

Synthesis and Photovoltaic Properties of Polymers Based on Cyclopentadithiophene and Benzimidazole Units

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The new semiconducting copolymers with 4,4-dialkyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene and 2,2-dimethyl-2*H*-benzimidazole units were synthesized. The fused aromatic rings, such as cyclopentadithiophene (CPDT) unit, can make the polymer backbone more rigid and coplanar, which induces long conjugation length, narrow band gap, and strong intermolecular π - π interaction. The stacking ability was controlled through attaching of linear or branched alkyl side chains. The spectra of PEHCPDTMBI and PHCPDTMBI in the solid films show absorption bands with maximum peaks at 401, 759 and 407, 768 nm, and the absorption onsets at 925 and 954 nm, corresponding to band gaps of 1.34 and 1.30 eV, respectively. The devices comprising PHCPDTMBI with TiO_x showed a V_{OC} of 0.39 V, a J_{SC} of 1.14 mA/cm², and a FF of 0.34, giving a power conversion efficiency of 0.15%. The PHCPDTMBI with linear alkyl chain on CPDT shows good solubility in organic solvent with higher PCE value than that of PEHCPDTMBI.

Key Words : Polymer, Photovoltaic cells, Synthesis, Dimethyl-2*H*-benzimidazole

Introduction

In the recent years, organic photovoltaics (OPVs) with bulk heterojunction (BHJ) architecture have become an active research area due to its possibility to be an alternative source of renewable energy with low cost and lightweight for making flexible large area devices.^{1,2} In order to increase the absorption of the solar spectrum, low bandgap polymers that cover the near infrared region have become available in OPVs.^{3,4} Low bandgap conjugated polymers harvesting wide range of the solar spectrum by controlling the intramolecular charge transfer (ICT) from the donors to the acceptors have been widely used to enhance the efficiency of OPVs.^{1,5,6} Among these, benzothiadiazole based copolymers have been showing high power conversion efficiencies (PCEs) in the range of ~1.0-5.5%,⁷⁻⁹ ascribed to high hole mobility, structural stability in the charged state and broad absorption spectrum.¹⁰ Several donor acceptor type (D-A) conjugated polymers with narrow band gaps, including poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT),¹¹ have shown promising performances with the PCE values as high as 6%.

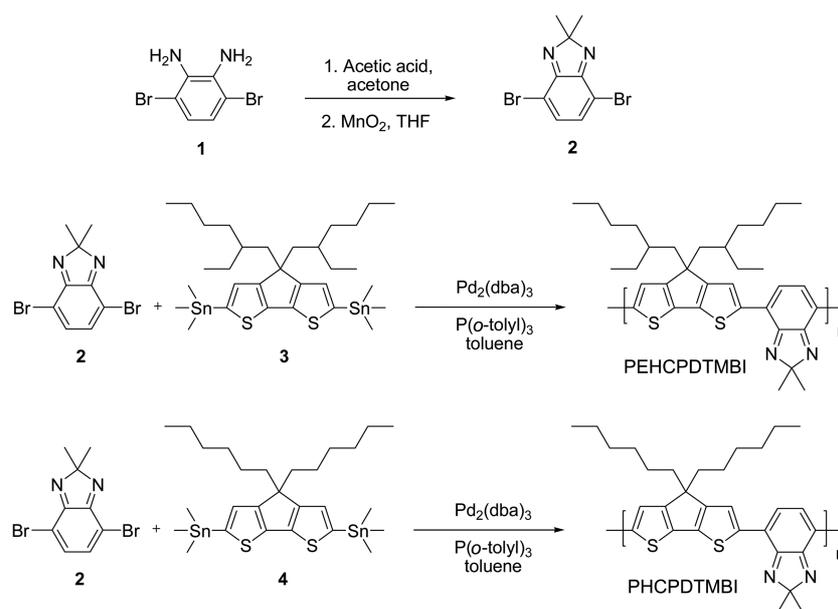
The stacking ability of conjugated polymers was modified through attaching of linear or branched alkyl side chains.¹² The bulky alkyl side chains interrupt the ICT caused by the distortion of the conjugation of the backbone.^{13,14} Bulky side

chain is disadvantageous in the construction of solar cells caused by reducing the strong interaction between donor and acceptor units leading to strong phase separation.^{13,14} Even if the bulky alkyl side chain improves the solubility of the polymers in organic solvents, selection of suitable alkyl chain has been important research area in the synthesis of polymers for OPVs.

