Polythiophenes Bearing Electron-Withdrawing Groups in the Side Chain and Their Application to Bulk Heterojunction Solar Cells

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ABSTRACT: Soluble polythiophenes bearing strong electron withdrawing groups, dicyanoethenyl $[-CH=C(CN)_2]$ (PTDCN) and cyano-methoxycarbonylethenyl $[-CH=C(CO_2Me)CN]$ (PTCNME), in the side chains have been prepared. Optical band gaps calculated from onset absorption were 1.70 eV and 1.73 eV for PTDCN and PTCNME, respectively. Highest occupied molecular orbital energy levels measured with a surface analyzer (AC-2) were -5.53 eV and -5.29 eV for PTDCN and PTCNME, respectively, which were much lower than that of poly(3-hexylthiophene) (-4.81 eV). To investigate photovoltaic properties, bulk heterojunction polymer solar cells based on PTDCN and PTCNME were fabricated with a structure of ITO/PEDOT:PSS/active layer/LiF/AI, where the active layer was a

INTRODUCTION Organic photovoltaics (OPVs) based on π conjugated polymers are of interest because of their potential to be low cost, lightweight, and flexible. Bulk heterojunction (BHJ) devices based on a π -conjugated polymer as a donor and a fullerene derivative as an acceptor have emerged as the most efficient solar cells to date.¹ BHJ solar cells using π -conjugated polymers have afforded very high power conversion efficiencies (PCEs; 5-7%).² PCE depends on three factors: short-circuit current (J_{sc}) , open-circuit current (V_{oc}) , and fill factor (FF). For attaining enhanced J_{sc} , the polymers should have a broad absorption in the solar spectrum to ensure effective harvesting of the solar photons and high charge carriers mobility.³ Generally, such a broad absorption can be achieved by designing more planar molecular geometries and more rigid structures in π -conjugated polymer. Recently, π -conjugated polymers composed of electron-donating and electron-withdrawing units in the polymer backbone have been prepared with expecting that the absorbance can be shifted to longer wavelength because of the formation of inter- and/or intramolecular charge-transfer complex. In addition, morphology of the donor-acceptor blend film plays very important role in an enhancement of J_{sc} . The optimizablend film of polymer and [6,6]-phenyl C₆₁ butyric acid hexyl ester (PC₆₁BH). Solar cell parameters were estimated from current density–voltage (*J–V*) characteristics under the illumination of AM1.5 at 100 mW/cm². The solar cell based on the blend film of PTCNME:PC₆₁BH (1:1) showed power conversion efficiency (PCE) of 0.72% together with the open current voltage (*V*_{oc}) of 0.61 V, the short current density (*J*_{sc}) of 3.90 mA/cm², and the fill factor of 30.3%. The PCE of a solar cell fabricated from PTDCN in a similar way was 0.56%. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 234–241, 2011

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tion of the phase separation and domain size of polymer and fullerene in the blend film has been performed by several methods such as varying component ratio of polymer and fullerene, annealing of blend film, and addition of cosolvents or additives.⁴ V_{oc} of OPV is proportional to the gap between highest occupied molecular orbital (HOMO) level of donor polymer and lowest unoccupied molecular orbital (LUMO) level of the acceptor fullerene material.⁵ Currently, polymers with lower HOMO energy level are used as electron-donating polymer for polymer solar cells (PSCs) with high V_{oc} . Several strategies to lower HOMO energy level of polymers have been reported so far. Hou et al.6 currently reported that P3HDTTT bearing an alkyl group in the side chain of terthiophene repeating unit showed lower HOMO energy level than poly(3-hexylthiophene) (P3HT). HOMO energy level of the polymer was lowered with decreasing the number of electron-donating alkyl group in the polythiophene side chain. The $V_{\rm oc}$ of PSC based on P3HDTTT exhibited higher value than that based on P3HT, implying that the $V_{\rm oc}$ value directly depends on the HOMO energy level of a donor polymer. The introduction of strong electron-withdrawing groups such as nitro, cyano, halogen, ester, and ketone into the side chain is

