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# Low-bandgap poly(4*H*-cyclopenta[*def*]phenanthrene) derivatives with 4,7-dithienyl-2,1,3-benzothiadiazole unit for photovoltaic cells

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#### ABSTRACT

A series of conjugated polymer bearing 4*H*-cyclopenta[*def*]phenanthrene (CPP) unit have been synthesized and was evaluated in bulk heterojunction solar cell. The alternating copolymers with CPP unit were incorporated with 4,7-dithienyl-2,1,3-benzothiadiazole (DTBT) unit by Suzuki conditions. The newly synthesized copolymers, poly(2,6-((4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene))-*alt*-(4,7-((2-thienyl)-2,1,3-benzothiadiazole))) (PCPP-DTBT), and poly(2,6-((4,4-bis(4-((2-ethylhexyl)oxy)phenyl)-4*H*-cyclopenta[*def*]phenanthrene)-*alt*-(4,7-((2-thienyl)-2,1,3-benzothiadiazole))) (PBEHPCPP-DTBT), contain dialkyl and bis(alkoxyphenyl) groups in the CPP unit, respectively. The HOMO–LUMO energy bandgaps of these materials, estimated from UV–vis spectroscopy and cyclic voltammetry (CV), were 2.00 eV for PCPP-DTBT and 1.80 eV for PBEHPCPP-DTBT. Bulk heterojunction solar cells based on the blends of the polymers with [6,6]phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) gave power conversion efficiencies as 1.00% for PCPP-DTBT and 1.12% for PBEHPCPP-DTBT under AM 1.5, 100 mW/cm<sup>2</sup>.

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#### 1. Introduction

The most representative configuration of polymer solar cells is bulk heterojunction device which is composed of a blend of an electron-donating material (n-type), and an electron-accepting material (p-type) such as (6,6)-phenyl C<sub>61</sub>-butyric acid methyl ester or (6,6)-phenyl C<sub>71</sub>-butyric acid methyl ester (PC<sub>x</sub>BM). Many new conjugated polymers with a small band gaps are being researched for polymer solar cells (PSCs) to cover the long-wavelength region for the improvement of total photovoltaic current [1–6].

Several examples have been known to show that utilization of the donor and acceptor functionalities in conjugate backbone of the alternative copolymer structures is an efficient way to decrease the band gaps. In the donor/acceptor (D–A) combinations, 4,7-dithien2-yl-2,1,3-benzothiadiazole (DTBT) unit has been used effectively as an acceptor, and copolymerized with many kinds of donor segments, such as fullerene [7,8], silafluorene [9,10], carbazole [11], dithienosilole [12], and cyclopenta[2,1-*b*:3,4-*b*]dithiophene [13]. When these D–A types of copolymers were applied to photovoltaic solar cells (PSCs), the power conversion efficiencies (PCEs) in the range of 0.18%–5.4% have been reported [14,15].

Recently, we reported new blue-emitting polymers, dialkyl substituted poly(2,6-(4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phen anthrene)) (PCPP) [16,17], and bis(alkoxyphenyl) substituted poly(2,6-(4,4-bis(4-((2-ethylhexyl)oxy)phenyl)-4*H*-cyclopenta[*def*]phenanthre ne)) (BEHPCPP) [18] with a rigid backbone, which generates stabilized and efficient blue electroluminescence without exhibiting any peak in the long-wavelength region even after prolonged annealing or operation of the devices in air. In addition to the stability of the CPP unit, it's combination with DTBT unit can generate the larger difference between the donor HOMO level and the acceptor LUMO level of the copolymer, which could be an essential key for the enhanced open circuit voltage ( $V_{OC}$ ) of the PSCs [19].

