Novel Conjugated Copolymers Based on Dithiafulvalene Moiety for Bulk Heterojunction Solar Cells

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ABSTRACT: New conjugated copolymers, **P1-P3**, based on dithiafulvalene-fused entity and different conjugated segments have been synthesized. Incorporation of electron-deficient conjugated segments into the conjugated copolymers results in red shifting the absorption band and lowering the hole mobility. Bulk heterojunction solar cells using on these polymers as the donor and [6,6]-phenyl-C61-butyric acid methyl ester (PC₆₁BM) as the acceptor were fabricated by solution process. The cells based on the blend of **P1-P3**/PC₆₁BM (1:1, w/w) have

power conversion efficiencies (PCEs) ranging from 0.53 to 0.93%. Among these, the cell of **P1**/PC₆₁BM exhibited the highest open-circuit voltage at 0.85 V, and the cell of P3/PC₆₁BM exhibited the best PCE at 0.93% with the short-circuit current (J_{SC}) of 4.88 mA/cm². © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 2121–2129, 2012

KEYWORDS: bulk heterojunction; dithiafulvalene; organic photovoltaics

INTRODUCTION Due to limited natural reserves and continually increasing consumption rate of fossil fuel, and concerns over global warming, renewable energy has become an important issue of policy maker and subject of researchers.^{1,2} Among these, the polymer solar cells (PSCs) have been attractive because of their low cost, large area manufacture, and flexibility.^{3,4} PSCs normally have a bulk heterojunction (BHJ) architectures which consists of the fullerene derivatives of [6,6]-phenyl C₆₁-butyric acid methyl ester (PC₆₁BM) as electron acceptor and conjugated polymers as the donor part.⁵ Recently, high power conversion efficiencies (PCEs) of >7% were reported for the blend of some conjugated polymers, such as PBnDT-DTffBT,⁶ PTBF1,⁷ PBDTTT-CF,^{8a} PBnDT-FTAZ,^{8b} PCDTBT⁹ and so forth, with fullerene derivatives. The design rules for donor polymers in BHJ devices include low HOMO energy level for higher open-circuit voltage, low band gap for good solar light harvesting, appropriate crystallinity and morphology for high carrier mobility, and wellmatched HOMO and LUMO energy levels between polymers and fullerenes for efficient charge separation.^{3,10} Conjugated polymers of alternating donor-acceptor (D-A) type have attracted considerable attention because their band gaps, energy levels, and carriers mobilities can be easily tuned.¹¹ The desired photophysical, electrochemical, and other properties are normally achievable via appropriate choice of donor or acceptor.

A tetrathiafulvalene (TTF) moiety has three stable oxidation states including the TTF^0 , TTF^+ , and TTF^{2+} . Thus, the charge

storage capacity of conjugated polymer may be significantly increased upon grafting with TTF units.¹² Moreover, large number of sulfur atoms in TTF-fused polymers increase the polarizability of the molecules and reduce intramolecular and intermolecular Coulomb repulsions between the charged species. Consequently, there is increased dimensionality of charge transport.¹³ Gautier et al. investigated a TTF derivative in which two quinones were connected by TTF backbone and found that the quinone units could readily communicate with each other through the TTF backbone. Therefore, the charge transport of the conjugated polymers can be increased via incorporation of TTF units.¹⁴ Solar cells based on TTF derivatives with TTF units either in the main chain or side chain of the conjugated polymers have been studied by several groups.^{15,16} Chen et al. prepared a novel TTFfused poly(aryleneethynylene) with an acceptor main chain and donor side chains. Intramolecular charge transfer (CT) exists between the electron-rich TTF side chains and the electron-deficient main chain. The PCE was reported to be 0.25% under AM 1.5 sunlight.15 Skabara et al. development a series of polymers derived from thiophene and TTF moieties. Despite very low band gap (1.44 eV) of the polymer, the PCE only reached 0.13%.¹⁶ Nonetheless, the excellent intramolecular CT and good π -stacking characteristics of this kind of TTF-fused polymers render them promising materials for photovoltaic and other organic electronic devices.

