

## Supporting Information

### Simultaneous Enhancement of Solar Cell Efficiency and Photostability via Chemical Tuning of Electron Donating Units in Diketopyrrolopyrrole-based Push-Pull Type Polymers

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**General:** Unless described otherwise, all chemicals used in the experiment were purchased from Aldrich and used without additional purification processes. PC<sub>71</sub>BM for the device fabrication was purchased from EM index Co., ltd.. Tetrahydrofuran (THF) and toluene were distilled with sodium metal and benzophenone. 3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione,<sup>1</sup> 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene,<sup>2</sup> 4,8-bis(2-ethylhexyl)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene ditin compound<sup>3</sup>, and dithieno[3,2-*b*:2',3'-*d*]thiophene ditin compound<sup>4</sup> were synthesized according to the synthetic procedures reported in the literature. To verify the molecular structures of all the synthesized products, <sup>1</sup>H-NMR (400 MHz) and <sup>13</sup>C-NMR (100 MHz) spectra were recorded using a Bruker Ascend 400 spectrometer. Standard abbreviations indicating multiplicity are used as follows: s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, and b = broad. The molecular weights and polydispersity indices in of the polymers were determined by a Waters Gel-Permeation

Chromatography (GPC) system at 80 °C which equipped with the 1515 isocratic pump and the 2414 refractive index detector. *o*-Dichlorobenzene (ODCB) was used as the eluent and polystyrene as the standard. The optical absorption spectra were obtained by a PerkinElmer Lambda 35 UV/vis spectrometer. The thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a TA instruments Q50 thermal analysis and TA instruments Q20 system, respectively. Atomic force microscopy (AFM) images were recorded on a XE-100 (Park systems) with PPP-NCHR 10M cantilever in the non-contact mode. AFM samples were fabricated in the same method for OPV devices without TiO<sub>2</sub>/Al deposition. FT-IR spectra were performed on a Spectrum 100 (Perkin Elmer) FT-IR spectrometer with a PerkinElmer Universal Attenuated Total Reflectance (UATR) sampling accessory. The spectrum scope was set in the range of 400–4000 cm<sup>-1</sup> and the resolution factor was selected to be 4 cm<sup>-1</sup>.

### *Synthesis of Monomers and Polymers*

**3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione.** Into a 100 mL flask, 3,6-bis(5-bromothiophen-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione (2.4 g, 3.86 mmol) and chloroform (80 mL) were added and the resulting mixture was cooled using an ice water bath. *N*-bromosuccinimide (0.6 g, 3.86 mmol) dissolved in chloroform (80 mL) was added slowly into the flask using a dropping funnel. After removing the ice water bath, the temperature of the flask was increased to R.T. and the resulting mixture was kept at R.T. with stirring under a dark condition for 12 h. The reaction solution was extracted with CHCl<sub>3</sub> and H<sub>2</sub>O. The combined organic part was dried with anhydrous magnesium sulfate and evaporated in vacuum. After column purification on silica

gel with a eluent (Hexane:CH<sub>2</sub>Cl<sub>2</sub>=1:1), a purple-black solid was obtained (1.96, 45.0%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.85-0.89 (m, 12H), 1.10-1.40 (br, 80H), 1.87 (br, 2H), 3.91 (d, 4H), 7.20 (d, 2H), 8.61 (d, 2H).

**2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene.** Under argon protection, 4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (4.1 g, 9.18 mmol) was dissolved in anhydrous THF (200 mL). The mixture was cooled using an acetone/dry ice bath and then, *n*-butyllithium solution (2.5 M in hexanes) (8.26 mL, 20.66 mmol) was added dropwise with stirring. After keeping the mixture in a dry ice bath for 40 min followed by reaction at R.T. for 20 min, the reaction solution was cooled in the acetone/dry ice bath, and 27.5 mL (27.5 mmol) of trimethyltin chloride solution (1 M in THF) was added with dropwise and stirred at R.T. for 12 h. The reaction mixture was quenched with 60 mL of water and extracted with diethyl ether. The organic part was dried with anhydrous magnesium sulfate and evaporated in vacuum. After recrystallization of the residue from isopropanol, the titled compound was obtained (5.24 g, 74.0%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.44 (t, 18H), 0.94 (t, 6H), 1.02 (t, 6H), 1.38-1.73 (m, 16H), 1.78-1.81 (m, 2H), 4.18 (d, 4H), 7.51 (s, 2H).