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also well-known method to lower HOMO energy level of the corresponding polymers. Heeger and coworkers⁷ reported the preparation of poly(3,4-dicyanothiophene) (PDCTh) from 2,5-diiodo-3,4-dicyanothophene by in situ thermal polymerization. PDCTh showed very low HOMO energy level of -6.7eV because of electron-deficient cyano groups substituted directly on thiophene unit. Casalbore-Miceli et al.⁸ reported the polythiophene composed of 3,3'-dialkoxy-2,2'-bithiophene unit and 3-dicyanoethenylthiophene in the main chain (PolyCN), which was prepared by chemical and electrochemical polymerization. They described an intramolecular charge transfer between the oxygen lone pair of the alkoxy group and the dicyanoethenyl group, which led an appearance of absorption peak in the longer wavelength. However, in terms of HOMO energy level, PolyCN showed slightly lowered HOMO energy level (-5.1 eV) compared with P3HT (-4.8 to)-5.1 eV).

Herein, we report the synthesis and characterization of novel polythiophenes PTDCN and PTCNME composed of a thiophene unit substituted with long alkyl chains that assured the high solubility of the polymers and terthiophene units with strong electron-withdrawing groups, 2,2-dicyanoethenyl $[-CH=C(CN)_2]$ and 2-cyano-2-methoxycarbonylethenyl $[-CH=C(CO_2Me)CN]$ in the side chains. Their optical and thermal properties were also investigated by UV-vis spectroscopy and thermogravimetric analysis (TGA). We also describe the photovoltaic properties of the polymers by their utilization for fabricating solar cells with the structure of ITO/PDOT:PSS/polymer:PCBH/LiF/Al.

EXPERIMENTAL

Materials

THF and toluene were dried over sodium/benzophenone ketyl and distilled before use. Chloroform and DMF were distilled over CaH₂. Methanol and dichloromethane were used as received. 3-Thiophenecarboxaldehyde, 3,4-dibromothiophene, 2-tributylstannyl thiophene, Pd(PPh₃)₂Cl₂, Pd(PPh₃)₄, magnesium, bromooctane, trimethylstannyl chloride, a hexane solution of *n*-BuLi, *N*-bromosuccinmide (NBS), acrylronitrile, cyanoacetic acid, and piperidine were used without purification. 2,5-Dibromo-3-thiophenecarboxyaldehyde (**1**),⁹ [2,2';5',2"]terthiophene-3'-carboxyaldehyde (**3**),¹⁰ 5,5"-dibromo-[2,2';5',2"]terthiophene-3'-carboxyaldehyde (**4**),¹¹ cyanoacetic acid methyl ester,¹² and 3,4-dioctylthiophene (**8**)¹³ were prepared according to the literature.

Measurements and Characterization

¹H NMR spectra were recorded on a Varian INOVA 400 NMR spectroscopy using tetramethylsilane as an internal standard in chloroform-*d* (CDCl₃). IR spectrum was recorded on Thermo fishier Scientific NICOLET iS10. UV-vis spectrometer was measured in chloroform $(1.0 \times 10^{-5} \text{ M})$ on a JASCO V570 spectrometer. Polymer films for UV-vis measurement were prepared on a glass substrate with a spin coater (700 rpm for 10 s and then 3000 rpm for 60 s) using 10 mg/mL chloroform solution. Number-average (M_n) and weight-average (M_w) molecular weights were determined by size exclu-

sion chromatography with TOSOH HLC-8120GPC using a calibration curve of polystyrene standards and THF as an eluent. TGAs were conducted with a TA instrument TG-DTA6200 at a heating rate of 10 °C/min under nitrogen. HOMO levels of polymers were measured using a photo-electron spectrometer AC-2 (Riken Keiki) by measuring ionic potential of polymer film in air.¹⁴

Device Fabrication and Characterization of Polymer Solar Cell

The photovoltaic cell structure used in this study is ITO/ PEDOT:PSS/active layer/LiF/Al, where the active layer is the blend film of a polymer as an electron donor and [6,6]-phenyl C₆₁ butyric acid hexyl ester (PC₆₁BH) as an electron acceptor in the weight ratio of 1:1 or 1:2 (wt/wt). PEDOT:PSS was spin coated on the precleaned ITO glass substrate and heated at 150 °C for 10 min. Subsequently, active layer was prepared by spin casting of the blend solution of polymer and PC₆₁BH in chlorobenzene (10 mg/mL) on the PEDOT: PSS layer. The thickness of active layer is about 100 nm. LiF (1 nm) and Al anode (100 nm) were deposited on the active layer to complete solar cell fabrication. Solar cell parameters were estimated from current density-voltage (J-V) characteristics under air mass 1.5 global solar simulated light (AM1.5G at 100 mW/cm², highly uniform irradiation system using 150W Xe lamp as light source, Wacom Electric) irradiation. We calibrated the light intensity using a standard cell for amorphous silicon (a-Si) solar cells. J-V characteristics were measured using a Current-Voltage Source Meter (Keithley 2410, Keithley) at room temperature in the glove box filled with inert gas.

