen-2-yl)thiophen-2-yl)-6-(thiophen-2-yl)pyrrolo [3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione) (DT-TDPP2T-TT), which is structurally very similar [6] and is close to that of poly (2,5-bis(2-octyldodecyl)-3-(5-phenylthiophen-2-yl)-6-



Scheme 1. Synthetic scheme for pDPPTTi-OD.



Fig. 1. TGA and DSC curves of pDPPTTi-OD polymer.



Fig. 2. (a) UV-visible spectra of pDPPTTi-OD in chloroform solution and in firm state. (b) Cyclic voltammogram of pDPPTTi-OD film.

(thiophen-2-yl) pyrrolo [3,4-c]pyrrole-1,4(2H, 5H)-dione) (PDPPTPT) [23].

The electrochemical properties of the pDPPTTi-OD film were evaluated by cyclic voltammetry (CV). A three-electrode cell was used with a degassed 0.1 M TBAPF₆ acetonitrile solution as the supporting electrolyte. Fig. 2b shows the CV curve of the pDPPTTi-OD polymer film. The onset oxidation potential was 0.60 V and the onset reduction potential was -1.06 V. From these values, the HOMO and LUMO levels of the polymer film were estimated to be -5.40 and -3.74 eV, respectively, and its electrochemical bandgap was determined to be 1.66 eV (Table 1). The HOMO level is slightly deeper than the HOMO levels of typical DPP-based polymers, including the DT-TDPP2T-TT polymer [6,32].

The torsional angle between the backbone aromatic rings and the energy-minimized structure of pDPPTTi-OD was determined by density functional theory (DFT) calculations. To save calculation cost and time, three repeating units of the pDPPTTi backbone were used and the attached long OD groups were replaced with methyl groups to form the (DPPTTi)₃ model molecule. The (DPPTTi)₃ geometry was optimized to an energy minimum using Gaussian 09 software at the DFT B3LYP level with the 6-31 + G (d, p) basis set. Fig. 3 shows the energy levels of the frontier orbitals, surface plots and geometric models of the structure. The molecular backbone is almost planar. All of the dihedral angles are less than 23.6°, which forms between the thiophene and TTi rings. The calculated HOMO and LUMO levels were -5.04 and -3.06 eV, respectively. The electronic density was well-distributed along the two repeating units in the HOMO level, whereas the middle DPP unit electronically contributed to the LUMO level. This fact may be associated with carrier transport behavior in the OTFT measurements, where the HOMO is a major transporting channel (see below). Additionally, time-dependent (TD) DFT was conducted to investigate the origin of the electronic transitions upon light absorption. A strong absorption at 703 nm corresponding to the HOMO \rightarrow LUMO transition was predicted, which is closely related to the strong absorption at ca. 700 nm in the UV–visible absorption spectrum (Fig. 2a).

Charge transport behavior was characterized for bottom-gate top-contact (BG/TC) OTFTs using 50-nm-thick pDPPTTi-OD films as the channel semiconductor. The polymer thin films were spin-coated onto the ODTS-treated SiO₂/Si wafer and heated at 150 °C in a vacuum chamber. Gold source/drain electrodes were then vacuum-deposited through a shadow mask. Electrical measurements of the devices were performed under vacuum. Fig. 4a shows

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UV-visible absorption			CV data				TGA		
Solution (λ_{max}, nm)	Film (λ _{max} ,nm)	Onset (nm)	$E_{g}^{Opt}\left(eV\right)$	Oxidation Potential (V)	HOMO (eV)	Reduction Potential (V)	LUMO (eV)	$E_{g}^{EC}\left(eV ight)$	T _d (°C)
655, 706	653, 723	792	1.57	0.60	-5.40	-1.06	-3.74	1.66	387



Fig. 3. Density functional theory calculation of (DPPTTi)₃. (a) Molecular geometry, (b) surface plots and electronic structure of frontier orbitals. and (c) UV–visible spectrum predicted by DT-DFT.