The present study is aimed at the identification of the effect of the alkyl side chain on cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT) unit which is coupled with 2,2-dimethyl-2*H*-benzimidazole (MBI) unit. The D-A-D type conjugated copolymers were synthesized by Stille coupling reaction of CPDT as the electron rich unit and MBI as the electron poor unit to generate poly(2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene)-*alt*-4,7-(2,2-dimethyl-2*H*-benzimidazole)) (PEHCPDTMBI) and poly(2,6-(4,4-dihexyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene)-*alt*-4,7-(2,2-dimethyl-2*H*-benzimidazole)) (PHCPDTMBI). The photovoltaic properties of the polymers were investigated by fabrication of the polymer solar cells with the configuration of ITO/PEDOT:PSS/polymer:PCBM/TiO_x/Al.

Results and Discussion

Synthesis and Characterization. The general synthetic routes toward the monomers and polymers are outlined in Scheme 1. In the first step, 3,6-dibromobenzene-1,2-diamine



Scheme 1. Synthetic route for the synthesis of the monomers and polymers.

(1)¹⁵ was treated with acetone to generate 4,7-dibromo-2,2-dimethyl-2*H*-benzimidazole (2). Copolymers that consist of 4,4-bis-(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (3)¹⁶ (or 4,4-dihexyl-2,6-bis(trimethylstannyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (4)¹⁷) as electron rich units and 4,7-dibromo-2,2 dimethyl-2*H*-benzimidazole (2) as electron poor moiety were synthesized by Pd(0)-catalyzed Stille coupling polymerization in toluene. All of the polymers show good solubility at room temperature in organic solvents such as chloroform, THF, chlorobenzene, and *o*-dichlorobenzene (ODCB).

Table 1 summarizes the polymerization results including molecular weight, polydispersity index (PDI) and thermal stability of the polymers. The number-average molecular weight (M_n) of 8500 and 4700 and weight-average molecular weight (M_w) of 18000 and 11000 with polydispersity index (PDI, M_w/M_n) of 2.1 and 2.3 of the resulting polymers were determined by GPC for PEHCPDTMBI and PHCPDTMBI, respectively. The thermal properties of the polymers were characterized by both differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). Data of DSC and TGA of the polymers are shown in Figure 1 and summarized in Table 1. DSC analysis was performed under a nitrogen atmosphere (50 mL/min) on a DSC 822 at heating rates of 10 °C/min. TGA was performed

with a Dupont 951 TGA instrument in a nitrogen atmosphere at a heating rate of 10 °C/min to 600 °C. TGA showed that PEHCPDTMBI and PHCPDTMBI are thermally stable with only about 5% weight loss at temperatures of 385 and