**2,6-Bis(trimethyltin)dithieno[3,2-*b*:2',3'-*d*]thiophene.** Dithieno[3,2-*b*:2',3'-*d*]thiophene (1.0 g, 5.10 mmol) was dissolved in 50 mL of anhydrous THF and cooled down to -78 °C. *n*-Butyllithium solution (5.12 mL, 12.8 mmol, 2.5 M in hexane) was added dropwise into the reaction mixture at the same temperature. After stirring for 30 min, the temperature was increased to R.T. and the solution was further stirred for 2 h at R.T. After cooling down to -

78 °C again, 15 mL of trimethyltin chloride solution (15 mL, 15 mmol, 1 M in THF) was added dropwise into the resulting solution. After further stirring for 12 h at R.T., the reaction was quenched by addition of 60 mL of water. After extraction with diethylether, the organic phase was washed with water, and then dried anhydrous magnesium sulfate and evaporated in vacuum. Recrystallization of the residue from CH<sub>2</sub>Cl<sub>2</sub> and isopropanol yields the ditin compound (1.86 g, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.43 (t, 18H), 7.28 (s, 2H).

**2,7-bis(trimethyltin)-5,10-bis(2-hexyldecyl)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene.** 2,7-Dibromo-5,10-bis(2-ethylhexyl)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene (1.2 g, 1.72 mmol) was dissolved in 40 mL of anhydrous THF and then the resulting solution was cooled in an acetone/dry ice bath under argon protection. *n*-Butyllithium solution (2.5 M in hexanes) (1.4 mL, 3.52 mmol) was added dropwise. The mixture was kept at the same temperature for 25 min with stirring and trimethyltin chloride solution (4.48 mL, 4.48 mmol, 1 M in THF) was added with small portions. The resulting solution was stirred at R.T. for 12 h and then, quenched with 80 mL of water and extracted with diethylether. The organic phase was dried with anhydrous magnesium sulfate and evaporated in vacuum. Recrystallization of the residue from CH<sub>2</sub>Cl<sub>2</sub> and isopropanol yields the ditin compound (0.9 g, 60%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.46 (t, 18H), 0.85 (t, 6H), 0.89 (t, 6H), 1.20-1.59 (m, 16H), 2.17-2.20 (m, 2H), 3.21-3.33 (m, 4H), 7.38 (s, 2H).

**PDPPBDT:** 3,6-Bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione (0.43 g, 0.38 mmol) and 2,6-Bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (0.30 g, 0.38 mmol) were weight into a 10 mL

round-bottom flask and then, tetrakis(triphenylphosphine)palladium(0) ( $\text{Pd}(\text{PPh}_3)_4$ ) (19 mg) was added. The flask was subjected to five successive cycles of vacuum followed by refilling with argon. Anhydrous toluene (5.8 mL) and anhydrous dimethylformamide (DMF) (1.5 mL) were added via a syringe and the resulting solution was heated with stirring at 120 ° C for 36 h under argon protection. The resulting mixture was precipitated into methanol and collected by filtration. The small molecules and oligomers were removed by Soxhlet extraction using hexane, methanol, and chloroform. The resulting polymer was obtained from the chloroform fraction after drying in vacuo for 12 h. (0.41 g, 76.6 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_2\text{CDCl}_2$ )  $\delta$  0.65-2.19 (b, 124H), 3.53-4.89 (b, 8H), 6.51-8.10 (b, 4H), 8.43- 9.85 (b, 2H). GPC:  $M_n = 122$  kg/mol: PDI = 5.6.