Synthesis

2-(5,5"-Dibromo-[2,2';5',2"]terthiophen-3'ylmethylene)malononitrile (5)

To a solution of **4** (0.33 g, 0.76 mmol) in acetonitrile (5 mL) were added malononitrile (59.4 mg, 0.90 mmol) and piperidine (3 μ L) at room temperature. After refluxing for 30 min, the solution was cooled to room temperature. Methanol (10 mL) was added into the resulting solution to give a precipitate, which was collected by filtration and then recrystallized from chloroform/methanol to afford 0.33 g (76%) of **5** as a reddish solid.

mp: 155.5–156.5 °C. ¹H NMR (400 MHz, CDCl₃, *δ*, ppm): 6.94 (d, J = 4.0 Hz, th-H, 1H), 7.03 (d, J = 4.0 Hz, th-H, 1H), 7.04 (d, J = 4.0 Hz, th-H, 1H), 7.77 (s, th-H, 1H), 7.94 (s, >C=CH—, 1H). ¹³C NMR (100 MHz, CDCl₃, *δ*, ppm): 82.30, 112.74, 113.82, 113.95, 117.34, 121.54, 125.98, 130.25, 130.95, 131.11, 131.73, 133.11, 135.97, 137.97, 144.84, 149.84. Anal Calcd for C₁₆H₆Br₂N₂S₃: C 39.85, H 1.25, Br 33.14, N 5.81, S 19.95. Found: C 39.48, H 1.09, Br 32.74, N 5.64, S 19.54.

2-Cyano-3-(5,5"-dibromo-[2,2';5',2"]terthiophen-3'-yl) Acrylic Acid Methyl Ester (6)

To a solution of **4** (1.00 g, 2.30 mmol) and cyanoacetic acid methyl ester (0.30 g, 3.00 mmol) in acetonitrile (30 mL) was added piperidine (5 μ L) at room temperature. After refluxing



FIGURE 1 ¹H NMR spectra of monomers 5 (a) and 6 (b) in CDCl₃ at room temperature.

for 1 h, the solution was cooled to room temperature to afford a precipitate, which was collected by filtration and washed with methanol. Obtained solid was purified by recrystallization from chloroform/methanol to afford 0.96 g (81%) of **6** as an orange solid.

mp: 193.5–195.0 °C. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 3.94 (s, —CH₃, 3H), 6.94 (d, J = 4.0 Hz, th-H, 1H), 7.02 (d, J = 4.0 Hz, th-H, 1H), 7.03 (d, J = 4.0 Hz, 1H), 7.15 (d, J = 4.0 Hz, th-H, 1H), 8.05 (s, th-H, 1H), 8.32 (s, >C=CH—, 1H). ¹³C NMR (100 MHz, CDCl₃, δ , ppm): 53.36, 102.50, 113.34, 115.43, 116.48, 122.59, 125.55, 129.63, 130.97, 131.15, 131.55, 134.00, 136.53, 137.04, 143.74, 145.61, 163.15. Anal Calcd for C₁₇H₉Br₂NO₂S₃: C 39.63, H 1.76, Br 31.01, N 2.72, O 6.21, S 18.67. Found: C 39.69, H 1.62, Br 30.98, N 2.58, S 18.20.

2,5-Bis(trimethylstannyl)-3,4-dioctylthiophene (9)

To a solution of **8** (3.22 g, 10.4 mmol) in hexane (10 mL) was added *n*-BuLi (13.9 mL, 21.9 mmol) (1.58 M in hexane). The solution was refluxed for 30 min and then cooled to -45 °C. After Me₃SnCl (4.78 g, 24.0 mmol) was added to the solution at -45 °C, the solution was stirred at the temperature for 2 h. The reaction was finished by adding water and the mixture was extracted with ether. The extract was dried over MgSO₄ and organic solvent was removed under reduced pressure to give a reside which was purified by column chromatography (silica gel, hexane—5% Et₃N) to afford 6.11 g (92%) of **9** as a colorless oil.

