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Synthesis and photovoltaic properties of low-bandgap alternating copolymers consisting of 3-hexylthiophene and [1,2,5]thiadiazolo[3,4-g]quinoxaline derivatives

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ABSTRACT

Two different kinds of low-bandgap alternating copolymers consisting of 3-hexylthiophene and [1,2,5]thiadiazolo[3,4-g]quinoxaline were synthesized via the Stille coupling reaction. The copolymers show broad absorption band from visible to infrared region. The bandgaps (1.02–1.35 eV) of the copolymers are successfully tuned by changing the substituent on the acceptor unit. The copolymers are highly soluble in common organic solvents due to three 3-hexylthiophenes in the repeating unit. By optimizing the device parameters such as the blend ratio of copolymer to PCBM and the choice of processing solvent, the power conversion efficiency reaches as high as 1.27% under the standard solar radiation condition (AM 1.5G, 100 mW/cm²).

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1. Introduction

Polymer solar cells have attracted great interest due to their unique advantages, such as low cost, light weight, and potential use in flexible devices. Among the concepts for polymer photovoltaic devices, bulk heterojunction (BHJ) solar cells have been mostly used, since they have advantages of ease processability and high efficiency [1-5]. The active layer of BHI solar cells forms an interpenetrating network of electron-donor and electron-acceptor domains. Currently, BHJ solar cells fabricated by simple blending of regioregular poly(3-hexylthiophene) (P3HT) as an electron-donating polymer and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as an electron acceptor have reached the power conversion efficiency (PCE) as high as 5% under AM 1.5G (AM = air mass) illumination [6,7]. Although possessing several advantageous properties, P3HT has a relatively high bandgap of 1.9 eV and thus harvests photons only up to 22% of available photons. To absorb photons at longer wavelengths, where more photon flux from the emission of the sun is found, development of low-bandgap polymer is inevitably needed.

In recent years, donor-acceptor alternating copolymers have attracted extensive interest because their electronic properties could be easily manipulated [8-11]. The internal charge transfer (ICT) between donor and acceptor units in the donor-acceptor copolymers can effectively reduce the bandgaps of the polymers. Very recently, some new low-bandgap polymers with high efficiency over 6% have been reported [12,13]. The acceptor units that have been used for donor-acceptor alternating copolymers include 2,1,3-benzothiadiazole, thieno[3,4-b]pyrazine, quinoxaline, benzo[1,2-c,3,4-c']bis[1,2,5]thiadiazole, pyrazino[2,3g]quinoxaline, and [1,2,5]thiadiazolo[3,4-g]quinoxaline (TQ) [14–19]. We are particularly interested in TQ as an acceptor unit because of the strong electron-withdrawing property of four imine groups in the TQ unit. The donoracceptor alternating copolymers containing TQ as the acceptor unit have been reported to have bandgaps of 0.90-1.50 eV, depending on the electron-donating power





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of donor unit and the bulkiness of side group of the acceptor unit. Although several research groups have synthesized TQ-based low-bandgap copolymers and reported the photovoltaic properties of those copolymers, the molecular weights of the copolymers were very low because of the lack of solubility, and therefore the power conversion efficiencies were below 0.7% [17,20–23].

Herein we report the synthesis and characterization of a new class of donor–acceptor alternating copolymers comprising 3-hexylthiophene (3HT) unit and TQ derivatives as electron-donating and electron-withdrawing unit, respectively. The optical and electrochemical properties of the copolymers and the performance of the copolymers/PCBM BHJ solar cells are reported.