***PDPPDTT***: The polymer was synthesized according to the similar procedure as that for PDPPBDT with 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-decyltetradecyl)pyrrolo[3,4-*c*]pyrrole-1,4(2H,5H)-dione (0.43 g, 0.38 mmol) and 2,6-bis(trimethyltin)dithieno[3,2-*b*:2',3'-*d*]thiophene (0.20 g, 0.38 mmol). (0.23 g, 55%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_2\text{CDCl}_2$ )  $\delta$  0.75~1.68 (b, 90H), 8.40~9.90 (b, 2H). GPC:  $M_n = 43$  kg/mol: PDI = 1.5.

***PDPPDTBDT***: The polymer was synthesized according to the similar procedure as that for PDPPBDT with 3,6-bis(5-bromo-thiophene-2-yl)- *N, N'*-bis(2-decyltetradecyl)-1,4-dioxopyrrolo[3,4-*c*]pyrrole (0.23 g, 0.2 mmol) and 2,7-bis(trimethyltin)-5,10-bis(2-hexyldecyl)dithieno[2,3-*d*:2',3'-*d'*]benzo[1,2-*b*:4,5-*b'*]dithiophene (0.17 g, 0.2 mmol). (0.21 g, 81.0%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_2\text{CDCl}_2$ )  $\delta$  0.68-1.77 (b, 124H), 2.82-4.59 (b, 8H), 6.45-7.78 (b, 4H), 8.32-9.79 (b, 2H). GPC:  $M_n = 29$  kg/mol; PDI = 2.6.

### ***Electrochemical Studies***

Cyclic voltammetry (CV) was performed to study the electrochemical properties of the polymers. The polymer thin film was coated on a glassy carbon electrode and measured using a 0.1 M tetrabutylammoniumhexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) acetonitrile solution as an electrolyte with a scan rate of 50 mV/s. The Ag/Ag<sup>+</sup> was used as a reference electrode. The oxidation potentials of PDPPBDT, PDPPDTT, and PDPPDTBDT were 1.05, 1.04, and 1.03 V, respectively and the reduction potentials of the polymers are -0.93, -0.74, and -0.97 V for PDPPBDT, PDPPDTT and PDPPDTBDT, respectively. The redox potential of ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) was measured using the same conditions for calibration and it was positioned at 0.48 V to the Ag/Ag<sup>+</sup> electrode. The redox potential of  $\text{Fc}/\text{Fc}^+$  is assumed to have an absolute energy level of -4.80 eV to vacuum.<sup>5</sup> The HOMO and LUMO energy levels of each polymer were then estimated according to the following equations.

$$E_{\text{HOMO}} = -4.8 - (\varphi_{\text{ox}} - 0.48) \text{ (eV)}$$

$$E_{\text{LUMO}} = -4.8 - (\varphi_{\text{red}} - 0.48) \text{ (eV)}$$

where  $\varphi_{\text{ox}}$  is the onset oxidation potential vs. Ag/Ag<sup>+</sup> and  $\varphi_{\text{red}}$  is the onset reduction potential vs. Ag/Ag<sup>+</sup>.

### ***Grazing Incidence Wide-Angle X-ray Scattering (GIWAXS) Studies***

Grazing incidence X-ray diffraction (GIWAXS) measurements were performed in vacuum at the 3C beamline in the Pohang Light Source, Korea. To make the results comparable to those of OPV devices, the samples for the measurements were prepared on PEDOT:PSS modified Si substrates under the same conditions as those used for fabrication of solar cell devices. The wavelength of X-rays was 0.1651 nm and the incidence angle was 0.13°, the angle between

the critical angle of the sample and that of Si. The 2D- GIWAXS patterns were recorded using a 2D CCD detector (Rayonix SX165), and the X-ray irradiation time was set at 0.5–10 sec depending on the saturation level of the detector. The 2D- GIWAXS images from the films were analyzed according to the relationship between the scattering vector  $q$  and the  $d$  spacing,  $q = 2\pi/d$ .