In this paper, we report the synthesis and photovoltaic properties of new CPP-based conjugated copolymers for solar cell, poly(2,6-

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((4,4-bis(2-ethylhexyl)-4*H*-cyclopenta[*def*]phenanthrene))-*alt*-(4,7-((2-thienyl)-2,1,3-benzothiadiazole))) (PCPP-DTBT), and poly(2,6-(4,4-bis(4-((2-ethylhexyl)oxy)phenyl)-4*H*-cyclopenta[*def*]phenanth rene)-*alt*-(4,7-((2-thienyl)-2,1,3-benzothiadiazole))) (PBEHPCPP-DTBT).

#### 2. Experimental section

#### 2.1. Instruments

IR spectra were recorded on a Perkin-Elmer 16F PC FTIR spectrometer with samples prepared as KBr pellet. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Varian Gemini-300 (300 MHz) spectrometer and chemical shifts were recorded in ppm units with TMS as the internal standard. Flash column chromatography was performed with Merck silica gel 60 (particle size 230-400 mesh ASTM) with ethyl acetate/hexane or methanol/methylene chloride gradients unless otherwise indicated. Analytical thin layer chromatography (TLC) was conducted using Merck 0.25 mm silica gel 60F precoated aluminum plates with fluorescent indicator UV254. UV spectra were recorded with a Varian CARY-5E UV/vis spectrophotometer. Cyclic voltammetric waves were produced by using a EG&G Parc model 273 potentiostat/galvanostat. The differential scanning calometry analysis was performed under a nitrogen atmosphere (50 mL/min) on a DSC 822 at heating rates of 10 °C/min. Thermo gravimetric analysis was performed with a Dupont 951 TGA instrument in a nitrogen atmosphere at a heating rate of 10 °C/min to 700 °C. High resolution mass spectra (HRMS) were recorded on a IEOL IMS-700 mass spectrometer under fast atom bombardment (FAB) conditions in the Korea Basic Science Institute Daegu Branch. Solar cells were fabricated on an indium tin oxide (ITO)-coated glass substrate with the following structure; ITO-coated glass substrate/ poly(3,4-ethylenedioxythiophene)(PEDOT:PSS)/polymer:PC71BM/  $TiO_x/Al$ . The ITO-coated glass substrate was first cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried overnight in an oven. PEDOT:PSS (Baytron PH) was spin-cast from aqueous solution to form a film of 40 nm thickness. The substrate was dried for 10 min at 140 °C in air and then transferred into a glove box to spin-cast the charge separation layer. A solution containing a mixture of polymer:PC71BM (1:4) in dichlorobenzene solvent with concentration of 7 mg/ml was then spin-cast on top of the PEDOT/PSS layer. The film was dried for 60 min at 70 °C in the glove box. The  $TiO_x$  precursor solution diluted by 1:200 in methanol was spin-cast in air on top of the polymer:PC<sub>71</sub>BM layer (5000 rpm for 40 s). The sample was heated at 80 °C for 10 min in air. Then, an aluminum (Al, 100 nm) electrode was deposited by thermal evaporation in a vacuum of about 5  $\times$  10<sup>-7</sup> Torr. Current density–voltage (*J–V*) characteristics of the devices were measured using a Keithley 236 Source Measure Unit. Solar cell performance utilized an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 100  $Wm^{-2}$ . An aperture (12.7 mm<sup>2</sup>) was used on top of the cell to eliminate extrinsic effects such as cross-talk, waveguiding, shadow effects etc. The spectral mismatch factor was calculated by comparison of solar simulator spectrum with AM 1.5 spectrum at room temperature. The FETs were fabricated on heavily doped *n*type silicon (Si) wafers each covered with a thermally grown silicon dioxide (SiO<sub>2</sub>) layer with thickness of 200 nm. The active layer was deposited by spin coating at 2500 rpm. Prior to active layer deposition, SiO<sub>2</sub> surfaces were treated with octyltrichlorosilane (OTS) to make surface hydrophobic. All solutions were of 0.5 wt % concentration in chlorobenzene. The thickness of the deposited films was about 60 nm. Prior to deposition of source drain electrodes, the films were dried on hot plate stabilized at