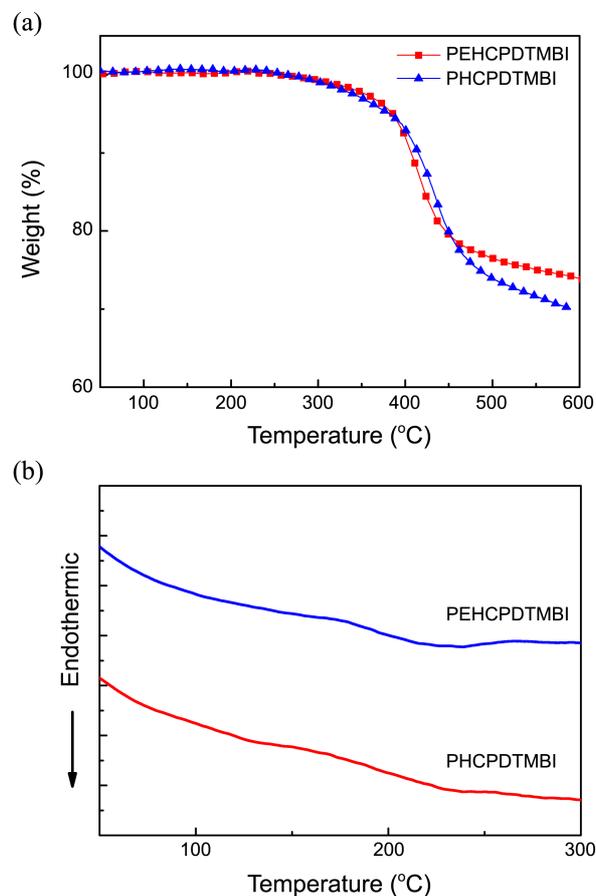


Figure 1. (a) Thermogravimetric analysis of the polymers under N₂. (b) Differential scanning calorimetry of the polymers under N₂.

Table 1. Polymerization Results and Thermal Properties of Polymers

Polymer	M_n^a	M_w^a	PDI ^a	DSC (T_g)	TGA (T_d) ^b
PEHCPDTMBI	8500	18000	2.1	128	385
PHCPDTMBI	4700	11000	2.3	177	378

^aMolecular weight (M_w) and polydispersity (PDI) of the polymers were determined by gel permeation chromatography (GPC) in THF using polystyrene standards. ^bOnset decomposition temperature (5% weight loss) measured by TGA under N₂.

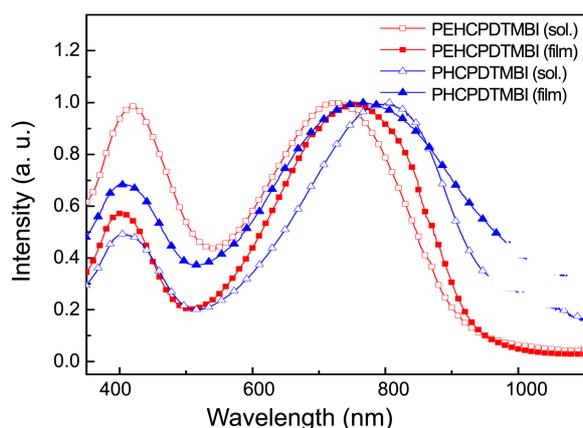


Figure 2. UV-visible absorption spectra in ODCB solution and in the solid state.

378 °C, respectively. The T_d values of PEHCPDTMBI and PHCPDTMBI was not affected by the type of alkyl chain. High thermal stability is required to prevent the degradation of polymers in photovoltaic devices upon annealing.¹⁸ The PEHCPDTMBI and PHCPDTMBI showed good thermal stability with a glass transition temperature (T_g) of 128 and 177 °C, using DSC performed at a temperature range of 30 to 350 °C. As compared to PEHCPDTMBI, PHCPDTMBI with dihexyl chains shows higher T_g value caused by stacking ability of linear alkyl chains. The high thermal stability of the resulting polymers prevents the deformation of the polymer morphology and is important for organic photovoltaics application.

Optical and Photoluminescence Properties. The solution was prepared using ODCB as a solvent and the thin film was obtained by spin-coating on quartz plates from the solution in ODCB at room temperature. The UV-vis absorption spectra of the polymers in solution and as thin films are shown in Figure 2 and summarized in Table 2. The solutions of PEHCPDTMBI and PHCPDTMBI present two absorption bands with maximum peaks at 417, 725 and 405, 807 nm, respectively. The spectra of PEHCPDTMBI and PHCPDTMBI in the solid films show absorption bands with maximum peaks at 401, 759 and 407, 768 nm, and the

Table 2. Characteristics of the UV-vis Absorption Spectra

Polymer	in solution	in thin film
PEHCPDTMBI	417, 725	401, 759
PHCPDTMBI	405, 807	407, 768

Table 3. Electrochemical Potentials and Energy Levels of the Polymers

Polymers	Optical band gap ^a (eV)	HOMO ^b (eV)	LUMO ^c (eV)	E_{ox}^d (V)	E_{red}^d (V)	Electrochemical band gap ^e (eV)
PEHCPDTMBI	1.34	-5.21	-3.70	0.41	-1.10	1.51
PHCPDTMBI	1.30	-5.26	-3.79	0.46	-1.01	1.47

^aOptical energy band gap was estimated from the onset wavelength of the optical absorption. ^bCalculated from the oxidation potentials. ^cCalculated from the reduction potentials. ^dOnset oxidation and reduction potential measured by cyclic voltammetry. ^eCalculated from the E_{ox} and E_{red} .