### ***Hole Mobility Measurement***

Hole-only devices with a structure of ITO/PEDOT:PSS/polymer:PC<sub>71</sub>BM/Au were fabricated. The hole mobilities of the polymer devices were determined with the space-charge-limited current (SCLC) method by using the next equation:

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu_h \frac{V^2}{L^3}$$

where  $\varepsilon_0$  is the permittivity of free space,  $\varepsilon_r$  is the dielectric constant of the polymer: PC<sub>71</sub>BM blend,  $\mu_h$  is the hole mobility,  $V = V_{\text{appl}} - V_{\text{bi}} - V_a$  ( $V_{\text{appl}}$ , the applied bias;  $V_{\text{bi}}$ , the built-in potential due to the difference in electrical contact work functions;  $V_a$ , the voltage drop due to contact resistance and series resistance across the electrodes), and  $L$  is the thickness of active layer.<sup>6,7</sup> The dielectric constant was assumed to be 3 in our analysis, which is a typical value for conjugated polymers. The current density versus voltage characteristics were measured on a Keithley model 2400 source measuring unit.

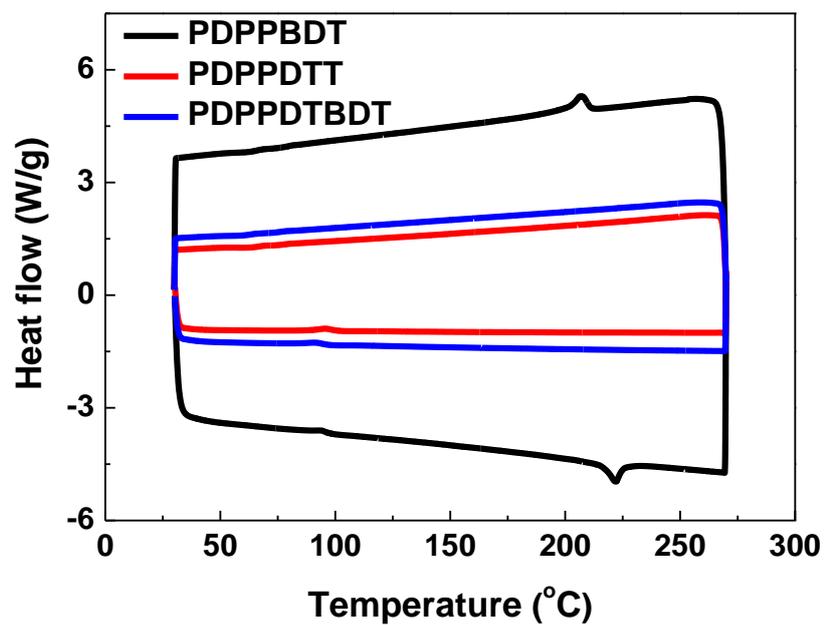
### ***Solar Cell Devices Fabrication and Measurement***

Solar cell devices were fabricated with a device configuration of ITO/PEDOT:PSS/polymer:PC<sub>71</sub>BM/TiO<sub>2</sub>/Al as follows: indium tin oxide (ITO) glass