Fig. 4. (a) Transfer and (b) output characteristics of a BG/TC OTFT device based on the pDPPTTi-OD polymer as the semiconductor. (c) GIXD image of the pDPPTTi-OD film and (d) linecut profiles in the in-plane and out-of-plane directions.

the transfer characteristics of the BG/TC OTFTs based on the ascoated and 150°C-annealed pDPPTTi-OD films. The pDPPTTi-OD films displayed ambipolar characteristics. The field-effect mobilities were calculated in the respective saturation regimes of the transfer curves according to the relationship $I_{\rm D} = C_i \mu W (V_{\rm G} - V_{\rm th})^2 / V_{\rm C}$ 2L, where W and L are the channel width and length, respectively, C_i is the specific capacitance of the gate dielectric (11 nF cm⁻²), V_{th} is the threshold voltage and μ is the field-effect mobility. The hole and electron mobilities of the pristine pDPPTTi-OD film were 0.015 (± 0.003) and 3.08 $(\pm 1.04) \times 10^{-5}$ cm²V⁻¹s⁻¹, respectively. After the pDPPTTi-OD film was heated at 150 °C for 60 min, the mobilities greatly improved to 0.16 (±0.04) and 2.41 (±0.89) $\times~10^{-3}$ cm²V⁻¹s⁻¹, respectively. The mobility enhancements suggested that the thermal annealing promoted planar pDPPTTi-OD interchain interactions. The higher mobility of the holes compared with the electrons was primarily attributed to different electronic coupling features in the polymer backbone for carrier transport: electronic overlapping at the HOMO level was well-spread along the chain, whereas the LUMO orbital was mainly localized on one of the DPP units. A second reason is that the Fermi level of gold is closer to the HOMO level, hence hole injection is easier than electron injection. The on/off current ratios of the OFETs based on the 150°C-annealed pDPPTTi-OD film were ca. 10⁴ for hole transport. Fig. 4b shows the output characteristics of the devices made with the 150°C-annealed pDPPTTi-OD film, which displayed saturation behavior at low gate voltages and diode-like behavior at high gate voltages. The good transport characteristics were also associated with the crystallinity of the pDPPTTi-OD polymer. Grazing incidence X-ray diffraction (GIXD) experiments revealed a high-order crystalline lamellar organization of polymer chains (Fig. 4c). Fig. 4d shows that the (100), (200), (300) and (400) peaks appeared in the out-of-plane (q_z) direction with a lamellar spacing of 19.6 Å, which suggested that the long alkyl chains of the polymer were interdigitated in the crystalline domains. In the in-plane (q_v)

direction, a clear indication of $\pi-\pi$ stacking of the polymer chains was observed at 1.63 Å⁻¹, with a corresponding spacing of 3.85 Å. These features implied that the pDPPTTi polymer chains mainly assumed an edge-on orientation, thereby allowing twodimensional charge transport in the OTFT device. Considering the polymer chemical structure, film crystallinity and carrier transport results, the TTi moiety would be a good construction unit for D–A polymers to achieve highly crystalline polymer films and high carrier mobilities in OTFT devices.

The photovoltaic performance of the polymer was investigated by fabricating PSC devices with the ITO/PEDOT:PSS/photoactive/Al and ITO/PEDOT:PSS/photoactive/TiO2/Al structures. Their electrical properties were measured under 100 mW cm⁻², AM 1.5G sunlight illumination. The photoactive materials with a blend ratio of pDPPTTi-OD:PC71BM (1:1.5, w/w) were dissolved in the mixed solvent of chlorobenzene/1,8-diiodooctane (DIO) (97/3, v/v). The pDPPTTi-OD:PC71BM blends were dissolved at 25, 70 and 90 °C for 12 h. After filtering the solutions through an Acrodisc[®] syringe filter (0.45 µm pore size), the photoactive layer was formed by spincoating the polymer solutions on the ITO/PEDOT:PSS surface at each dissolving temperature. The current density-voltage (J-V)characteristics are shown in Fig. 5a,b and the corresponding photovoltaic results are summarized in Table 2. Several important observations can be made. First, the use of the TiO₂ nanoparticle layer improved the PCE. This was attributed to the efficient holeblocking role of the TiO₂ layer, which reduced free carrier recombination at the interface between the photoactive layer and the Al electrode [33]. Second, the device performance improved with increasing solution temperature: with the TiO₂ laver, the PCEs of the devices processed at 25, 70 and 90 °C were 2.05, 2.30 and 2.90%, respectively. The PCE improvement mainly resulted from the increase in *I*_{sc}. The 90°C-devices had a 27%-higher *I*_{sc} than the 25°Cdevices. The J_{sc} results were consistent with the external quantum efficiency (EQE) spectra (Fig. 5c,d). High-temperature-processed