2. Experimental

2.1. Materials

All reagents were obtained from Aldrich unless otherwise specified and used as received. Tetrahydrofuran (THF) was dried over sodium/benzophenone under nitrogen and freshly distilled before use. Hexane was dried over calcium hydride under nitrogen and freshly distilled before use. 5,6-Diamino-4,7-di(4-hexylthien-2-yl)-2,1,3-benzothiadiazole (2), 6,7-dimethyl-4,9-di(4-hexylthien-2-yl)[1, 2,5]-thiadiazolo[3,4-g]quinoxaline (3b), and 6,7-dimethyl-4,9-di(5'-bromo-(4-hexylthien-2-yl))[1,2,5]-thiadiazolo[3, 4-g]quinoxaline (4b) were synthesized by following the literature method [24]. [6,6]-Phenyl-C₆₁-butyric acid methyl ester (PCBM) was obtained from Nano-C. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (Baytron P VP AI 4083) was purchased from H.C. Stark and passed through a 0.45 µm PES syringe filter before spin-coating.

2.2. Synthesis

2.2.1. 2,5-Bistrimethylstannyl-3-hexylthiophene (1)

3-Hexylthiophene (5.0 g, 0.03 mol) and tetramethylethylenediamine (TMEDA) (13.5 ml, 3.0 equiv) were added into 150 ml of anhydrous hexane. After cooled to -78 °C with isopropanol/dry ice bath, *t*-BuLi (52.4 ml, 3.0 equiv) was added dropwise to the solution over 30 min. After the cooling bath was removed, the reaction mixture was stirred at room temperature for 48 h under nitrogen atmosphere. Then the reaction mixture was cooled back down to -78 °C, and the reaction solution was stirred overnight at room temperature after 92.0 ml of trimethyltinchloride solution (3.0 equiv) was added. The product mixture was washed with saturated solution of NaHCO₃, water, and brine, then dried over anhydrous MgSO₄ and filtered. After evaporation of the solvent under reduced pressure, the residue was further purified by flash chromatography on silica gel (99:1 hexane/triethylamine as eluent), yielding viscous light yellow liquid as a product. Yield: 12.44 g (85%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 7.21 (t, 1H), 2.56 (t, 2H), 1.60 (t, 2H), 1.52-1.41 (m, 6H), 0.86 (t, 3H), 0.43-0.30 (m, 18H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 151.88, 143.79, 137.82, 137.61, 32.77, 32.19, 31.55, 29.48, 22.08, 13.73, -8.18. Anal. Calcd for C₁₆H₃₂S₁Sn₂ (%): C, 38.91; H, 6.48; S, 6.50. Found (%): C, 38.92; H, 6.47; S, 6.49.

2.2.2. 6,7-Diphenyl-4,9-di(4-hexylthien-2-yl)[1,2,5]thiadiazolo[3,4-g]quinoxaline (**3a**)

To a suspension of 5,6-diamino-4,7-di(4-hexylthien-2vl)-2,1,3-benzothiadiazole (0.815 g, 1.64 mmol) in 80 ml of acetic acid, 1,2-diphenyl-1,2-ethanedione (0.862 g, 4.1 mmol) was added in one portion. When the mixture was stirred at room temperature for 8 h, green-colored precipitate was obtained. The precipitate was filtered, washed thoroughly with methanol, and then dried in vacuum to afford green powder as product. Yield: 1.01 g (92%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.86 (d, 2H), 7.83 (d, 4H), 7.44 (m, 6H), 7.30 (d, 2H), 2.80 (t, 4H), 1.78 (m, 4H), 1.48–1.35 (m, 12H), 0.93 (t, 6H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 153.11, 152.12, 143.23, 138.37, 135.80, 135.38, 135.04, 130.94, 130.79, 129.87, 128.27, 121.53, 32.01, 29.82, 29.37, 28.90, 22.91, 14.07. Anal. Calcd for C₄₀H₄₀N₄S₃ (%): C, 71.41; H, 5.95; N, 8.33; S, 14.31. Found (%): C, 71.14; H, 5.96; N, 8.30; S, 14.55.