Similar to TTFs, dithiafulvalene (DTFs) also have good charge transport property because of π - π and S...S interactions.

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SCHEME 1 Synthesis of monomer 1.

However, monomeric and polymeric DTF derivatives¹⁷ were not explored as intensively as TTF congeners. To our knowledge, no OPVs using DTF-based polymers have been reported. Therefore, we chose 2-(9H-fluoren-9-ylidene)-4,5bis(hexylthio)-1,3-dithiole entity (Scheme 1; monomer 1) an the electron-donating motif for D-A alternating copolymer based on the following reasons: (1) bis(hexylthio)-1,3dithiole entity (BTDT) may have a lower HOMO level compared with its TTF congener, and a higher open-circuit voltage is expected; (2) BTDT may function as the hole-hopping sites; (3) the two hexylthio substituents may not only enhance the solubility of the polymer for device fabrication but also help intermolecular stacking; (4) large number of sulfur atoms along the structure may facilitate molecular aggregation. In this article, conjugated polymers constructed from 2-(9H-fluoren-9-ylidene)-4,5-bis(hexylthio)-1,3-dithiole and different acceptor moieties will be reported. Their

photophysical, electrochemical, and thermal properties, as well as the BHJ type photovoltaic cells are also included.

EXPERIMENTAL

General Information

Infrared spectra were recorded on a Perkin–Elmer FT-IR spectrometer spectrum 100. ¹H NMR and ¹³C NMR spectra were taken on a Bruker AMX-400 or Bruker AV-400 spectrometer using CDCl₃ as the solvent. Fast atom bombardment mass spectrometry (FABMS) analysis was performed on a JEOL Tokyo Japan JMS-700 mass spectrometer equipped with the standard FAB source. Elemental analyses were performed on a Perkin–Elmer Model 2400 analyzer. Absorption spectra were recorded on a Dynamica DB-20 UV–Vis spectrophotometer. Low-energy photoelectron spectra were taken from a photoelectron spectrometer (AC-2, Riken-Keiki PT5-0210).

Gel permeation chromatography (GPC) was performed with a Waters apparatus equipped with Waters Stygel columns and a refractive index detector using tetrahydrofuran (THF) as the eluent (polystyrene calibration). Glass transition temperature (T_g) and thermal decomposition temperature (T_d) of the copolymer were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) using Seiko DSC 6220 SII Extra 6000 and Thermo Cahn Versa Therm analyzer systems, respectively. The photoelectrochemical characterizations on the solar cells were carried out using an Oriel Class A solar simulator (Oriel 91195A, Newport). Photocurrent-voltage characteristics of the OPVs were recorded with a potentiostat/galvanostat (CHI650B, CH Instruments) at a light intensity of 100 mW/cm² calibrated by an Oriel reference solar cell (Oriel 91150, Newport). The monochromatic quantum efficiency was recorded at shortcircuit condition using a monochromator (Oriel 74100, Newport). The morphology of the thin films was analyzed by atomic force microscopy (AFM) (Digital instrument NS 3a controller with D3100 stage).

Device Fabrication

The fabricated BHJ device has a configuration of ITO/ PEDOT:PSS/active layer/Ca/Al. They were prepared according to the following procedures: (1) Glass/ITO substrates (8 Ω/\Box) were sequentially patterned by hydrochloric acid (HCl_{aq}), followed by cleaning with acetone, cleanser, deionized water, and isopropyl alcohol, dried and treated with oxygen plasma for 5 min; (2) PEDOT:PSS (Clevios P-VP AI4083) was passed through a 0.45- μ m filter before being deposited on ITO through spin-coating at 4000 rpm in air; (3) the sample was then dried at 100° C for 1 h and 130° C for 30 min; (4) A blend of fullerene derivatives (PCBM) and the polymers (P1-P3) [ratios of (w/w), 1.2 wt % in odichlorobenzene (o-DCB)] were stirred overnight in o-DCB, filtered through a $0.22 - \mu m$ poly(tetrafluoroethylene) filter, and then spin-coated with 800 rpm for 40 s on top of the PEDOT:PSS layer. Subsequently, the devices were thermal annealed at 130°C for 10 min. Then, the device was completed by depositing a 30-nm thick layer of Ca and a 120-nm thick layer of Al at pressures of less than 10^{-6} torr. Finally, the devices were transferred to the glove box and encapsulated using UV-curing glue (Lumtec, Taiwan). The active area of the device was 0.1 cm^2 .