¹H NMR (400 MHz, CDCl₃, δ , ppm): 0.35 (s, -SnMe₃, 18H), 0.89 (t, J = 6.6 Hz, -CH₃, 6H), 1.29-1.52 (m, -CH₂-, 24H), 2.51-2.60 (m, -CH₂-, 4H). ¹³C NMR (100 MHz, CDCl₃, δ ,



SCHEME 1 Preparation of monomers.



SCHEME 2 Preparation of PTDCN and PTCNME.

ppm): -7.89, 14.11, 22.69, 29.26, 29.48, 30.23, 31.19, 31.90, 32.96, 138.68, 151.00.

PTDCN

To a mixture of **5** (0.32 g, 0.50 mmol), **9** (0.24 g, 0.50 mmol), and Pd(PPh₃)₄ (11.6 mg, 0.010 mmol) were added anhydrous toluene (10 mL) and anhydrous DMF (2.5 mL). The solution was bubbled with argon for 10 min and then stirred for 48 h at 120 °C under argon atmosphere. After cooling to room temperature, the solution was poured into hexane (300 mL) to afford black precipitate, which was collected with filtration. The collected solid was dissolved in THF (50 mL) and then purified by column chromatography (silica gel, PSQ100B) using THF as an eluent. After organic solvent was removed under reduced pressure, hexane (200 mL) was added to give precipitate, which was collected with filtration to afford 0.19 g (59%) of PTDCN as a black solid.

¹H NMR (400 MHz, CDCl₃, δ, ppm): 0.89 (br, -CH₃, 6H), 1.18-1.49 (br, -CH₂-, 16H), 1.55-1.80 (br, -CH₂-, 8H), 2.51-2.79 (m, -CH₂-, 4H), 6.90-7.26 (m, th-H, 4H), 7.91 (br, th-H, 1H), 8.02 (br, >C=CH-, 1H). IR (ATR, cm⁻¹): 3064 (aromatic C-H), 2922, 2852 (aliphatic C-H), 2222 (C=N). UV-vis (chloroform) λ_{max} , nm (ε): 439 (22,900). Anal Calcd for C₃₆H₄₀N₂S₄: C 68.74, H 6.41, N 4.45, S 20.39. Found: C 66.28, H 6.11, N 3.80, S 17.35.

PTCNME

PTCNME was prepared under the same conditions as that for the preparation of PTDCN using **6** (0.32 g, 0.50 mmol) and **9** (0.26 g, 0.50 mmol). After purification by column chromatography, 0.27 g (81%) of PTCNME was obtained as a black solid.

¹H NMR (400 MHz, CDCl₃, δ , ppm): 0.88 (br, -CH₃, 6H), 1.15-1.52 (br, -CH₂-, 16H), 1.68 (br, -CH₂-, 8H), 2.51-2.85 (m, -CH₂-, 4H), 3.95 (s, -CH₃, 3H), 6.90-7.24 (m, th-H, 4H), 8.10 (br, th-H, 1H), 8.48 (br, >C=CH-, 1H). IR (ATR, cm⁻¹): 3061 (aromatic C-H), 2922, 2851 (aliphatic C-H), 2220 (C=N), 1726 (C=O). UV-vis (chloroform) λ_{max} , nm (ε): 452 (23,500). Anal Calcd for C₃₇H₄₃NO₂S₄: C 67.13, H 6.55, N 2.12, O 4.83, S 19.37. Found: C 64.56, H 6.55, N 2.02, S 16.99.

RESULTS AND DISCUSSION

Preparation of Monomers

2,5-Dibromo-3-thiophenecarboxyaldehye (1) was prepared by the reaction of 3-thiophenecarboxyalhedye with NBS.⁹ The Stille coupling of 1 with 2-tributylstannyl thiophene afforded terthiophene carboxyaldehyde **3** in 81% yield.¹⁰ Dibromoterthiophene **4** was obtained by the bromination of **3** with NBS in 62% yield.¹¹ Knoevenagel reaction of **4** with malononitrile or cyanoacetic acid methyl ester afforded monomers **5** and **6** in 88% and 81% yields, respectively. ¹H NMR spectra of dibromoterthiophene monomers **5** and **6** are shown in Figure 1. Distannylthiophene monomer **9** was prepared as follows: first, the reaction of 3,4-dibromothiophene **7** with octylmagnesium bromide in the presence of Ni catalyst afforded dioctylthiophene **8**, quantitatively.¹³ Lithiation of **8** with *n*-BuLi followed by an addition of trimethylstannyl chloride gave **9** as colorless oil in 92% yield (Scheme 1).