2.2.3. 6,7-Diphenyl-4,9-di(5'-bromo-(4-hexylthien-2-yl))-[1,2,5]-thiadiazolo[3,4-g]quinoxaline (**4a**)

The compound **3a** (0.890 g, 1.32 mmol) was dissolved in 40 ml of THF, to which *N*-bromosuccinimide (NBS) (0.483 g, 2.71 mmol) was added in the dark. After stirring the mixture at room temperature for 3 h, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (1:3 chloroform/ hexane as eluent) to yield the dark-green product. Yield: 0.804 g (74%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.79 (d, 2H), 7.70 (d, 4H), 7.45 (m, 6H), 2.80 (t, 4H), 1.78 (m, 4H), 1.50–1.35 (m, 12H), 0.93 (t, 6H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) 153.02, 150.77, 141.79, 137.45, 135.22, 134.29, 134.03, 130.85, 129.44, 127.69, 119.78, 118.25, 31.87, 29.88, 29.59, 28.71, 22.66, 13.89. Anal. Calcd for C₄₀H₃₈N₄S₃Br₂ (%): C, 57.83; H, 4.58; N, 6.75; S, 11.59. Found (%): C, 57.98; H, 4.65; N, 6.52; S, 11.79.

2.2.4. Poly(3-hexylthiophene-alt-6,7-diphenyl-4,9-bis-(4-hexylthien-2yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (P(3HT-PhTDQ))

Under nitrogen atmosphere, monomer 1 (102.0 mg, 0.206 mmol) and 4a (171.3 mg, 0.206 mmol) were dissolved in 10 ml of anhydrous 1,2-dichlorobenzene. The solution was flushed with N₂ for 20 min, and then 7.2 mg of Pd(PPh₃)₂Cl₂ was added. After the reaction mixture was stirred at 130 °C for 48 h, the polymer was precipitated by addition of 70 ml of methanol. The crude product was filtered through a Soxhlet thimble, and then subjected to Soxhlet extraction with methanol, hexane, acetone, and chloroform. The polymer was recovered from the chloroform fraction by rotary evaporation as dark green solid. Yield: 107.7 mg (63%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 9.18-8.80 (m, 2H), 7.75 (s, 4H), 7.33 (d, 6H), 7.20-6.93 (m, 1H), 3.01-2.54 (m, 6H), 1.98-1.60 (m, 6H), 1.58-1.21 (m, 18H), 0.98-0.65 (m, 9H). Anal. Calcd for C₅₀H₅₂N₄S₄ (%): C, 71.75; H, 6.22; N, 6.70; S, 15.34. Found (%): C, 71.46; H, 6.22; N, 6.67; S, 15.41.

2.2.5. Poly(3-hexylthiophene-alt-6,7-dimethyl-4,9-bis-(4-hexylthien-2yl)-[1,2,5]thiadiazolo[3,4-g]quinoxaline (P(3HT-MeTDQ))

The polymerization process was the same as that of P(3HT-PhTDQ), except that the monomer **4b** was used instead of **4a**. Yield: 62.5 mg (55%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) 9.10–8.71 (m, 2H), 7.36–7.02 (m, 1H), 3.04–2.49 (m, 12H), 1.98–1.66 (m, 6H), 1.58–1.33 (m, 18H), 1.02–0.68 (m, 9H). Anal. Calcd for C₄₀H₄₈N₄S₄ (%): C, 67.39; H, 6.74; N, 7.86; S, 18.01. Found (%): C, 67.35; H, 6.78; N, 7.75; S, 17.96.

2.3. Measurement

The chemical structures of materials used in this study were identified by ¹H NMR and ¹³C NMR (Avance DPX-300). Elemental analysis was performed on EA1110 (CE Instrument) elemental analyzer. Molecular weight and its distribution were measured by gel permeation chromatography (PL-GPC 50 Integrated GPC System, Polymer Laboratories) equipped with a refractive index detector using THF as eluent, where the columns were calibrated against standard polystyrene samples. The optical absorption and photoluminescence spectra were obtained by UV-vis-NIR spectrophotometer (Lambda 850, Perkin-Elmer) and fluorescence spectrometer (814, Photon Technology International), respectively. Cyclic voltammetry experiments were carried out on potentiostat/galvanostat (Model 273 A, EG&G Princeton Applied Research) in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) in dichloromethane. Three-electrode cell was used for all experiments. Platinum wires (Bioanalytical System Inc.) were used as both counter and working electrodes, and silver/silver ion (Ag in 0.1 M AgNO₃ solution, Bioanalytical System Inc.) was used as a reference electrode.