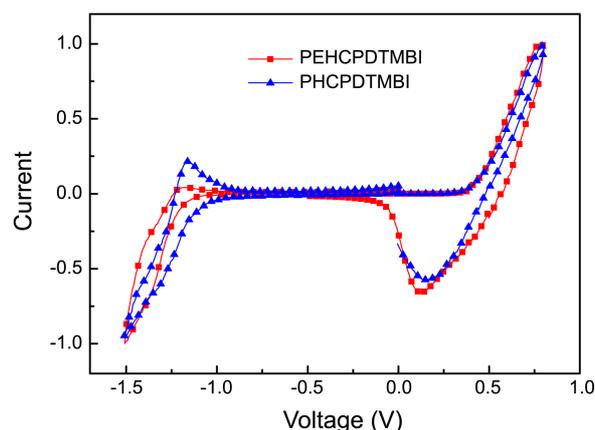


Figure 3. Electrochemical properties of polymers.

absorption onsets at 925 and 954 nm, corresponding to band gaps of 1.34 and 1.30 eV, respectively. The short-wavelength absorption peaks have been ascribed to a delocalized excitonic π - π^* transition in the conjugated chains and the long-wavelength absorption peaks attributed to the intramolecular charge transfer (ICT) between the cyclopentadithiophene and MBI units.⁸ In solution, the polymer with hexyl chain, PHCPDTMBI, exhibits red-shifted long-wavelength absorption peak by about 82 nm as compared to the case of PEHCPDTMBI caused by linear alkyl chain. In case of PEHCPDTMBI thin films, the long-wavelength absorption peak shows red-shift about 34 nm in comparison with the absorption spectrum of the solution. The long-wavelength absorption peak of the PHCPDTMBI thin film shows broader peak as compared to the case of the solution caused by linear hexyl chain.

Electrochemical Properties. The electrochemical property of the polymer was determined from the bandgap estimated from the absorption onset wavelength, and the HOMO energy level which was estimated from the cyclic voltammetry (CV). The CV was performed with a solution of tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) (0.10 M) in acetonitrile at a scan rate of 100 mV/s at room temperature under argon atmosphere. A platinum electrode (~ 0.05 cm²) coated with a thin polymer film was used as the working electrode. Pt wire and Ag/AgNO₃ 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⁺ redox system) was 4.8 eV below the vacuum level. The cyclic voltammograms are shown in Figure 3, and the oxidation potentials derived from the onsets of electrochemical p-doping are summarized in

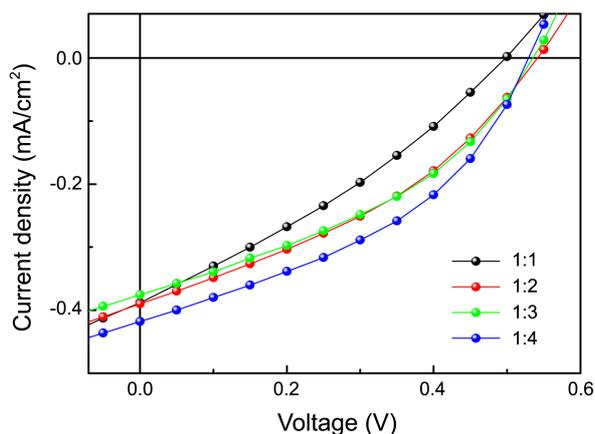


Figure 4. Current density-potential characteristics of the PEHCPDTMBI solar cells under the illumination of AM 1.5, 100 mW/cm².