Preparation of PTDCN and PTCNME

PTDCN and PTCNME were prepared by the Stille cross-coupling polymerization using Pd(PPh₃)₄ as a catalyst. The reactions of bis(trimethylstannyl)thiophene 9 with dibromoterthiophenes 5 and 6 afforded PTDCN and PTCNME in 61% and 63% yields, respectively (Scheme 2). Polymers were purified by reprecipitation from hexane to remove oligomeric compounds and subsequent column chromatography (silica gel, PSQ100B) using THF as an eluent to remove metal catalyst. Molecular weight (M_w) and distribution (M_w/M_n) of the resulting polymers were 2.20 \times 10⁴ and 3.3 for PTDCN and 2.30×10^4 and 3.8 for PTCNME, respectively (Table 1). The resulting polymers showed good solubility in organic solvents such as THF, chloroform, chlorobenzene, and dichlorobenzene. The structures of PTDCN and PTCNME were assigned by ¹H NMR and IR spectroscopies (Figs. 2 and 3). IR spectra of PTDCN and PTCNME exhibited CN stretching bands at 2222 cm⁻¹ and 2220 cm⁻¹, respectively. In addition, the peak intensity of CN bond of PTDCN was stronger than that of PTCNME. A strong signal assignable to C=0stretching band of PTCNME was observed at 1726 cm^{-1} . Thermal stability of the polymers was investigated with TGA

TABLE 1	Synthesis a	and Charact	erization	of PTDCN
and PTC	NME			

		Molecular Weight ^b		TGA (°C) ^c	
Polymer	Yield (%) ^a	M _w	$M_{\rm w}/M_{\rm n}$	T_{d5}	$T_{\rm d10}$
PTDCN	61	$2.2 imes 10^4$	3.3	405	435
PTCNME	63	$\textbf{2.3}\times \textbf{10}^{4}$	3.8	319	374

^a Insoluble part in hexane.

^b Measured by GPC (THF).

^c Under N₂, 10 °C/min.



FIGURE 2 ¹H NMR spectra of PTDCN (a) and PTCNM (b) in CDCl₃.

under nitrogen atmosphere. Both polymers were stable up to 250 °C. $T_{d5}s$ of PTDCN and PTCNME were observed at 405 °C and 319 °C, respectively. PTDCN with rigid dicyano groups showed higher thermal stability than PTCNME. Glass transition temperature (T_g) by differential scanning calorimetry measurement was not detectable for both polymers.

Optical Properties of PTDCN and PTCNME

Optical properties of PTDCN and PTCNME are summarized in Table 2. Absorption spectra obtained in solution and film states are shown in Figure 4. First, UV-vis spectra of a solution state were measured in chloroform to give absorption maxima at 439 nm and 452 nm for PTDCN and PTCNME, respectively. These results imply that methyl ester group in the side chain of polythiophene was more effective for elongation of π -conjugation length than cyano group in the solution state. PTCNME also showed slightly higher molar absorption coefficient than PTDCN (Table 2). Absorption spectra of both polymer films prepared by spin cast on a glass substrate were measured as well. Absorption maxima of polymer films appeared at 473 nm and 466 nm for PTDCN and PTCNME, respectively. Absorption maxima of both polymers were observed at longer wavelength than those in a solution state, indicating the effective planarization and $\pi - \pi$ interaction of the polymer backbone in the solid state. Interestingly, PTDCN film revealed an absorption maximum at longer wavelength than that of PTCNME, which is a different result from that in a solution state. This may be attributed to the formation of more planar polymer structure by rigid dicyanoethenyl groups in a film state. Both polymer films also showed broad shoulders at 600 nm and 560 nm for PTDCN and PTCNME, respectively. Optical band gaps calculated from the absorption onset of polymer films are 1.70 eV and 1.73 eV for PTDCN and PTCNME, respectively. HOMO levels of both polymers were measured to be -5.53 eV for PTDCN and -5.29 eV for PTCNME. For a comparison, optical band gap and HOMO energy level of P3HT