2.4. Fabrication of photovoltaic devices

Polymer solar cells were fabricated on ITO glass cleaned by stepwise sonication in acetone and IPA, followed by O₂ plasma treatment for 10 min. The substrate was spincoated with PEDOT:PSS at 4500 rpm for 1 min and annealed at 120 °C for 30 min to yield 40 nm thick film. A mixture of polymer and PCBM were dissolved in anhydrous chlorobenzene (30 mg/ml), and spin-coated on the top of the ITO/PEDOT:PSS film at 800 rpm for 60 s. The typical thickness of the active layer was 70-80 nm. LiF (0.5 nm) and Al (100 nm) were evaporated under vacuum lower than 10^{-6} Torr on the top of active layer through a shadow mask. The effective area of one cell was ca. 4 mm^2 . The current–voltage (*I–V*) curve of the device was obtained on a computer-controlled Keithley 4200 source measurement unit under AM 1.5G (100 mW/cm²) simulated by an Oriel solar simulator (Oriel 91160A). The light intensity was calibrated using a NREL-certified photodiode prior to each measurement. The external quantum efficiency (EQE) was measured using a Polaronix K3100 IPCE measurement system (McScience) where the light intensity at each wavelength was calibrated with a standard single-crystal Si cell.

3. Results and discussion

3.1. Synthesis and characterization

We synthesized alternating copolymers for preparation of low-bandgap polymers. The synthetic routes for preparation of the monomers and polymers are shown in Fig. 1. We used the palladium-catalyzed Stille coupling reaction to synthesize alternating copolymers of 3HT and TO derivatives which are electron-donating and electronwithdrawing unit, respectively. At first, 3HT was dilithiated with 3 equiv amount of t-BuLi and TMEDA, followed by reaction with trimethyltin chloride to yield 2,5bistrimethylstannyl-3-hexylthiophene (1). In a separate experiment, the comonomer 4a was synthesized by condensation reaction of diamino compound with 1,2-diphenyl-1,2-ethanedione, followed by bromination with NBS in THF. Stille coupling of 1 with 4a or 4b resulted in the corresponding polymers, P(3HT-PhTDQ) and P(3HT-MeT-DQ), with moderate yield. The polymers are highly soluble in common organic solvents, such as chloroform, toluene, and THF at room temperature. The number-average molecular weight (M_n) and polydispersity index (PDI) of P(3HT-PhTDQ) are 7200 and 1.6, respectively, and those of P(3HT-MeTDQ) are 11,100 and 1.5, respectively.

3.2. Optical properties

The optical absorption spectra of the two polymers in chloroform solutions and films on glass substrate are shown in Fig. 2a and b, respectively. Both of two polymers have broad absorption from visible to infrared region. The lower energy absorption peaks of P(3HT-PhTDQ) and P(3HT-MeTDO) in solution are 784 nm and 703 nm, respectively. As expected, the broad and longer wavelength absorption of the polymers is attributed to the intermolecular charge transfer induced by the donoracceptor structure of the 3HT and TO units. When the maximum absorption of polymers in solution is compared with that in solid state (Fig. 2a vs. b), it reveals that the maximum absorption wavelengths (λ_{max}) of the two polymers are red-shifted in solid state by 76 nm and 30 nm, respectively, indicating that polymer chains are associated in solid state. The optical bandgaps ($E_g(opt)$) as determined from the onset of the absorption spectra of P(3HT-PhTDQ) and P(3HT-MeTDQ) are 1.02 eV and 1.35 eV, respectively. Particularly, the bandgap of P(3HT-PhTDQ) is lower than that of P(3HT-MeTDQ) because the electron-withdrawing phenyl group in P(3HT-PhTDQ) makes the TQ unit more electron-deficient while the electron-donating methyl group in P(3HT-MeTDQ) weakens the electron-withdrawing power of TO unit. Since it has generally been accepted that the strong electron-withdrawing power of acceptor unit results in a decrease of bandgap for alternating copolymer, our results are very consistent with the prediction and other reports [11,25].