Table 3. HOMO and LUMO levels were calculated according to the empirical formula ($E_{\text{HOMO}} = -([E_{\text{onset}}]^{\text{ox}} + 4.8) \text{ eV}$) and ($E_{\text{LUMO}} = -([E_{\text{onset}}]^{\text{red}} + 4.8) \text{ eV}$), respectively. The PEHCPDTMBI and PHCPDTMBI exhibited the absorption onset wavelengths of 925 and 954 nm in solid thin films, which corresponds to band gaps of 1.34 and 1.30 eV, respectively. The oxidation onsets of the polymers, PEHCPDTMBI and PHCPDTMBI, were estimated to be 0.41 and 0.46 V, which correspond to HOMO energy levels of -5.21 and -5.26 eV, respectively. The reduction potential onsets of PEHCPDTMBI and PHCPDTMBI are -1.10 and -1.01 V, which corresponds to LUMO energy levels of -3.70 and -3.79 eV, respectively. The electrochemical band gaps, calculated from cyclic voltammetry data, are about 1.51 and 1.47 eV, somewhat higher than the optical band gaps estimated from the onset wavelengths of the absorption spectra. The optical and electrochemical bandgaps of PHCPDTMBI is lower than that of PEHCPDTMBI, caused by the good stacking ability of the linear alkyl chain.

Polymer Photovoltaic Properties. The photovoltaic properties of PEHCPDTMBI and PHCPDTMBI were investigated by fabricating the OPVs with ITO as anode, the blend

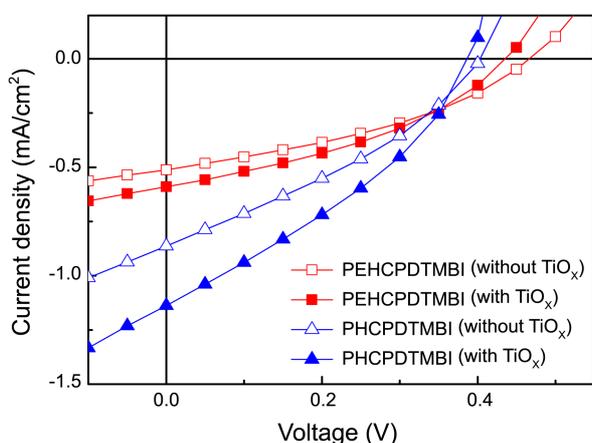


Figure 5. Current density-potential characteristics of the polymer solar cells under the illumination of AM 1.5, 100 mW/cm².

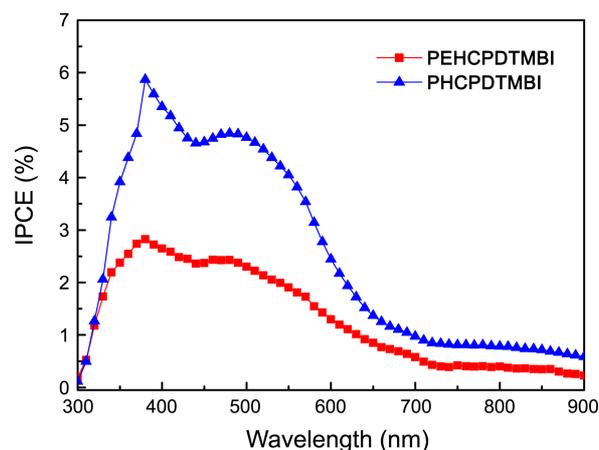


Figure 6. IPCE curves of the polymer:PCBM (1:4) under the illumination of AM 1.5, 100 mW/cm².

with PEHCPDTMBI and PHCPDTMBI and PC₇₁BM as active layer, and Al as cathode. Figure 5 and 6 shows the current-voltage (I - V) curves of the OPVs under AM 1.5G irradiation (100 mW/cm²) and summarized in Table 4 and 5. BHJ devices were fabricated by spin-coating of 1% (w/v) chlorobenzene solutions comprising a blend of polymer and PC₇₁BM. To optimize the device performance of the most efficient polymer, PEHCPDTMBI, various compositions of PEHCPDTMBI and PC₇₁BM in the device were investigated to find that 1:4 was the optimum ratio. The devices comprising PEHCPDTMBI with PC₇₁BM showed an open circuit voltage (V_{OC}) of 0.53 V, a short circuit current density (J_{SC}) of 0.42 mA/cm², and a fill factor (FF) of 0.41, giving a power conversion efficiency of 0.10%. The devices comprising PEHCPDTMBI:PC₇₁BM (1:4) with TiO_x showed an open circuit voltage (V_{OC}) of 0.44 V, a short circuit current density (J_{SC}) of 0.59 mA/cm², and a fill factor (FF) of 0.33, giving no change of the power conversion efficiency to provide 0.10%. The devices comprising PHCPDTMBI without TiO_x showed a V_{OC} of 0.40 V, a J_{SC} of 0.86 mA/cm²,