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80 °C for 30 min. All fabrication processes were carried out in the glove box filled with N<sub>2</sub>. Source and drain electrodes using Au were deposited by thermal evaporation using shadow mask. The thickness of source and drain electrodes was 50 nm. Channel length (*L*) and channel width (*W*) were 50  $\mu$ m and 1.5 mm, respectively. Electrical characterization was performed using a Keithley semiconductor parametric analyzer (Keithley 4200) under N<sub>2</sub> atmosphere. Atom force microscopy (AFM) measurements were obtained with a Veeco NanoScope III AFM at room. Commercial silicon cantilevers (Veeco) with typical spring constants of 21–78 N m<sup>-1</sup> was used to operate the AFM in taping mode. Images were taken continuously with the scan rate 2.0 Hz.

#### 2.2. Materials

All reagents were purchased from Aldrich or TCI, and used without further purification. Solvents were purified by normal procedure and handled under moisture-free atmosphere. 2-(4,4-Bis(2-ethylhexyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4H-cyclopenta[*def*]phenanthren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6**) [20], and 2,6-dibromo-4,4-bis(4-((2-ethyl-hexyl)oxy)phenyl)-4H-cyclopenta[*def*]phenanthrene (**8**) [18] were synthesized using similar methods reported by us.

#### 2.3. Synthesis of monomer and polymer

#### 2.3.1. Synthesis of 4,7-di-2-thienyl-2,1,3-benzothiadiazole (4) [20]

To a stirred solution of 1 mL (12.2 mmol) of thiophene (1) in 30 mL of anhydrous THF was added 5.50 mL (8.72 mmol) of nbuthyllithium (1.6 M in Hexane) at -78 °C. After 2 h at -78 °C, the reaction mixture was added 2.58 g (7.90 mmol) of tributyltin chloride over 30 min. After stirring over 6 h at room temperature, the mixture was quenched with 20 mL of saturated aqueous NaHCO<sub>3</sub>. The organic phase was dried with MgSO<sub>4</sub>, concentrated under reduced pressure, and the resulting residue was dried under vacuum (4 Torr) for 15 h to give 3 g of tributyl(2-thienyl)stannane (2). To a solution of 1.00 g (3.40 mmol) of 4,7dibromobenzo-2,1,3-thiadiazole (3) in 50 mL of THF were added 3.00 g (8.16 mmol) of compound 2 and 97.0 mg (2.00 mol%) of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> under nitrogen atmosphere. After 3 h at reflux, the solvent was removed under reduced pressure, and then the residue was purified by flash chromatography ( $60 \times 150 \text{ mm}$ column, SiO<sub>2</sub>, 50% methylene chloride/n-hexane) to give 750 mg of compound **4** as red needles.: mp 124–125 °C, R<sub>f</sub> 0.5 (SiO<sub>2</sub>, 50% methylene chloride/*n*-hexane). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.08 (dd, 2H, J = 3.85 and 1.1 Hz), 7.79 (s, 2H), 7.45 (dd, 2H, I = 5.22and 1.1 Hz), 7.19 (dd, 2H, J = 5.22 and 3.85 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, *b*): 152.472, 139.261, 127.924, 127.408, 126.710, 125.822, 125.618; HRMS (FAB<sup>+</sup>, *m*/*z*) Calcd for C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>S<sub>3</sub> 299.9850; found 299.9852.