Fig. 3 compares photoluminescence (PL) spectra of P(3HT-MeTDQ) and P(3HT-MeTDQ)/PCBM composite in solid state. P(3HT-MeTDQ) shows strong PL with a maximum at 990 nm whereas P(3HT-PhTDQ) does not show



Fig. 1. Synthetic route of alternating copolymers.

PL below 1000 nm wavelength. The PL intensity of P(3HT-MeTDQ) is largely quenched by addition of PCBM, indicating that the charge transfer takes place effectively from the polymer to PCBM.

3.3. Electrochemical properties

The electrochemical data of all the polymers were obtained from the oxidation and reduction cyclic voltammograms, as shown in Fig. 4, and are summarized in Table 1. The onset oxidation and reduction potential of P(3HT-PhTDQ) are 0.38 eV and -0.48 eV (vs. Ag/Ag⁺), respectively, and those of P(3HT-MeTDQ) are 0.52 eV and -0.65 eV (vs. Ag/Ag⁺). The HOMO energy levels of the polymers can be calculated using the equation: HOMO = $-[E_{ox} - E_{1/2}(\text{ferro$ $cene}) + 4.8]$ V, where E_{ox} is the onset oxidation potential of polymer and $E_{1/2}(\text{ferrocene})$ is the onset oxidation potential of ferrocene vs. Ag/Ag⁺. The LUMO energy levels can be estimated by using the equation: LUMO =

 $-[E_{red} - E_{1/2}(ferrocene) + 4.8]$ V, where E_{red} is the onset reduction potential of polymer. The calculated HOMO and LUMO energy levels of P(3HT-PhTDQ) are -4.82 eV and -3.94 eV, and those of P(3HT-MeTDQ) are -4.96 eV and -3.79 eV, respectively, from which the electrochemical bandgaps $(E_g(ec))$ for each polymer can be determined. It is noted that the $E_g(ec)$ values of the copolymers are smaller than their corresponding values of $E_{g}(opt)$. It has generally been accepted that a LUMO-LUMO offset of 0.3-0.4 eV is necessary for efficient electron transfer from polymer to PCBM [26]. Since the LUMO energy level of PCBM has the value ranging between -4.0 and -4.3 eV [27,28], the LUMO-LUMO offset between P(3HT-MeTDQ) and PCBM is larger than 0.3 eV and therefore it is expected that exciton can be easily dissociated at the interface between P(3HT-MeTDQ) and PCBM, whereas the LUMO-LUMO offset between P(3HT-PhTDQ) and PCBM is small, and thus the charge separation is difficult to occur. Furthermore, the HOMO energy level of P(3HT-PhTDQ) is



Fig. 2. UV-vis-NIR absorption spectra of the copolymers in chloroform (a) and in film (b).



Fig. 3. Photoluminescence spectra of P(3HT-MeTDQ) and P(3HT-MeTDQ):PCBM composite films.

higher than that of PEDOT:PSS (-5.0 eV), while the HOMO energy level of P(3HT-MeTDQ) is almost the same as that of PEDOT:PSS, indicating that holes can be easily trans-



Fig. 4. Cyclic voltammograms of P(3HT-MeTDQ) and P(3HT-PhTDQ).

ported from P(3HT-MeTDQ) to PEDOT:PSS whereas holes can be trapped at the interface between P(3HT-PhTDQ) and PEDOT:PSS. Consequently, it can be expected that P(3HT-MeTDQ) is better candidate for active material in photovoltaic device.