Fabrication of Hole- and Electron-Only Devices

The hole- and electron-only devices in this study were fabricated according to the literature with modification.¹⁸ The hole only device has a configuration of ITO/PEDOT:PSS/ active layer/MoO₃/Al, and MoO₃ was thermally evaporated to a thickness of 20 nm. The electron-only device has a configuration of ITO/CS₂CO₃/active layer/Ca/Al, in which CS₂CO₃ (0.2 wt % in methoxyethanol) was deposited by spin-coating process.

Materials

All the starting materials were used as received without any further purification. All the solvents such as dichloromethane, THF, and dimethylformamide, and toluene were



Synthesis of Monomer 1b²⁴

The bis(tetraethylammonium)bis(1,3-dithiole-2-thione-4,5dithiolato)zincate (zincate) (0.83 g, 1.15 mmol) and 1-bromohexane (0.58 mL, 4.18 mmol) in MeCN (12 mL) under N₂. The mixture was stirred at reflux for 24 h. After the reaction was complete, the solvent was removed under vacuum and 1b was obtained as a brown viscous liquid (0.70 g, 82%). ¹H NMR: (400 MHz, CDCl₃, δ , ppm): 2.86 (*t*, *J* = 7.2, 4H), 1.67-1.62 (m, 4H), 1.43-1.36 (m, 4H), 1.28-1.26 (m, 8H), 0.89-0.86 (m, 6H).

Synthesis of Monomer 2-(2,7-Dibromo-fluoren-9-ylidene)-4,5-bis-hexylsulfanyl-[1,3]dithiole (1)

Triethylphosphite (15 mL) was added slowly to a solution of 1a (1.40 g, 4.14 mmol) and 1b (0.76 g, 2.07 mmol) in toluene (20 mL) under N2. The mixture was stirred at 120°C for 3 h. After the reaction was complete, the excess 1a was filtered off. The solvent of the filtrate was removed under vacuum. Addition of methanol to the resulting viscous solution led to precipitation of monomer 1. The precipitate was separated by filtration and washed with methanol thoroughly to provide pure 1 in 46% yield (0.62 g). FT-IR: 1683 (C=C stretch), 1587 (S—C=C stretch), 1448, 1276 cm⁻¹ (S—C stretch). ¹H NMR: (400 MHz, CDCl₃, δ , ppm): 7.82 (s, 2H), 7.61 (d, J = 8.0 Hz, 2H), 7.41 (dd, J = 8.4, 1.6 Hz, 2H), 2.97 (t, J = 7.2, 4H), 1.74-1.67 (m, 4H), 1.50-1.42 (m, 4H), 1.33-1.29 (m, 8H), 0.90–0.87 (m, 6H). ¹³C NMR (100 MHz, CDCl₃, δ, ppm): 142.01, 138.28, 135.58, 129.52, 128.36, 125.74, 121.07, 120.89, 36.97, 31.57, 29.96, 28.48, 22.76, 14.25. (FAB): m/z 656 (M⁺). Anal. Calcd: C, 51.22; H, 4.91. Found: C, 51.34; H, 4.71.