#### 2.3.2. Synthesis of 4,7-bis(5-bromo-2-thienyl)-2,1,3benzothiadiazole (5)

To a solution of 1 g (3.33 mmol) of compound **4** in 50 ml of *N*,*N*-dimethylformamide (DMF) was added 1.24 g (6.99 mmol) of *N*-bromosuccinimide (NBS). After being stirred for 12 h at room temperature, the dark red precipitate was filtered off and recrystallized with DMF to give 1 g of **5**, red solid.: mp 251–252 °C,  $R_f$  0.75 (SiO<sub>2</sub>, 50% methylene chloride/*n*-hexane). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 7.82 (d, 2H, *J* = 3.85 Hz), 7.80(s, 2H), 7.17 (d, 2H, *J* = 3.85 Hz). HRMS (*m*/*z*, FAB<sup>+</sup>) Cald for C<sub>14</sub>H<sub>6</sub>Br<sub>2</sub>N<sub>2</sub>S<sub>3</sub> 455.8060; Found 455.8055.

### 2.3.3. Synthesis of 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,4-bis(4-((2-ethylhexyl)oxy)phenyl)-4H-

cyclopenta[def]phenanthrene (**9**)

To a stirred solution of 0.720 g (0.950 mmol) of 2,6-dibromo-4,4-bis(4-((2-ethylhexyl)oxy)phenyl)-4*H*-cyclopenta[*def*]phenanthrene (**8**) in 40 mL of DMF were added 1.20 g (4.80 mmol) of bis(pinacolato)diboron, 0.470 g (4.80 mmol) of potassium acetate, and 50.0 mg (0.050 mmol) of Pd(dppf)Cl<sub>2</sub>. After 12 h at 60 °C, the reaction mixture was treated with 200 mL of water and 150 mL of diethyl ether. The organic phase was dried (MgSO<sub>4</sub>), and concentrated under reduced pressure. The residue was purified by column chromatography (40 × 150 mm column, SiO<sub>2</sub>, 5% ethyl acetate/*n*hexane) to give 0.7 g, yellow liquid.:  $R_f$  0.36 (SiO<sub>2</sub>, 10% ethyl acetate/ *n*-hexane). FTIR (KBr, cm<sup>-1</sup>): 3744, 2914, 2852, 1617, 1521, 1469, 1381, 1328, 1245, 1130, 1020, 951, 841, 718, 525. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 0.84–0.93 (m, 12H), 1.27–1.50 (m, 40H), 1.64–1.70 (m, 2H), 3.79 (d, 4H, J = 5.7 Hz), 6.77 (d, 4H, J = 8.8 Hz), 7.23 (d, 4H, J = 9 Hz) 7.86 (s, 2H), 8.00 (s, 2H), 8.37 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 158.29, 150.47, 138.30, 137.23, 131.43, 129.59, 128.55, 127.43, 126.08, 114.30, 84.08, 70.51, 67.59, 39.62, 30.76, 29.31, 25.21, 24.09, 23.29, 14.32, 11.35. HRMS (m/z, FAB<sup>+</sup>) Cald for C<sub>55</sub>H<sub>72</sub>B<sub>2</sub>O<sub>6</sub> 850.5515; Found 850.5507.

## 2.3.4. Synthesis of poly(2,6-((4,4-bis(2-ethylhexyl)-4H-cyclopenta[def]phenanthrene))-alt-(4,7-((2-thienyl)-2,1,3-benzothiadiazole))) (7, PCPP-DTBT)

To a stirred solution of 0.260 g (0.400 mmol) of 2-(4,4-Bis(2-ethylhexyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4*H*-cyclopenta[*def*]phenanthren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6**) in 7 mL of toluene were added 0.180 g (0.400 mmol)



Scheme 1. Synthetic routes for the monomers and the polymers.

of 4,7-bis(5-bro-mo-2-thienyl)-2,1,3-benzothiadiazole (**5**), and 14.0 mg (3.00 mol%) of (PPh<sub>3</sub>)<sub>4</sub>Pd(0), and 2 mL (4.00 mmol) of aqueous 2 M K<sub>2</sub>CO<sub>3</sub>. The reaction mixture was further heated at 80 °C for 2 days. After cooling to room temperature, the reaction mixture was poured into the solution of 100 mL of acetone, and 300 mL of methanol. After being stirred for 1 h, the precipitate was filtered and dried in vacuum. The precipitate was dissolved with minimum amount of chloroform and poured into the 300 mL of methanol. After filtration by glass filter, the precipitate was purified by Soxhlet extraction with methanol and dried in vacuum for 24 h to generate 47 mg of polymer **7**, PCPP-DTBT.