3.4. Photovoltaic properties

The polymer solar cells were fabricated with layered configuration of glass/ITO/PEDOT:PSS/polymer:PCBM/LiF/ Al. The current-voltage characteristics of photovoltaic devices with two different polymers, P(3HT-PhTDQ) and P(3HT-MeTDQ), are shown in Fig. 5, and the photovoltaic parameters of open circuit voltage (V_{oc}), short circuit current (I_{sc}) , fill factor (FF), and power conversion efficiency (PCE) are summarized in Table 2. When the PCEs of P(3HT-MeTDQ) are compared with those of P(3HT-PhTDQ), it reveals that the PCEs of P(3HT-MeTDQ) are higher than those of P(3HT-PhTDQ). It should be noted here that P(3HT-MeTDQ) device reaches 0.48% of PCE at the mixing ratio of 1:2 (polymer:PCBM) with $V_{oc} = 0.58$ V, $J_{sc} =$ 1.58 mA/cm², and FF = 0.53. The values of V_{0c} and FF of P(3HT-MeTDQ) are comparable to or slightly higher than those of other TQ-based polymer solar cells [17,20-23], while the J_{sc} value is lower than others. When the external quantum efficiencies (EQE) of P(3HT-PhTDQ) and P(3HT-MeTDQ) are compared (Fig. 6), P(3HT-MeTDQ) exhibits 7.3% efficiency at 700 nm while P(3HT-PhTDQ) shows very low efficiency. This can be explained by the small offset of LUMO levels of P(3HT-PhTDQ) and PCBM, which implies that only a small fraction of the absorbed photons is dissociated at the polymer/PCBM interface.

It is important to optimize the morphology of active layer for achieving high efficiency. The AFM image of P(3HT-MeTDQ):PCBM blend film shows smooth and homogeneous film surface without exhibiting any characteristic feature of phase separation, as can be seen in Fig. 7a and b. This homogeneous morphology may cause low current density because it does not provide the pathway for charge carriers to pass through. It has recently

Table 1

Table 2

Optical and electrochemical properties of polymers.

Sample	Absorption		$E_{\rm g}({\rm opt})^{\rm a}~({\rm eV})$	HOMO (eV)	LUMO (eV)	$E_{\rm g}({\rm ec})^{\rm b}~({\rm eV})$
	$\lambda_{\max}(CHCl_3)$ (nm)	$\lambda_{\max}(\text{film}) (\text{nm})$				
P(3HT-PhTDQ) P(3HT-MeTDQ)	784 703	860 733	1.02 1.35	-4.82 -4.96	-3.94 -3.79	0.88 1.17

^a Determined from the onset of UV-vis-NIR absorption spectra.

^b Calculated from the cyclic voltammetry.



Fig. 5. Current–voltage characteristics of photovoltaic devices based on P(3HT-PhTDQ) (a) and P(3HT-MeTDQ) (b) with different mixing ratio of copolymer to PCBM by weight.

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	400	600	800	1000		
	Wavelength (nm)					

Fig. 6. External quantum efficiency spectra of polymer/PCBM solar cells.

been reported that the morphology of active layer can be effectively modified by the use of specific additives [29-32]. Peet and coworkers [29] have demonstrated that addition of 1,8-octanedithiol (ODT) to polymer:PCBM composite induces phase separation of active layer and thereby improves the PCE of BHJ solar cells. Accordingly, when we add 5 vol.% of ODT to chlorobenzene solution of P(3HT-MeTDO):PCBM (1:2 w/w), the morphology of active laver shows a phase-separated structure, as shown in Fig. 7c and d. When the surface roughness and phase morphology of film with addition of ODT are compared with those of film without ODT, as shown in Fig. 7, it is realized that the surface roughness of film with ODT is larger than the film without ODT and that the film morphology with ODT exhibits more phase-separated structure as compared to the film without addition of ODT.