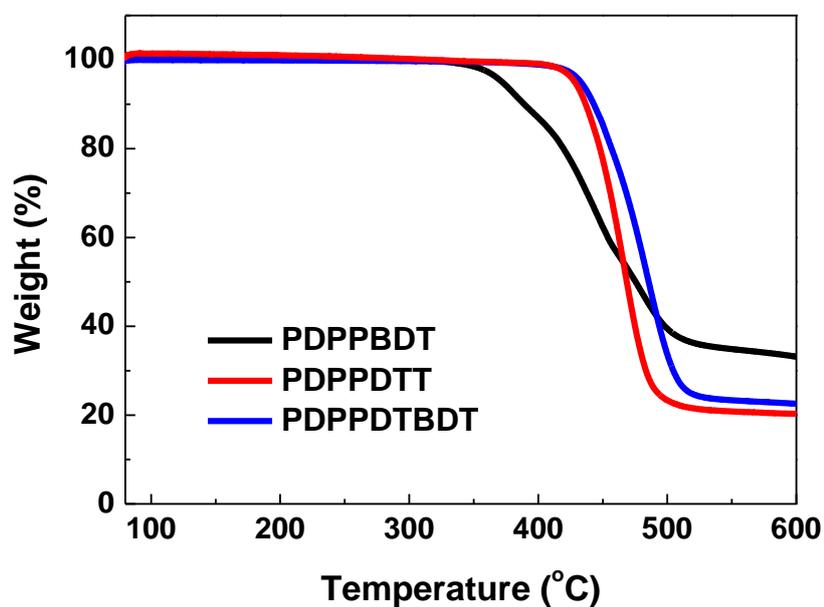
substrates were successively cleaned by sonication in isopropanol, acetone, and isopropanol for 10 min, and dried in vacuum. The ITO substrates were then treated with UV ozone for 20 min. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS) layers were spin-coated onto a cleaned ITO glass with a PEDOT:PSS solution at 4000 rpm for 35 s, and then dried in a vacuum oven at 120 °C for 10 min. The PEDOT:PSS solution was prepared by diluting CLEVIOS P VP AI4083 PEDOT:PSS solution with methanol in a 1:1 volume ratio. A solution of each polymer and PC<sub>71</sub>BM blend (3~10 mg/mL) was prepared by dissolving a mixture of the polymer and PC<sub>71</sub>BM in chlorobenzene with 3 volume% of 1,8-diiodooctane (DIO). The polymer:PC<sub>71</sub>BM ratios are 1:2, 1:1.5, and 1:2 for PDPPBDT, PDPPDTT, and PDPPDTBDT, respectively. The polymer:PC<sub>71</sub>BM blend solutions were then spin-coated onto the ITO/PEDOT:PSS substrates at 2000 rpm for 25 s. A TiO<sub>2</sub> nanoparticle layer was formed on top of each active layer via spin-casting at 4000 rpm from a TiO<sub>2</sub> nanoparticle dispersion in ethanol. An aluminum layer (100 nm) was vacuum-deposited through a shadow mask at a base pressure of  $2 \times 10^{-6}$  Torr with a deposition rate of 3 Å/s. The current-density versus voltage (*J-V*) characteristics of the solar cells were recorded with a Keithley model 2400 source meter. A class-A solar simulator with a 1000 W Xenon lamp (Yamashita Denso) equipped with an AM 1.5 G filter was used as the light source. Its light intensity was adjusted to 1 sun light intensity (100 mW/cm<sup>2</sup>) by using a NREL-calibrated Si solar cell equipped with a KG-5 filter. The external quantum efficiency (EQE) of each cell was measured as a function of wavelength from 300 to 1000 nm on incident photon-to-current conversion equipment (PV Measurements Inc.). Calibration was performed using a NIST-calibrated G425 silicon photodiode as a standard.