Fig. 5. (a, b) J–V curves and (c, d) EQE spectra of pDPPTTi-OD:PC₇₁BM-based BHJ solar cells showing different treatment conditions under 1 sun illumination. Device structures of (a,c) ITO/PEDOT:PSS/Photoactive/Al and (b,d) ITO/PEDOT:PSS/Photoactive/TiO₂/Al.

 Table 2

 Photovoltaic properties of pDPPTTi-OD:PC₇₀BM-based BHJ solar cell under 1 sunlight illumination.

	Photoactive layer (processing temperature)	$V_{\rm oc} ({\rm V})$	J _{sc} (mA/cm ²)	FF	PCE (%)
w/o TiO ₂	pDPPTTi-OD:PC ₇₁ BM (25 °C)	0.75	5.83	0.43	1.90
	pDPPTTi-OD:PC ₇₁ BM (70 °C)	0.76	6.78	0.44	2.27
w/TiO ₂	pDPPTTI-OD:PC ₇₁ BM (90 °C)	0.75	6.93	0.45	2.35
	pDPPTTi-OD:PC ₇₁ BM (25 °C)	0.77	5.65	0.47	2.05
	pDPPTTi-OD:PC ₇₁ BM (70 °C)	0.76	6.55	0.46	2.30
	pDPPTTi-OD:PC ₇₁ BM (90 °C)	0.79	7.17	0.51	2.90



Fig. 6. UV-visible spectra of pDPPTTi-OD:PC71BM films processed at 25, 70, and 90 °C.

devices showed enhanced EQE values. More specifically, the 70°Cdevices displayed more improved EQE values for all absorption wavelengths compared with the 25°C-devices. The 90°C-devices exhibited even further improved EQE values, and the more improvements occurred in the PC₇₁BM absorption range than in the pDPPTTi-OD absorption range. These enhanced EQE behaviors appeared to be strongly related to morphological features (see below). Third, the V_{oc} of 0.79 V was obtained, which is one of the highest V_{oc} values reported for DPP-based polymers such as PDPPDTP [23]. The high V_{oc} was ascribed to the low-lying HOMO level, which illustrates that the TTi moiety can be a good donor unit to achieve high V_{oc} values in PSC devices.

The UV—visible absorption properties of pDPPTTi-OD:PC₇₁BM blend films processed at 25, 70 and 90 °C, were measured (Fig. 6) to understand the interchain interaction between polymer chains as a function of the processing temperature. The 25°C-processed blend film absorbed up to 1000 nm, which is significantly longer than that of pDPPTTi-OD films cast from chloroform solution (Fig. 2). This unusually low wavelength absorption might be caused by severe aggregation of pDPPTTi-OD polymer fibers that were identified by GIXD, transmission electron microscopy (TEM) and atomic force microscopy (AFM) (discussed below). The 70- or 90°C-processed blend films, however, had normal light absorption features. This result suggested that processing at elevated temperatures could be used to take advantage of the favorable intrinsic characteristics of the pDPPTTi-OD polymer.