Photovoltaic parameters of devices testing under standard AM 1.5G conditions.								
Polymer	Polymer:PCBM	Solvent	$V_{\rm oc}~({ m V})$	$J_{\rm sc}$ (mA/cm ²)	FF	PCE (%)		
P(3HT-PhTDQ)	1:1	CB	0.46	0.39	0.32	0.06		
	1:2	CB	0.47	0.85	0.36	0.14		
	1:3	CB	0.51	0.56	0.43	0.12		
	1:4	CB	0.52	0.46	0.42	0.10		
P(3HT-MeTDQ)	1:1	CB	0.59	0.89	0.54	0.28		
	1:2	CB	0.58	1.58	0.53	0.48		
	1:3	CB	0.63	1.03	0.51	0.33		
	1:4	CB	0.59	1.06	0.44	0.28		
	1:2	CB/ODT	0.55	4.64	0.50	1.27		

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Fig. 7. AFM images of P(3HT-MeTDQ):PCBM (1:2 weight ratio) thin films cast from chlorobenzene (a, height; b, phase), and chlorobenzene with 1,8-octanedithiol as an additive (c, height; d, phase). Scale bars are 150 nm.

To investigate the effect of phase-separated morphology on the charge transport property, we measured hole and electron mobilities from the space charge limited current (SCLC) *I–V* curve obtained in the dark for hole-only device (ITO/PEDOT:PSS/P(3HT-MeTDO):PCBM/Au) and electron-only device (Al/P(3HT-MeTDQ:PCBM)/Al) (Fig. 8). The SCLC behavior can be analyzed using the Mott-Gurney law [33]: $J = (9/8)\varepsilon\mu(V^2/L^3)$, where ε is the static dielectric constant of the medium, μ is the carrier mobility, $V = V_{a} - V_{bi}$ (V_{a} , the applied bias; V_{bi} , the built-in potential due to the difference in electrical contact work functions), and L is the layer thickness. When the hole and electron mobilities of the device with ODT, determined from the slope of plot of $I^{1/2}$ vs. V, are compared with those of the device without ODT, it is found that both the hole and electron mobilities of the device with ODT are enhanced compared to those of the device without ODT: the hole mobility increases from 6.37×10^{-6} to 2.30×10^{-5} cm²/ Vs: the electron mobility increases from 1.10×10^{-5} to 3.60×10^{-5} cm²/Vs. This can be attributed to effective formation of phase-separated structure induced by the addition of ODT, which leads to better connectivity of each phase.

Fig. 9 compares J–V curves of devices with and without ODT, from which V_{oc} , J_{sc} , FF, and PCE are determined (Table 2). The PCE of the device with ODT (1.27%) is much higher

than that of device without ODT (0.48%). Particularly, the addition of ODT causes a large increase in J_{sc} , because polymer/PCBM composite is phase-separated in nanometer scale as ODT is added, which provides effectively the pathway for charge carriers to pass through the active layer. On the other hand, the photovoltaic performance of P(3HT-PhTDQ) device is not improved by addition of ODT, indicating that the low PCE of the device is attributed mainly to the small difference between LUMO energy levels of the polymer and PCBM.

4. Conclusion

We have synthesized two types of 3-hexylthiophenethiadiazoloquinoxaline alternating copolymers via the Stille coupling polymerization. Introduction of three hexyl side groups in a repeating unit results in highly soluble polymers with moderate molecular weight. The copolymers exhibited a wide range of optical absorption up to near-IR region. The device fabricated with P(3HT-MeTDQ) shows the PCE of 1.27%, one of the highest values among the TQ-based copolymers, when a small amount of ODT is added to polymer/PCBM composite. Our results demonstrate that P(3HT-MeTDQ) is a potential candidate for application of near-IR absorbing polymer solar cells.



Fig. 8. Dark *J*–*V* characteristics for hole-only (a) and electron-only (b) devices of P(3HT-MeTDQ):PCBM (1:2 w/w) fabricated using different processing solvents. The solid lines are the best linear fit of the data points.



Fig. 9. Current–voltage characteristics of photovoltaic devices of P(3HT-MeTDQ):PCBM (1:2 w/w) fabricated using different processing solvents.

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