Table 4. Photovoltaic Properties of the Polymer Solar Cells

Polymers	Polymer:PC ₇₁ BM	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	PCE (%)
PEHCPDTMBI	1:1	0.50	0.39	0.31	0.06
	1:2	0.54	0.39	0.36	0.08
	1:3	0.54	0.38	0.38	0.08
	1:4	0.53	0.42	0.41	0.10

Table 5. Photovoltaic Properties of the Polymer Solar Cells based on polymer:PC₇₁BM (1:4) blends

Polymers	TiO _x	V_{OC} (V)	J_{SC} (mA/cm ²)	FF	PCE (%)
PEHCPDTMBI	without	0.53	0.42	0.41	0.10
	with	0.44	0.59	0.33	0.10
PHCPDTMBI	without	0.40	0.86	0.33	0.12
	with	0.39	1.14	0.34	0.15

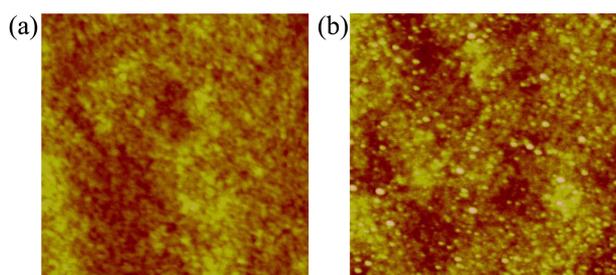


Figure 7. Atomic force microscopy images of PEHCPDPTMBI/PC₇₁BM (a) and PHCPDPTMBI/PC₇₁BM (b).

and a *FF* of 0.33, giving a power conversion efficiency of 0.12%. The devices comprising PHCPDPTMBI with TiO_x showed a *V*_{OC} of 0.39 V, a *J*_{SC} of 1.14 mA/cm², and a *FF* of 0.34, giving a power conversion efficiency of 0.15%, which is attributed higher short circuit current caused by TiO_x.

The incident-photon-to-current efficiency (IPCE) spectra of the photovoltaic devices from small molecule:PCBM blends are presented in Figure 5. The IPCE spectra of the polymers show maxima of 2.83% at 380 nm for PEHCPDPTMBI and 5.87% at 380 nm for PHCPDPTMBI. The enhanced efficiency of PHCPDPTMBI results from the higher IPCE value between 300 and 630 nm.

Atomic force microscopy (AFM) studies of polymer blends (polymer:PCBM = 1:4 w/w) revealed that the morphology of the polymer/PCBM blend film exhibited very fine domains and no large phases can be found in Figure 7, where the images were obtained in a surface area of 1 × 1 μm² by the tapping mode. The AFM image of both PHCPDPTMBI exhibited typical amorphous morphology with crystalline domains, as shown in Figure 7 (b). The coarser grained film morphology consequences in enhanced photovoltaic property.¹²

Conclusions

The new semiconducting copolymers with 4,4-dialkyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene and 2,2-dimethyl-2*H*-benzimidazole units were synthesized. The spectra of PEHCPDPTMBI and PHCPDPTMBI in the solid films show absorption bands with maximum peaks at 401, 759 and 407, 768 nm, and the absorption onsets at 925 and 954 nm, corresponding to band gaps of 1.34 and 1.30 eV, respectively. The polymer with hexyl chain, PHCPDPTMBI, exhibits red-shifted long-wavelength absorption peak by about 82 nm in solution as compared to PEHCPDPTMBI caused by the linear alkyl chain. The long-wavelength absorption peak of the PHCPDPTMBI thin film shows broader peak as compared to the case of the solution caused by the linear hexyl chain. The devices comprising PHCPDPTMBI with TiO_x showed a *V*_{OC} of 0.39 V, a *J*_{SC} of 1.14 mA/cm², and a *FF* of 0.34, giving a power conversion efficiency of 0.15%.