Synthesis of P1

Compound 1 (0.66 g, 1.00 mmol), 2,5-bis(trimethylstannyl)thiophene (0.41 g, 1.00 mmol), Pd₂(dba)₃ (18.3 mg), and P(o-tol)₃ (48.7 mg) were placed in a 25 mL round-bottomed flask. The degassed chlorobenzene (8 mL) was added to the flask as the solvent. The resulting mixture was heated at 110°C for 3 days under N₂. After cooling to room temperature, the mixture was poured into methanol. The precipitate formed was collected by filtration through a frit and then purified by Soxhlet extraction first with hexane and acetone to remove soluble impurities, and then with chloroform to extract the polymer. The chloroform solution was concentrated by rotary evaporation followed by precipitation with methanol. The solid was dried under vacuum and obtained as a red solid in 50% yield. FT-IR: 1595 (C=C stretch), 1530 (S-C=C stretch), 1456, 1261 cm⁻¹ (S-C stretch). ¹H NMR: (400 MHz, CDCl₃, δ, ppm): 8.05–6.90 (br, 8H), 2.95 (br, 4H), 1.80–1.23 (br, 16H), 0.86 (br, 6H). GPC (THF) polydispersity index (PDI) = 3.18, $M_{\rm w} = 17155$.



SCHEME 2 Structure and synthesis of DTF-based copolymers (P1-P3).

Synthesis of P2

Compound 1 (0.33 g, 0.50 mmol), 2,5-bis(trimethylstannyl)thiophene (0.41 g, 1.00 mmol), 4,7-dibromo-benzo[1,2,5]thiadiazole (0.15 g, 0.50 mmol), Pd₂(dba)₃ (18.3 mg), and P(otol)₃ (48.7 mg) were placed in a 25 mL round-bottomed flask. The degassed chlorobenzene (8 mL) was added to the flask as the solvent. The resulting mixture was heated to 110°C for 3 days under N₂. After being cooled to room temperature, the mixture was poured into methanol. The precipitate was collected by filtration through a frit and then purified by Soxhlet extraction, first with hexane and acetone to remove soluble impurities, and then with chloroform to extract the polymer. The chloroform solution was concentrated by rotary evaporation followed by precipitation with methanol. The solid was dried under vacuum and obtained as a black solid in 15% yield. FT-IR: 1595 (C=C stretch), 1527 (S-C=C stretch), 1456, 1261 cm⁻¹ (S-C stretch). ¹H NMR: (400 MHz, CDCl₃, δ, ppm): 8.05-6.90 (br, 12H), 2.97 (br, 4H), 1.78–1.23 (br, 16H), 0.87 (br, 6H). GPC (THF) PDI = 3.20, $M_{\rm w} = 10149$.

P3 was obtained as a black solid following the procedure described for P2. The yield was 16%. FT-IR: 1743, 1701 (imide C=O stretch), 1595 (C=C stretch), 1531 (S-C=C stretch), 1456, 1259 cm⁻¹ (S-C stretch). ¹H NMR: (400 MHz, CDCl₃, *δ*, ppm): 8.05–6.90 (br, 10H), 3.35 (br, 2H), 2.94 (br, 4H), 1.65–1.24 (br, 25H), 0.86 (br, 12H). GPC (THF) PDI = 3.14, *M*_w = 13233.

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthetic protocol of the novel electron-donating monomer bearing DTF moiety (1) is illustrated in Scheme 1. The monomer **1a** was prepared according to the literature procedures,¹⁹ while monomer $\mathbf{1b}^{24}$ was obtained from zincate metal complex²⁰ and 1-bromohexane. Condensation reaction of **1a** and **1b** mediated by P(OEt)₃ was then carried out in refluxing toluene to afford **1**. Elemental analysis, FT-IR, and NMR and mass spectra (FAB-MS) were used to identify structures of the target monomer **1**. The monomer has three characteristic bands at 1587, 1448, and 1276 cm⁻¹ (Supporting Information Fig. S1). The first band is attributed to S—C=C stretching, and the latter two are attributable to S—C stretching. Both the NMR spectra (Supporting Information Fig. S2) and elemental analysis of the monomer **1** agree well with the proposed molecular structure.