were measured by the same methods to be 1.90 eV and -4.81 eV, respectively. Energy diagram of PTDCN, PTCNME, and P3HT are shown in Figure 5. It is clearly shown that polythiophenes bearing strong electron-withdrawing substituent in the side chain significantly reduce HOMO energy levels. PTDCN exhibited much lower HOMO energy level than P3HT by 0.72 eV. Optical band gaps of PTDCN and PTCNME are narrower than that of P3HT by about 0.2 eV, implying that the LUMO energy levels of PTDCN and PTCNME are significantly lowered as well by introducing strong electron-withdrawing substituents. PTDCN showed lower HOMO energy level than PTCNME by 0.24 eV. This result suggests dicyano ethenyl group works more effectively to reduce HOMO energy level than a single cyano ethenyl group. Our current results are comparable with those of PolyCN described in the Introduction section. The band gap of PTDCN (1.70 eV) was larger than that of PolyCN (1.3 eV). This result can be explained with a structural difference. PolyCN involves alkoxy groups as a strong electron-donating group and dicyanoethenyl groups a strong electron-withdrawing group in the side chain, which may lead the formation of intramolecular charge-transfer complex to give an absorption maximum in



FIGURE 3 IR spectra of PTDCN and PTCNME.

TABLE 2 Optical Properties and Energy Levels of Polymers

	UV–Vis (nm)				
	$\lambda_{\max} \operatorname{CHCl_3}^{a} (\varepsilon)^{b}$	λ_{\max} Film	HOMO (eV) ^c	LUMO (eV) ^d	$E_{\rm g.opt}$ (eV) ^e
PTDCN	439 (2.29 \times 10 ⁴)	473	-5.53	-3.83	1.70
PTCNME	452 (2.35 \times $10^4)$	466	-5.29	-3.56	1.73

^a Conc. = 1.0×10^{-5} M.

 $^{\rm b}$ Molar absorption coefficient (M $^{-1}\!/m).$

^c Measured with AC-2.

^d Calculated from the equation, $E_g = |HOMO - LUMO|$.

^e Calculated from the onset absorption, $E_{\rm g} = 1240 / \lambda_{\rm onset}$.



FIGURE 4 UV-vis spectra of PTDCN and PTCNME in solution (a) and film states (b).



FIGURE 5 HOMO and LUMO energy levels of P3HT, PTDCN, and PTCNME.

the longer wavelength. On the other hand, PTDCN contains soluble dialkyl groups, which are weaker electron-donating groups than alkoxy groups. Therefore, the formation of weak intramolecular charge-transfer complex is predicted for PTDCN. In terms of HOMO energy level, PTDCN revealed much lower energy level than PolyCN (-5.1 eV) probably because of no alkoxy groups as electron-donating substituents in the side chain of PTDCN.

Evaluation of Solar Cells Based on PTDCN and PTCNME

We previously investigated the PCE of solar cells based on the blend film of P3HT as electron donor and [6,6]-phenyl C_{61} butyric acid methyl ester (PC₆₁BM) or PC₆₁BH as an electron acceptor.¹⁵ Our previous results showed the solar cell based on P3HT:PC₆₁BH blend gave higher PCE than that based on P3HT:PC61BM blend. The higher miscibility between P3HT and PC₆₁BH may lead the increase in PCE. Our new polymers PTDCN and PTCNME were blended with PC₆₁BH as an electron acceptor and applied to solar cells with a configuration of ITO/PEDOT-PSS/polymer:PC61BH/ LiF/Al (Fig. 6). Polymer and PC₆₁BH were blended with a ratio of 1:1 or 1:2 (wt/wt) in chlorobenzene (10 wt/vol %) and spin coated on PEDOT-PSS layer, which was precasted on ITO electrode. The devices were finalized by the deposition of LiF and Al layer as top electrodes on the blend film. Figure 7 shows current density-voltage (J-V) curves of the solar cells estimated under AM1.5 at 100 mW/cm². The associated photovoltaic parameters $V_{\rm oc}$, $J_{\rm sc}$, FF, and PCE are summarized in Table 3. For comparison, the photovoltaic parameters of the solar cell based on P3HT are included. Solar cells based on PTDCN showed higher $V_{\rm oc}$ (0.69–0.73 V) compared with those based on PTCNME (0.60-0.61 V). This result is attributed to the lower HOMO energy level of PTDCN than that of PTCNME (Fig. 4). Jsc of solar cell was significantly affected by the blend ratio of polymer:PC₆₁BH; J_{sc}s



FIGURE 6 The structures of solar cell and PC₆₁BH.