#### 2.3.5. Synthesis of poly(2,6-(4,4-bis(4-((2-ethylhexyl)oxy)phenyl)-4H-cyclopenta[def]phenanthrene)-alt-(4,7-((2-thienyl)-2,1,3benzothiadiazole))) (**10**, PBEHPCPP-DTBT)

To a stirred solution of 560 mg (0.650 mmol) of 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,4-bis(4-((2-ethylhexyl)oxy)-phenyl)-4*H*-cyclopenta[*def*]phenanthrene (**9**) in 7 mL of toluene were added 0.300 g (0.650 mmol) of 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (**5**), and 23.0 mg (3.00 mol%) of (PPh<sub>3</sub>)<sub>4</sub>Pd(0), and 3.30 mL (6.50 mmol) of aqueous 2 M K<sub>2</sub>CO<sub>3</sub>. The reaction mixture was further heated at 80 °C for 2 days. After cooling to room temperature, the reaction mixture was poured into the solution of 100 mL of acetone and 300 mL of methanol. After being stirred for 1 h, the precipitate was filtered and dried in vacuum. The precipitate was dissolved with minimum amount of chloroform and poured into the 300 mL of methanol. After filtration by galss filter, the precipitate was purified by Soxhlet extraction with methanol and dried in vacuum for 24 h to generate 50 mg of polymer **10**, PBEHPCPP-DTBT.

#### 3. Results and discussion

#### 3.1. Synthesis and characterization of polymers

The general synthetic routes towards the monomer and polymers are outlined in Scheme 1. Commercially available thiophene (1) was lithiated using *n*-buthyllithium and then treated with tributylchlorostanne to afford tributyl(2-thienyl)stannane (2), which was coupled with commercially available 4,7-dibromobenzo-2,1,3-thiadiazole (3) in THF by Stille coupling reaction to give 4,7-di-2-thienyl-2,1,3-benzothiadiazole (4). Compound 4 was brominated using N-bromosuccinimide to generate 4,7-bis(5-bromo-2-thienyl)-2,1,3benzothiadiazole (5) [20]. Compound 8 was treated with bis(pinacolato)diboron, potassium acetate, and Pd(dppf)Cl<sub>2</sub> in DMF to get 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,4-bis(4-((2-ethylhexyl)oxy)phenyl)-4H-cyclopenta[*def*]phenanthrene (9). The alternating copolymer 7 (PCPP-DTBT) was affected under Suzuki coupling condition [21], using monomer 5, 2-(4,4-bis(2-ethylhexyl)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4H-cyclopenta-[def]phenanthren-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6) [18], Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst and aqueous 2 M potassium carbonate.

#### Table 1

Characterization of	the	Polymers.
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Copolymers	$M_n^a$	$M_w^a$	$M_{\rm w}/M_{\rm n}^{\rm a}$	$T_{g}^{b}(^{\circ}C)$	$T_{d}^{c}(^{\circ}C)$
PCPP-DTBT	8600	17,000	2.0	101	404
PBEHPCPP-DTBT	5000	8000	1.6	79	432

<sup>a</sup> The number-average molecular weight ( $M_n$ ) and the weight-average molecular weight ( $M_w$ ) were determined by GPC in THF using a calibration curvse of polystyrene as the standard.

<sup>b</sup> Glass transition temperature determined by DSC.

 $^{\rm c}\,$  Decomposition temperature corresponding to 5% weight loss in  $N_2$  determined by TGA.