Scheme 2 illustrates the synthetic route of the polymers P1-P3. They were obtained via Stille coupling reaction between a distannyl reagent and a dibromide. 2,5-Bis(trimethylstannyl)-thiophene was selected due to the reluctance of 1 in double stannylation. Only very low-molecular weight copolymers were obtained when Pd₂(PPh₃)₂Cl₂ was used as the catalyst. Consequently, $Pd_2(dba)_3$ and $P(o-tol)_3$ was used instead. The desired polymers could be obtained in 15-50% yields from the reaction of the monomers 1, an acceptor moiety (for P2 and P3) and 2,5-bis(trimethylstannyl)-thiophene in chlorobenzene as solvent. The crude polymers were purified by precipitating in methanol and washing off residual small molecules by hexane and acetone via Soxhlet extraction. The polymers were further purified by extraction with chloroform followed by precipitation with methanol. Typical IR spectra for all the copolymers are shown in Supporting Information Figure S1. All the copolymers showed characteristic IR absorption bands of the S-C=C and the S-C groups. The characteristic IR absorption bands

tion Fig. S3).

TABLE 1 Molecular Weight, Polydispersity (PDI) Value, and

 Thermal Properties of the Copolymers (P1-P3)

<i>M</i> _w ^a	(PDI) ^a	τ _d (°C) ^b
17155	3.18	325
10419	3.20	357
13233	3.14	346
	<i>M</i> _w ^a 17155 10419 13233	M _w ^a (PDI) ^a 17155 3.18 10419 3.20 13233 3.14

^a Copolymers was determined by GPC analysis in THF (calibration with polystyrene standards), $PDI = M_w/M_n$.

 $^{\rm b}$ Temperatures at which 5% weight loss were recorded by TGA at a heating rate of 10°C/min.

of the imide group for P3 were also observed at 1743 and 1701 cm⁻¹. The ¹H NMR spectra of the polymers are consistent with their structural formulation (Supporting Information Fig. S2). Compared with the precursor monomer 1, all the copolymers showed broadened ¹H NMR spectra. The peaks due to aromatic protons appear at around δ 8-7 ppm. The peaks at around δ 2.95 ppm are attributed to the CH₂—S group, and those at around δ 3.50-3.20 ppm are due to the N– CH_2 group (P3). The peaks of the hexyl substituent and the ethylhexyl substituent are in the range δ 1.80-0.86 ppm. The weight average molecular weight of P1-P3 determined by GPC in THF using polystyrene as the standard are 1.7, 1.0 and 1.3 kg mol⁻¹, and the corresponding PDIs are 3.18, 3.20, and 3.14, respectively (Table 1). From TGA (Fig. 1 and Table 1), the onset temperature with 5% weight loss (T_d) of these polymers was found in the range of 325-357°C. The thermal stability of the polymers is therefore good for optoelectronic device applications. No glass transition temperature (T_g) was noticeable from thermal DSC measurement.

Optical Properties

Absorption spectra of the monomer **1**, **P1-P3** in THF solution and thin films are shown in Figure 2 and the data are collected in Table 2. The monomer **1** exhibited a prominent absorption peak at 421 nm (Fig. 2) due to the π - π * transition of the backbone. Similar absorption peak due to this entity was observed at 422, 427, and 431 nm for P1, P2, and P3, respectively. However, all the polymers exhibited broader peaks with lower absorption onsets (λ_{onset}) than that of monomer **1**, indicating the peak was mixed with delocalized π - π^* transition band (**P1-P3**) and intramolecular CT transition band from the donor [2-(2,7-dibromo-9H-fluoren-9-ylidene)-4,5-bis(hexylthio)-1,3-dithiole] to the electron-deficient acceptor (P2 and P3).^{11,23} The absorption spectra of the polymers in the solid state are very similar to those in the solution. As the electron-withdrawing group becomes stronger, the absorption onsets (λ_{onset}) of the CT bands in these polymers are red shifted, and the optical band gap (E_g) decreases in the order of P1 > P3 > P2. The optical band gaps (E_g) of the three polymers calculated from absorption onset of the films are 2.25, 1.77, and 1.81 eV for P1, P2, and P3, respectively. The higher absorption intensity of P3 in the range of 500-550 nm is beneficial to enhancing the PCE (vide infra). It is interesting to note that impressively long wavelength absorption extending to >900 nm can be achieved when a strong electron-withdrawing group, diketopyrrolopyrrole, is used as the acceptor (Supporting Informa-