### ***Stability Test of Polymer Solar Cells***

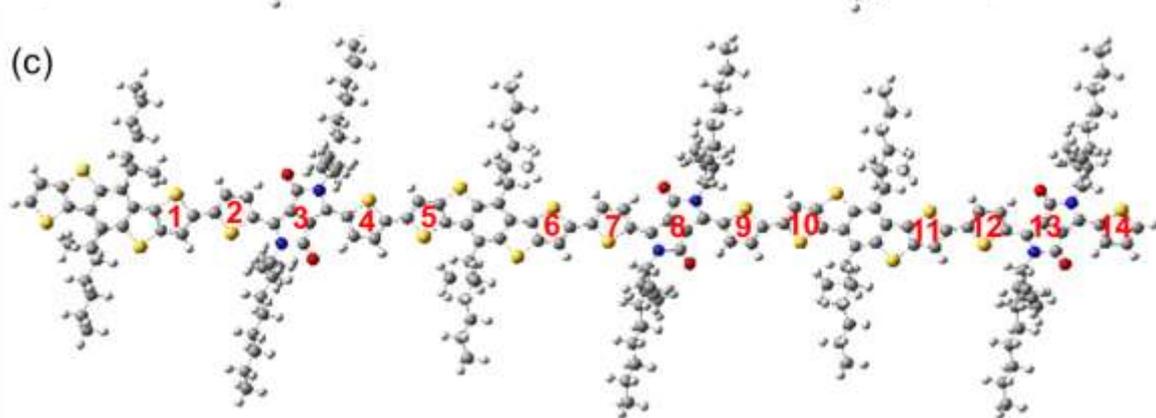
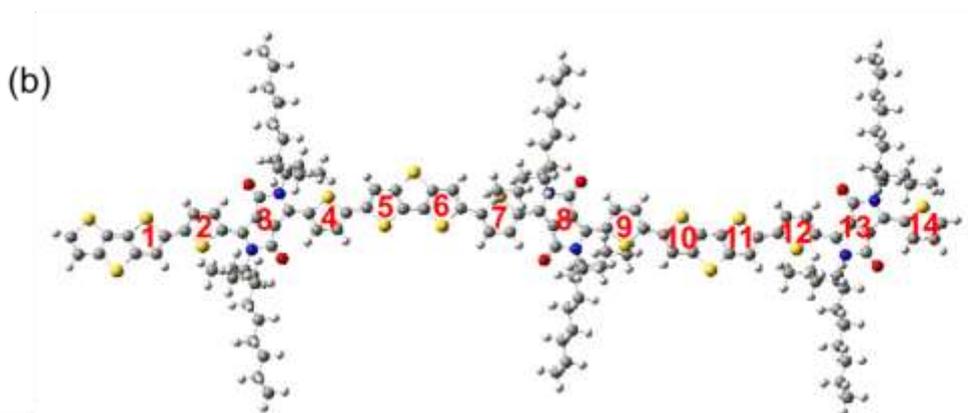
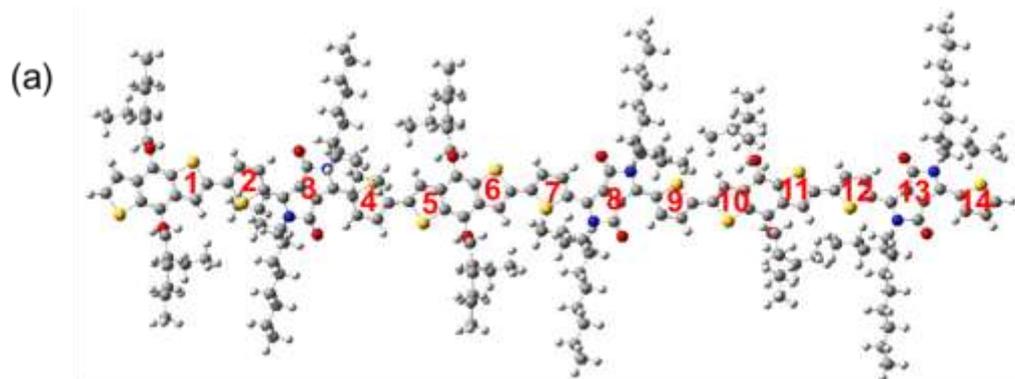
The fabricated solar cell devices were encapsulated with the next procedure; a glass substrate was placed on top of the cell and then the device was sealed using a UV curable epoxy resin. Sulfur lamp with a light intensity equivalent to 1 sun was used for the device degradation. Photovoltaic property changes of the polymer solar cells were monitored as a function of light-soaking time and the degraded cells were measured using the same conditions described above in the session of 'Solar Cell Devices Fabrication and Measurement'.