PBEHPCPP-DTBT (**10**) was obtained under Suzuki coupling condition, using monomer **5**, 2,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4,4-bis(4-((2-ethylhexyl)oxy)phenyl)-4*H*-cyclopenta [*def*]phenanthrene (**9**), Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst and aqueous 2 M potassium carbonate.

The PCPP-DTBT and PBEHPCPP-DTBT were soluble in organic solvents such as chloroform, tetrahydrofuran, dichloromethane, and chlorobenzene. Molecular weights and polydispersities of the



**Fig. 1.** The normalized UV–visible absorption spectra of PCPP-DTBT and PBEHPCPP-DTBT (a) in THF solution and (b) in thin film and fluorescence spectra (c) in THF.

polymers were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. As shown in Table 1, the number-average molecular weight ( $M_n$ ) and the weight-average molecular weight ( $M_w$ ) of the PCPP-DTBT were 8600 and 17,000 with polydispersity index of 2.0.  $M_n$  and  $M_w$  of PBEHPCPP-DTBT were 5000 and 8000 with polydispersity index of 1.6. The thermal properties of the polymer were evaluated by differential scanning calorimetry (DSC) and thermo gravimetric analysis (TGA) in nitrogen. PCPP-DTBT shows loses less than 5% of its weight on heating to 404 °C. Glass transition temperature measured by DSC under N<sub>2</sub> was 101 °C. PBEHPCPP-DTBT shows loses less than 5% of its weight on heating to 432 °C. Glass transition temperature measured by DSC under N<sub>2</sub> was 79 °C.

#### 3.2. Optical properties

All spectroscopic properties were measured both in THF solutions and as thin films on glass slides. As shown in Fig. 1a, PCPP-DTBT shows absorption maxima at 375 and 527 nm. PBEHPCPP-DTBT shows similar absorption maxima at 379 and 527 nm. The short-wavelength absorption peak is attributed to a delocalized excitonic  $\pi$ - $\pi$ <sup>\*</sup> transition in the polymer chains and the longwavelength absorption peaks attributed to a localized transition between the D-A-D charge transfer. As shown Fig. 1b, PCPP-DTBT in solid state shows the maximum absorption peaks at 387 and 554 nm. PBEHPCPP-DTBT in solid state exhibits the maximum absorption peaks at 400 and 570 nm. The second absorption maxima of the solid thin films exhibit larger red shifts (27–43 nm) as compared to the corresponding peaks in dilute solutions. Fig. 1c shows that PCPP-DTBT and PBEHPCPP-DTBT emit deep red fluorescence in THF solution with maximum peaks at 621 and 612 nm, respectively. This suggests that there is a very efficient energy transfer from the CPP unit to the benzothiadiazole-cored unit.

#### 3.3. Electrochemical properties

The LUMO energy levels of the polymers were determined from the band gaps which were estimated from the absorption edges, and the HOMO energy levels which were estimated from the cyclic voltammetry [22]. The CVs were performed with a solution of tetrabutylammonium tetrafluoroborate (Bu<sub>4</sub>NBF<sub>4</sub>) (0.10 M) in acetonitrile at a scan rate of 80 mV/s at room temperature. Polymer films were prepared by dipping platinum working electrodes into the polymer solution, which was prepared with minimum amount of THF, and then air-drying. A platinum wire and an Ag/AgNO<sub>3</sub> electrode were used as the counter electrode and reference electrode, respectively. The energy level of the Ag/AgNO3 reference electrode (calibrated by the FC/FC<sup>+</sup> redox system) was 4.76 eV below the vacuum level. The oxidation potentials derived from the onset of electrochemical p-doping are summarized in Table 2. HOMO levels were calculated according to the empirical formula  $E_{\text{HOMO}} = -([E_{\text{onset}}]^{\text{ox}} + 4.76) \text{ (eV)} [22,23]$ . During the anodic scan, the oxidation onset potential of PCPP-DTBT was 0.64 V and

#### Table 2

Electrochemical Potentials and Energy Levels of the Polymers.