A low-energy photoelectron spectrometer (AC-2) was employed to measure the ionization potentials of these copolymers in the film state. The films were prepared by spin coating of the polymer solutions in o-dichlorobenzene. The AC-2 spectra of the polymers in this study (P1-P3) and commercial P3HT [poly(3-hexylthiophene)] polymer are shown in Figure 3. These were then used to estimate the HOMO energy levels of the polymers. The HOMO energy levels of P1-P3 are calculated to be 5.31, 5.25, and 5.34 eV, respectively, and the reference polymer P3HT was 4.75 eV. All the polymers show similar HOMO energy levels, possibly due to the dominance of the BTDT-fused entity. In contrast, the LUMO level, obtained from the HOMO energy level and the optical band gap, varies with the identity of the acceptor. The LUMO energy levels of P1-P3 are calculated to be 3.06, 3.48, and 3.53 eV, respectively.



FIGURE 1 TGA curves of the polymers P1-P3 in nitrogen atmosphere.



FIGURE 2 UV-Vis absorption spectra of monomer 1, P1-P3 in THF solution and in thin films.

TABLE 2 Electrochemical and Optical Properties of the Polymers

Polymer	λ _{max} (nm) solution ^a	λ _{em} (nm) solution ^a	λ _{max} (nm) film	E _g (eV) ^b	HOMO ^c / LUMO ^d (eV)
P1	343, 422	612	432	2.25	5.31/3.06
P2	374, 427, 588	643	429	1.77	5.25/3.48
P3	342, 431	695	434	1.81	5.34/3.53

^a Absorption and emission data was collected in THF solution.

^b Data taken by the absorption edge of the thin film.

^c HOMO energy level was determined by low-energy photoelectron spectrometer.

^d LUMO levels were derived via eq. $E_g = HOMO-LUMO$.

Organic Solar Cells and Relevant Characterization

Typical BHJ solar cells using these polymers as the electron donors and PC₆₁BM as the electron acceptor were fabricated and tested under simulated AM 1.5 illumination (100 $mWcm^{-2}$). The energy levels of relevant materials obtained from the optical measurements (vide supra) are shown in Figure 4. The devices have the layered configuration of ITO/ PEDOT:PSS/P1 (P2 or P3):PC61BM (w/w)/Ca (30 nm)/Al (120 nm). The effective area of the device was 0.1 cm^2 . The active layers of these devices were spin-coated from the odichlorobenzene (o-DCB) solutions of these polymers. The performance data of PSCs are listed in Table 3 and their J-V curves are shown in Figure 5 and Supporting Information Fig. S4. Figure 5 shows the *I–V* characteristics of the selected cells based on P1: PC61BM blend at different weight ratios (1:1, 1:2 and 1:4, w/w) after annealed at 130°C for 10 min. The cells performance data of P1/PC₆₁BM (1:1, 1:2, and 1:4, w/w) blends are as the following: PCE at 0.74, 0.73, and 0.49%; open-circuit voltage (V_{OC}) at 0.85, 0.80, and 0.77 V; short-circuit currents (J_{SC}) at 2.88, 2.85, and 1.93 mA/cm²; fill factor (FF) at 0.30, 0.32, and 0.33. The J-V curves in the dark (dark currents) are for $P1/PC_{61}BM$ cells also shown in Figure 5. The $P1/PC_{61}BM$ (1:1, w/w) cell exhibited the lowest dark current among the three devices, which is consist-



FIGURE 3 AC-2 spectra of all the polymers (P1-P3) and P3HT.