The crystallinity of pDPPTTi-OD and the blend with PC₇₁BM was examined again by GIXD experiments. Fig. 7 shows GIXD images of the pDPPTTi-OD:PC₇₁BM blend films. Highly crystalline peaks of pDPPTTi polymer lamellar domains were observed for the polymeronly film. In the out-of-plane (q_z) direction, (100), (200) and (300) peaks appeared at 0.336, 0.649 and 0.969 Å⁻¹, respectively, for a corresponding lamellar spacing of ca. 19.6 Å. In the in-plane (q_y) direction, weak signals for π – π stacking of the polymer chains were observed at 1.63 E⁻¹, corresponding to a distance of 3.85 Å. These features implied that the pDPPTTi polymer chains still



Fig. 7. GIXD images of pDPPTTi-OD:PC₇₁BM films processed at (a) 25, (b) 70, and (c) 90 °C, and the corresponding line-cut profiles of GIXD images in the in-plane $(q_y)(d)$ and out-of-plane $(q_z)(e)$ directions.



Fig. 8. TEM images of pDPPTTi-OD:PC71BM blend films. Films were prepared at temperatures of (a, b) 25 °C, (c, d) 70 °C, and (e, f) 90 °C.

maintained their crystalline features and edge-on orientation just as in the pDPPTTi-OD polymer-only film, even after blending with PC₇₁BM. Notably, while the polymer's crystalline features were less dependent on the processing temperatures, the crystalline semicircles of the PC₇₁BM domains at q = 1.33 Å⁻¹ significantly decreased with increasing processing temperature. This observation indicated that highly crystalline PC₇₁BM molecules disaggregated at high temperatures.

More detailed morphological features of the pDPPTTi-OD:PC₇₁BM blend films were revealed by TEM (Fig. 8) and AFM imaging. Clear morphological differences were observed that depended on the processing temperature. The 25°C-solution blend film with photoactive films exhibited large PC₇₁BM aggregates between randomly distributed fibrous crystalline pDPPTTi-OD polymer chains (Fig. 8a,d). With increasing solution temperature, the aggregation of PC₇₁BM molecules was significantly reduced and



Fig. 9. AFM images of pDPPTTi-OD:PC70BM blend films. Films were prepared at temperatures of (a, b) 25 °C, (c, d) 70 °C, and (e, f) 90 °C.

the fibril polymers were better-dispersed. Consequently, more desirable morphological features were obtained with increasing solution temperature by providing more intimate interactions between PC71BM molecules and the pDPPTTi-OD chains. This resulted in the higher I_{sc} values at the higher temperatures. Fig. 9 shows the surface morphologies of the pDPPTTi-OD:PC71BM blend films. The 25°C-solution blend films were quite rough with a root-meansquare (rms) value of 8.29 nm (Fig. 9a). The blend films appeared to contain aggregated nanoparticles in the phase image (Fig. 9b). In contrast, increased processing temperature decreased the surface roughness (rms = 4.25 and 4.12 nm for 70 and 90 °C, respectively) and the number of clearly visible aggregated nanoparticles (Fig. 9c-f). The lowering of the surface roughness and the nanoparticle numbers were in good agreement with TEM images. The reduction of PC₇₁BM aggregation was confirmed by AFM imaging. In conclusion, the various characterizations indicated that the observed increases in Jsc and PCE with processing temperature resulted from an enhancement in the polymer:PC71BM blend morphology, with particular impact on the disaggregation of PC71BM molecules.

4. Conclusions

A new polymer, pDPPTTi-OD, was synthesized and its electrical properties were investigated by OTFT and PSC test beds. The pDPPTTi-OD polymer showed a wide light absorption up to 800 nm with a deep HOMO (-5.42 eV) level. In the OTFT devices, it had a high hole mobility of 0.16 cm² V⁻¹ s⁻¹ after a 150 °C thermal treatment. PSC devices were fabricated at various temperatures. The pDPPTTi-OD:PC₇₁BM blend film processed at 90 °C displayed a PCE of 2.9%, mainly because of optimal phase separation between pDPPTTi-OD polymer chains and PC₇₁BM molecular domains. This work demonstrated that the TTi moiety can maintain the planarity of polymer backbones and keep the polymers' HOMO levels deep, which leads to a high hole mobility in thin-film transistors and a high open-circuit voltage in PSCs. Furthermore, high-temperature processing can help to control the morphology of semiconducting polymer or polymer blend films.

Competing financial interests

The authors declare no competing financial interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://

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