**Figure S1.** DSC analysis of PDPPBDT, PDPPDTT, and PDPPDTBDT



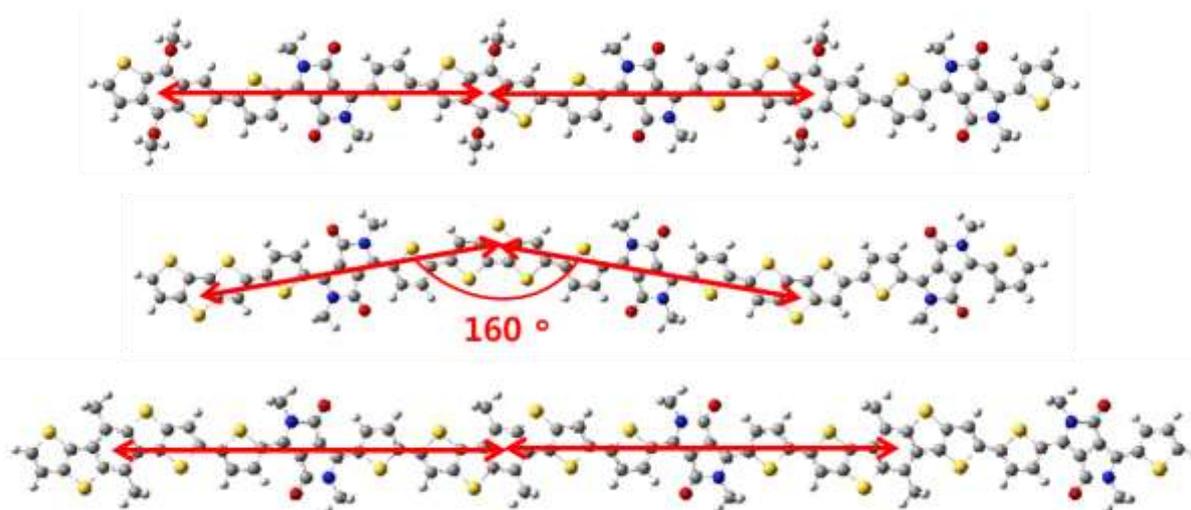
**Figure S2.** TGA analysis of PDPPBDT, PDPPDTT, and PDPPDTBDT



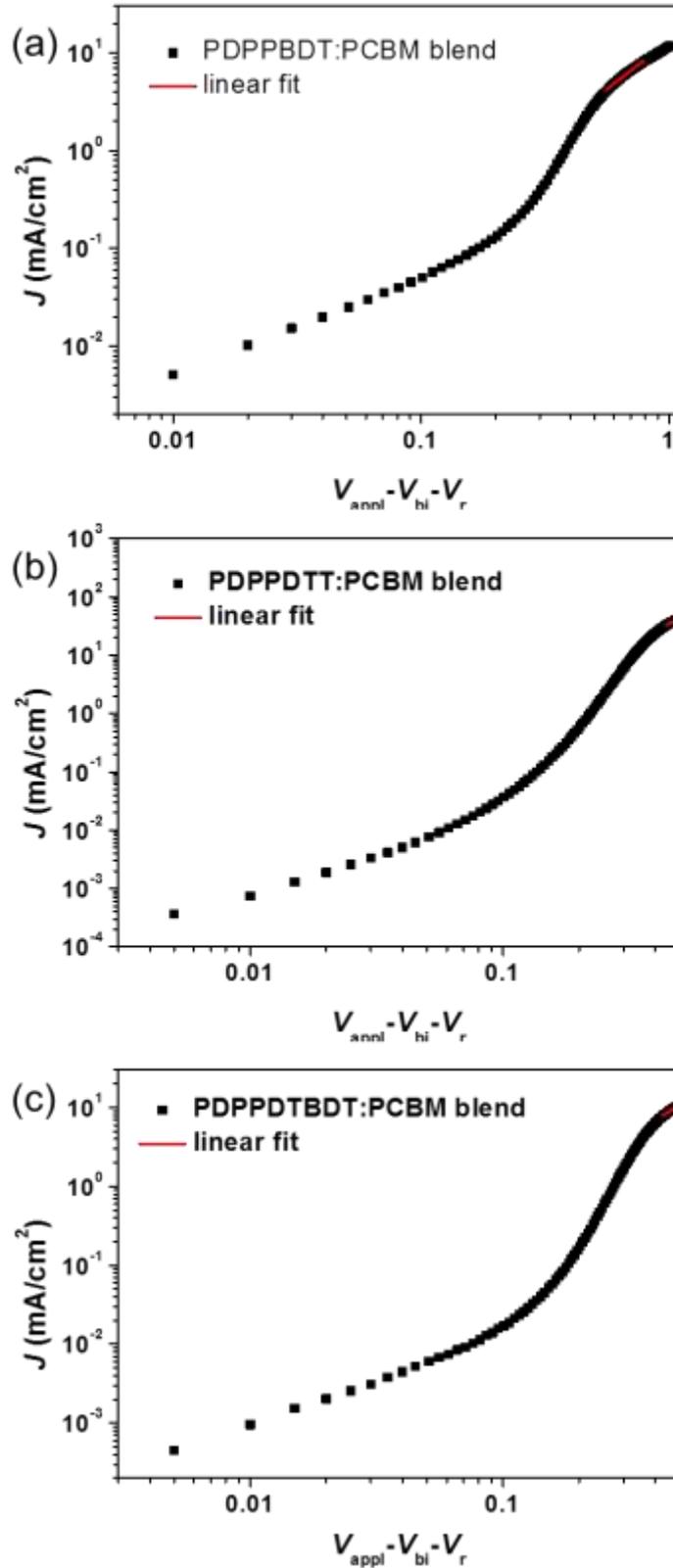
Aromatic ring position <sup>a</sup>	Dihedral angle (degree)		
	PDPPBDT	PDPPDTT	PDTTDTBDT
1-2	-3.87	-10.46	-10.81
2-3	14.47	14.23	1.06
3-4	-16.67	-16.12	-1.42
4-5	2.68	14.81	-15.42
6-7	-15.07	-1.12	-2.11
7-8	13.39	-18.90	2.01
8-9	-17.65	-13.71	-0.90
9-10	0.00	-7.40	-0.46
11-12	-8.96	-9.71	-4.37
12-13	-14.29	-14.51	2.38
13-14	-20.25	-19.92	-1.01