FIGURE 4 Energy levels for the polymers.

ent with its highest open-circuit voltage (Voc). Others polymers in various blend ratios were also tested in the same manner. The optimized weight ratio between the polymer and PC₆₁BM was found to be 1:1 for all polymers, and the cell performance drops as the wt % of PC_{61}BM increases (Table 3). All the cells exhibited photovoltages (V_{OC}) exceeding 0.68 V, which is much higher than that of pristine P3HT/ PC₆₁BM cell. This may be attributed to the lower HOMO level of the polymers compared with P3HT.²⁴ Compared with TTFfused polymers reported in the literature ($V_{\rm OC} = 0.42-0.52$ V),^{15,16} our systems show much higher $V_{\rm OC}$ value. Such an outcome can also be rationalized by the lower HOMO level of the BTDT moiety. Among the cells of polymers/PC₆₁BM at 1:1 (w/w) ratio, P3 exhibited the best PCE at 0.93%, which may be attributed to the better light absorption of P3 than the other two (vide supra).

The external quantum efficiencies (EQEs) of the devices based on the blend of $\mathbf{P1}/\mathbf{PC}_{61}\mathbf{BM}$ (1:1, 1:2, 1:4 w/w) illuminated by monochromatic light are shown in Figure 6. Good EQE values were achieved in the range of 350-550 nm, with the highest value reaching ~ 50% at ~ 400 nm for $\mathbf{P1}/\mathbf{PC}_{61}\mathbf{BM}$ (1:1, w/w) device. Figure 7 shows the EQE plots for the \mathbf{Pn} (n = 1-3)/ $\mathbf{PC}_{61}\mathbf{BM}$ blends in 1:1 ratio. Although the $\mathbf{P1}/\mathbf{PC}_{61}\mathbf{BM}$ device exhibited the highest EQE values at shorter wavelengths, its short-circuit current and conversion efficiency were inferior to those of the $\mathbf{P3}/\mathbf{PC}_{61}\mathbf{BM}$ device exhibited better EQE value ranging from 500 to 600 nm, and therefore better short-circuit current. This is consistent with the UV-Vis absorption.

The morphologies of the active layers with different weight ratios of polymer (**P1-P3**)/PC₆₁BM were investigated by AFM, and the tapping mode AFM images of these films are shown in Figure 8. All the films exhibited root-mean-square (rms) roughness smaller than 1 nm. Figure 8(a,b) show the images of the **P1**/PC₆₁BM blends in different weight ratios (1:1 and 1:4, w/w). The J_{SC} and PCE values of **P1**/PC₆₁BM (1:4, w/w) cell dropped to 1.93 mA/cm² and 0.49%, respectively, when compared with **P1**/PC₆₁BM (1:1, w/w) cell

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Device ^a	$V_{\rm OC}$ (V)	J _{SC} (mA/cm ²)	η (%)	FF	μ_h (\times 10^{-4} cm²/ V s)	μ_{e} (\times 10^{-4} cm²/Vs)
P1 /PC ₆₁ BM (1/1)	0.85	-2.88	0.74	0.30	1.04	2.15
P1 /PC ₆₁ BM (1/2)	0.80	-2.85	0.73	0.32	0.15	2.46
P1 /PC ₆₁ BM (1/4)	0.77	-1.93	0.49	0.33	0.07	3.24
P2 /PC ₆₁ BM (1/1)	0.69	-2.80	0.53	0.27	0.81	2.37
P2/PC ₆₁ BM (1/2)	0.68	-2.46	0.43	0.26	-	-
P2/PC ₆₁ BM (1/4)	0.68	-0.98	0.22	0.32	-	-
P3 /PC ₆₁ BM (1/1)	0.69	-4.88	0.93	0.28	0.77	2.26
P3/PC ₆₁ BM (1/2)	0.71	-2.49	0.55	0.31	-	-
P3 /PC ₆₁ BM (1/4)	0.68	-1.61	0.41	0.37	-	-

TABLE 3 Photovoltaic Properties of the Cells

^a Cell area: 0.1 cm².