Experimental Section

General. 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. ¹H and ¹³C 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 pre-coated aluminum plates with fluorescent indicator UV254. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 mass spectrometer under electron impact (EI) or fast atom bombardment (FAB) conditions in the Korea Basic Science Institute (Daegu). Molecular weight and polydispersity of the polymer were determined by gel permeation chromatography (GPC) analysis with a polystyrene standard calibration. The UV-vis absorption spectra were recorded by a Varian 5E UV/VIS/NIR spectrophotometer, while the Oriel InstaSpec IV CCD detection system with xenon lamp was used for the photoluminescence and electroluminescence spectra measurements.

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 40nm 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 in chlorobenzene solvent with concentration of 7 wt/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:PC₇₁BM layer (5000 rpm for 40 second). 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 × 10⁻⁷ Torr. Current density-voltage (*J-V*) characteristics of the devices were measured using a Keithley 236 Source Measure Unit. Solar cell performance was measured by using an Air Mass 1.5 Global (AM 1.5 G) solar simulator with an irradiation intensity of 100 mW/cm². An aperture (12.7 mm²) 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.

Synthesis of 4,7-dibromo-2,2-dimethyl-2*H*-benzimidazole (2). 3,6-Dibromobenzene-1,2-diamine (10 g, 37.65 mmol), acetone (10 mL), and acetic acid (10 mL) were dissolved in diethyl ether (200 mL) and heated to 50 °C overnight. After the reaction mixture was cooled to room temperature, water and ethyl acetate were added. The aqueous phase was extracted with ethyl acetate and combined organic layer were

dried over MgSO₄. The solvent was removed under vacuum and the residue was purified by column chromatography to give 4,7-dibromo-2,2-dimethyl-2,3-dihydro-1*H*-benzimidazole. To a stirred solution of 4,7-dibromo-2,2-dimethyl-2,3-dihydro-1*H*-benzimidazole in 50 mL of tetrahydrofuran (THF) at room temperature was added MnO₂ (10 g). After 3 h, the solid was filtered and washed with THF. The organic phase was concentrated under reduced pressure and the residue was purified by flash column chromatography to give 4.8 g of compound **2** as yellow powder. mp 132 °C; ¹H NMR (300 MHz, Acetone-*d*₆) δ (ppm) 1.52 (s, 6H), 6.49 (s, 2H); ¹³C NMR (75 MHz, Acetone-*d*₆) δ (ppm) 79.66, 98.31, 121.74, 121.80, 139.68. HRMS (*m/z*, EI⁺) calcd for C₉H₈N₂Br₂ 301.9054, found 301.9056.

Polymerization of poly(2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene)-*alt*-4,7-(2,2-dimethyl-2*H*-benzimidazole)) (PEHCPDTMBI). Carefully purified 4,7-dibromo-2,2-dimethyl-2*H*-benzimidazole (**2**), 4,4-bis-(2-ethylhexyl)-2,6-bis(trimethylstannyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (**3**), P(*o*-tolyl)₃ (1 eq) and Pd₂(dba)₃ (3 mol %) were dissolved in a mixture of toluene. The mixture was refluxed with vigorous stirring for 2 days under argon atmosphere. After cooling to room temperature, the mixture was poured into methanol. The precipitated material was recovered by filtration. The resulting solid material was reprecipitated using 100 mL of THF/1.0 L of methanol several times to remove residual amount of catalyst. The resulting polymer was soluble in THF, CHCl₃, ODCB and toluene. The yields of the polymers ranged from 50-60%.

Polymerization of poly(2,6-(4,4-dihexyl-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene)-*alt*-4,7-(2,2-dimethyl-2*H*-benzimidazole)) (PHCPDTMBI). This dark purple copolymer was prepared by a procedure similar to that for PEHCPDTMBI, using 4,4-dihexyl-2,6-bis(trimethylstannyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (**4**) as the monomer.

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