<sup>a</sup> Dihedral angles were calculated between the numbered aromatic rings.

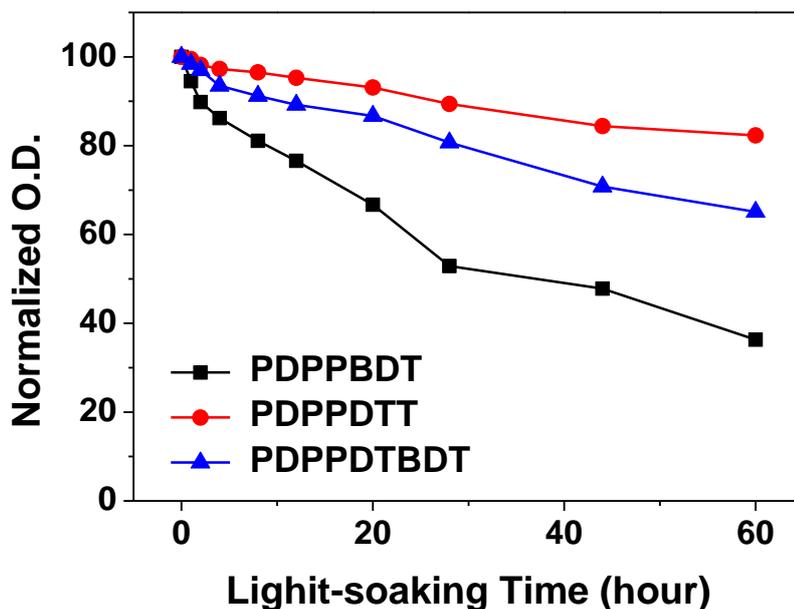
**Figure S3.** Optimized molecular conformations and calculated dihedral angles of the oligomers of (1) PDPPBDT, (2) PDPPDTT, and (3) PDPPDTBDT



**Figure S4.** Molecular conformations of the backbones of PDPPBDT, PDPPDTT, and PDPPDTBDT obtained through the DFT at the B3LYP/6-31G(d) level.



**Figure S5.**  $J$  vs.  $V$  plots for polymer:PC<sub>71</sub>BM blend films. The solid lines are fits of the data points.



**Figure S6.** Decrease in optical density (O.D.) at  $\lambda_{\max}$  of polymer films.

### References

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