FIGURE 5 The current density-voltage curves of the devices with $P1/PC_{61}BM$ (1/1, 1/2, and 1/4, w/w) under AM 1.5 solar simulator of 100 mW/cm² and in the dark.

(2.88 mA/cm² and 0.74%). Possibly the finer morphology observed for the **P1**/PC₆₁BM (1:4, w/w) blend resulted in inefficient charge separation and decreased the short-circuit current and the cell efficiency. Among the AFM images of the three polymer/PC₆₁BM (1:1, w/w) blends [Fig. 8(a,c,d)], the **P2**/PC₆₁BM film exhibited larger domain sizes, which is not favorable for efficient exciton diffusion and charge transport. Therefore, lower J_{SC} and PCE values were obtained in **P2**-based device.

The space-charge limited current (SCLC) flow technique was used to measure the electron and hole mobilities in the blend films.²⁵ The carrier mobility was determined by fitting the current versus voltage (*J*-*V*) curve to SCLC model for a single carrier device.²⁶ The carrier mobility can be calculated from $J = 9\varepsilon_n\varepsilon_r\mu V^2/8L^3$, where $\varepsilon_n\varepsilon_r$ is the dielectric permittivity of the polymer, μ is the carrier mobility, and *L* is the film thickness.²⁷ The relevant data are collected in Table 3 and their *J*-*V* curves are shown in Supporting Information Figure S5. In general, more balanced electron and hole mobility is beneficial to the device performance. Among **P1**-based devi



FIGURE 6 The external quantum efficiency (EQE) spectra of $P1/PC_{61}BM$ (1/1, 1/2, and 1/4, w/w).

ces of different weight ratios, the $P1/PC_{61}BM$ at 1:1 weight ratio exhibited more balanced electron and hole mobility than others. This may be the cause of its better performance.



FIGURE 7 The external quantum efficiencies (EQEs) of the cells based on $(P1-P3)/PC_{61}BM$ (1:1, w/w) blends.



FIGURE 8 AFM images (5 × 5 μ m²) of thin films spin-coated on ITO/PEDOT:PSS substrates and annealed at 130°C for 10 min. (a) **P1**:PCBM (1:1), (b) **P1**:PCBM (1:4), (c) **P2**:PCBM (1:1), and (d) **P3**:PCBM (1:1).

The better performance of $P1/PC_{61}BM$ (1:1 ratio) than $P2/PC_{61}BM$ (1:1 ratio) may also be attributed to the better balance of carrier mobility in the former, despite the shorter absorption wavelength of the P1. Despite the least balanced carrier mobility among three polymer/PC₆₁BM (1:1 ratio) cells, $P3/PC_{61}BM$ still exhibited the best efficiency among all. Obviously, light harvesting plays an important role in this system, although there is slightly favored root-mean-square (rms) roughness than and slightly better balanced electron/ hole mobility ratio than $P2/PC_{61}BM$.

CONCLUSIONS

In conclusion, a novel monomer based on DTF moiety was prepared and conjugated copolymers (**P1-P3**) have been synthesized from this entity and conjugated segments. These polymers have good thermal stability with decomposition temperatures higher than 300°C. Electron-deficient conjugated segments significantly red shift the absorption due to the CT transition. The BHJ PSCs based on these polymers and PC₆₁BM at 1:1 weight ratio have PCEs in the range of 0.53–0.93%, and open-circuit voltages in the range of 0.69–0.85 V, which are significantly higher than those of TTF-

based polymers. OPVs with more balanced carrier mobility or polymers of better light harvesting exhibit better cell performance.

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