Polymers	$E_{\text{onset}}^{a}(V)$	HOMO <sup>b</sup> (eV)	LUMO <sup>c</sup> (eV)	$E_{\rm g}^{\rm d}  ({\rm eV})$
PCPP-DTBT	0.64	-5.40	-3.40	2.00
PBEHPCPP-DTBT	0.54	-5.30	-3.50	1.80

<sup>a</sup> Onset oxidation potentials measured by cyclic voltammetry.

<sup>b</sup> Calculated from the oxidation potentials.

<sup>c</sup> Calculated from the HOMO energy levels and  $E_g$ .

<sup>d</sup> Energy band gaps were estimated from the onset wavelengths of the optical absorption.



Fig. 2. Energy diagram of HOMO/LOMO levels of PCPP-DTBT and PBEHPCPP-DTBT in relation to the work function of the ITO, PEDOT:PSS, PCBM, and Al.

exhibited irreversible p-doping process. HOMO energy level of the polymer was -5.40 eV. The absorption onset wavelength is 620 nm, which corresponds to band gap of 2.00 eV. The LUMO energy level, calculated from the value of the band gap and HOMO energy level, was -3.40 eV. The oxidation onset potential of PBEHPCPP-DTBT was 0.54 V and exhibited irreversible p-doping process. HOMO energy level of PBEHPCPP-DTBT was -5.30 eV. The absorption onset wavelength was 688 nm, which correspond to band gap of 1.80 eV. As shown in Fig. 2, the bandgap of PBEHPCPP-DTBT was decreased by 0.20 eV as compared to that of PCPP-DTBT. Such a decrease in the band gap can be explained by the extension of  $\pi$ -conjugation system of the polymer main chain to two aromatic substituents on the PCCP unit.

#### 3.4. Photovoltaic cell characteristics

The current-voltage characteristics of the solar cells, under simulated 100 mW/cm<sup>2</sup> AM 1.5 G white light illumination, based on the two blends of PCPP-DTBT/PCBM and PBEHPCPP-DTBT/PCBM are shown in Fig. 3. Table 3 lists the photovoltaic properties obtained from the *J*–*V* curves for the best devices. The PSCs had a layered structure of ITO/PEDOT:PSS/copolymers:PC<sub>71</sub>BM (1:4, w/ w)/TiO<sub>x</sub>/Al where the polymer was used as the electron donor and PCBM was used as the electron acceptor. The device with PCPP-DTBT: PCBM layer showed an open circuit voltage (*V*<sub>oc</sub>) of 0.71 V, a short-circuit current density (*J*<sub>sc</sub>) of 4.7 mA/cm<sup>2</sup>, and a fill factor (*FF*) of 0.30, giving a power conversion efficiency of 1.00%. The device with PBEHPCPP-DTBT:PC<sub>71</sub>BM blend demonstrated a *V*<sub>oc</sub> value of 0.61 V, a *J*<sub>sc</sub> value of 4.6 mA/cm<sup>2</sup>, and a *FF* of 0.40, leading to the power conversion efficiency of 1.12%, a slightly improved



**Fig. 3.** Current-voltage characteristics of polymers:PC<sub>71</sub>BM (1:4) bulk heterojunction solar cells under white light illumination (AM 1.5 conditions).

 Table 3

 Photovoltaric performances of the device with the configuration of ITO/PEDOT:PSS/ copolymers:PC71BM/TiOx/Al.

Copolymers	Acceptor	Ratio	$J_{\rm sc}({\rm mA/cm^2})$	$V_{\rm oc}\left({\rm V} ight)$	FF	Eff. (%)
PCPP-DTBT	PC <sub>71</sub> BM	1:4	4.70	0.71	0.30	1.00
PBEHPCPP-DTBT	PC <sub>71</sub> BM	1:4	4.60	0.61	0.40	1.12

performance as compared to the case of PCPP-DTBT. The  $V_{oc}$  value of PCPP-DTBT is higher than that of PBEHPCPP-DTBT, which is attributed to the larger difference between the HOMO energy levels of the polymer and LUMO energy level of PC<sub>71</sub>BM. The  $J_{sc}$  values of PCPP-DTBT and PBEHPCPP-DTBT based devices were about same. PBEHPCPP-DTBT exhibited higher *FF* value than that of PCPP-DTBT, resulting in the improved the power conversion efficiency of 1.12%.