FIGURE 7 Current density–voltage (J–V) characteristics of PV cells based on polymer PC₆₁BH with a ratio of 1:1 and 1:2.

of solar cells with a blend ratio of polymer: $PC_{61}BH = 1:1$ were relatively higher than those with polymer: $PC_{61}BH =$ 1:2. PCEs of solar cells based on both PTDCN and PTCNME are 0.56–0.72% and 0.22–0.30% for polymer: $PC_{61}BH = 1:1$ and 1:2 blend, respectively. When the ratio of $PC_{61}BH$ was increased in the blend, almost no change in $V_{\rm oc}$ and FF, and a drastic decrease of J_{sc} were observed. This is attributable to the relatively weak absorbance of polymer: $PC_{61}BH = 1:2$ blend film in UV-vis spectrum compared with that of polymer: $PC_{61}BH = 1:1$ blend film. Solar cells based on PTDCN revealed higher PCEs than those of PTCNME under the same fabrication conditions. This result can be explained with UVvis spectra of polymer:PC₆₁BH blend films. Unnormalized UV-vis spectra of polymer and PCBH blend films are shown in Figure 8. Absorbance of $PC_{61}BH$ was observed at 334 nm with a strong intensity. Both spectra showed very similar absorption pattern except for the shoulder peak at around 600 nm. The blend film of PTCNME exhibited stronger absorption at around 600 nm than that of PTDCN, which might lead higher J_{sc} and PCE for PTCNME (Table 3). In terms of Voc, the solar cells with new polymers PTDCN and PTCNME exhibited higher values than that with P3HT because of lower HOMO levels of PTDCN and PTCNME than P3HT. However, J_{sc} and FF of the solar cells with PTDCN and PTCNME gave much lower values than that with P3HT. It

TABLE 3 Characteristic Properties of Polymer Solar Cells

Polymer:PC ₆₁ BH	V _{oc} (V)	J _{sc} (mA/cm²)	FF (%)	PCE (%)
$PTDCN:PC_{61}BH = 1:1$	0.73	2.70	28.2	0.56
$PTDCN:PC_{61}BH = 1:2$	0.69	1.16	28.2	0.22
$PTCNME:PC_{61}BH = 1:1$	0.61	3.90	30.3	0.72
$PTCNME:PC_{61}BH = 1:2$	0.60	1.74	28.7	0.30
P3HT:PC ₆₁ BH = 1:0.7	0.59	9.87	60.4	3.54

 $V_{\rm ocr}$ open-circuit voltage; $J_{\rm scr}$ short-circuit current density; FF, fill factor; PCE, power conversion efficiency.



FIGURE 8 Absorption spectra of blend films of PTDCN:PC₆₁BH = 1:1 and PTCNME:PC₆₁BH = 1:1.

seems that the higher charge mobility of regioregular P3HT (97%) and the charge balance of the P3HT:PC₆₁BH device led enhanced $J_{\rm sc}$ and FF. It was also found that although band gaps of PTDCN and PTCNME are narrower than that of P3HT, the absorption intensity of P3HT:PC₆₁BH film was stronger than those of PTDCN:PC₆₁BH and PTCNME:PC₆₁BH, which may lead lowered $J_{\rm sc}$ and PCE of the solar cells with PTDCN and PTCNME compared to that with P3HT.

CONCLUSIONS

We prepared novel polythiophenes composed of dioctylthiophene as a soluble unit and a terthiophene having strong electron-withdrawing groups, dicyanoethenyl (PTDCN) and cyano-methoxycarbonylethenyl groups (PTCNME) via Stille cross-coupling polymerization. By using strong electron-withdrawing substitutes in the side chain, both polymers showed very low HOMO energy levels of -5.53 eV and -5.29 eV for PTDCN and PTCNME, respectively. Band gaps of PTDCN and PTCNME were 1.70 eV and 1.73 eV, respectively. Both polymers possessed high thermal stability up to 250 °C. The BHJ PSCs fabricated by using blend films of polymers as the electron donor and PC₆₁BH as the electron acceptor exhibited 0.56% and 0.72% of PCEs for PTDCN and PTCNME, respectively, under the illumination of AM1.5 at 100 mW/cm².

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