Fig. 4 shows the incident photon to concerted current efficiency (IPCE) of the PSCs for the best device as a function of wavelength, which follows the copolymer's UV–vis absorption spectrum, indicating that all the absorption of the polymers contributed to the photovoltaic conversion. The significant absorbance of the conjugated polymers up to 700 nm increased the total photovoltaic current because the solar photon flux is high in this energy range [24,25]. The IPCE spectra of PCPP-DTBT and PBEHPCPP-DTBT show the maximum of 38% at 379 nm for PCPP-DTBT and 40% at 380 nm for PBEHPCPP-DTBT. A broad plateau around the maximum in IPCE spectrum exists between 430–580 nm and 430–600 nm for PCPP-DTBT and PBEHPCPP-DTBT, respectively. The shape of IPCE spectrum of PCPP-DTBT:PC<sub>71</sub>BM film is almost identical with that of PBEHPCPP-DTBT:PC<sub>71</sub>BM film.



**Fig. 4.** The IPCE spectra (circled line) of photovoltaric devices with the configuration of ITO/PEDOT:PSS/polymers:PCBM(1:4)/TiO<sub>x</sub>/Al and the absorption spectra for the corresponding films of the blends of polymers and PCBM (black solid line).



Fig. 5. Tapping mode AFM topographies images at 0–10 nm height scale for polymer/ $PC_{71}BM$  (1:4) blend films of PBEHPPCPP-DTBT and PCPP-DTBT.

2.00

um

1.00

Parts (a) and (b) of Fig. 5 show AFM images of PBEHPPCPP-DTBT/ PC<sub>71</sub>BM and PCPP-DTBT/PC<sub>71</sub>BM blend films. The root mean square surface roughness (rms) of the two polymer films are 0.52 and 0.44 nm, respectively. PCPP-DTBT/PC<sub>71</sub>BM shows smaller domain size and more well-penetrated morphology than PBEHPPCPP-DTBT/ PC<sub>71</sub>BM, which leads to improved  $J_{sc}$  for PCPP-DTBT/PC<sub>71</sub>BM. But PBEHPPCPP-DTBT has higher hole mobility (5.79 × 10<sup>-5</sup> cm<sub>2</sub>V<sup>-1</sup> s<sup>-1</sup>) than that of PCPP-DTBT (8.22 × 10<sup>-6</sup> cm<sub>2</sub>V<sup>-1</sup> s<sup>-1</sup>), which lead to superior photovoltaic cell performance for PBEHPPCPP -DTBT.

#### 4. Conclusion

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In conclusion, the D–A type of alternating copolymers of PCPP-DTBT and PBEHPCPP-DTBT were synthesized by Suzuki coupling polymerization and characterized. The CPP unit was combined with DTBT unit to generate the larger difference between the donor HOMO level and the acceptor LUMO level of the copolymer, which could be an essential key for the enhanced open circuit voltage ( $V_{OC}$ ) of the PSCs. Both of conjugated polymers showed significant absorbance up to around 700 nm region. The HOMO–LUMO energy bandgaps of these materials show 2.00 eV for PCPP-DTBT and 1.80 eV for PBEHPCPP-DTBT. Bulk heterojunction solar cells based on blends of the polymers with [6,6]phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) gave power conversion efficiencies of 1.00% for PCPP-DTBT and 1.12% for PBEHPCPP-DTBT under AM 1.5, 100 mW/cm<sup>2</sup>.

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