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A highly crystalline low band-gap polymer consisting of perylene and diketopyrrolopyrrole for organic photovoltaic cells

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◆ EXPERIMENTAL

◆ Materials

Perylene, CCl_4 , and potassium phosphate were purchased from Aldrich. *Tris*(dibenzylideneacetone)dipalladium(0) and *tris-o*-tolylphosphine were purchased from Strem. [6,6]-Phenyl C_{71} -butyric acid methyl ester (PC_{71}BM) was purchased from EM-index. All starting organic compounds were purchased from Aldrich, Alfa Aesar, or TCI Korea, and used without further purification. Solvents were dried and purified by fractional distillation over sodium/benzophenone and handled in a moisture-free atmosphere. Column chromatography was performed using silica gel (Merck, Kieselgel 60 63-200 MYM SC). 3,6-Di(2-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)thien-5-yl)-2,5-di(2-octyl-1dodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione (DPP) was synthesized similarly to methods described in previous reports [1].

◆ Measurements

^1H - and ^{13}C NMR spectra were recorded using a Varian Mercury Plus 300MHz spectrometer, and the chemical shifts were recorded in units of ppm with chloroform as an internal standard (δ 7.26 ppm). Elemental analysis was performed using a Vario Micro Cube at the Korea Basic Science Institute (Busan, Korea). Absorption spectra were obtained using a JASCO JP/V-570 spectrometer. The molecular weights of the polymers were determined via gel permeation chromatography (GPC) analysis relative to a polystyrene standard using a Waters high-pressure GPC assembly (model M590). Thermal analyses were performed on a Mettler Toledo TGA/SDTA 851^e under a N_2 atmosphere with a heating and cooling rate of 10 °C/min. Cyclic voltammetry (CV) was performed on a CH Instruments Electrochemical Analyzer.

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Cyclic voltammetry was performed to investigate the redox behavior of the polymers and determine the HOMO and LUMO energy levels of the polymers. CV was carried out under an argon atmosphere at room temperature in a solution of TBABF₄ (0.10 M) in acetonitrile at a scan rate of 50 mV/s. A platinum plate, platinum wire, and Ag/AgNO₃ electrode were used as the working, counter, and reference electrodes, respectively. The HOMO energy level was determined by measuring the oxidation onsets (E_{ox}) of the polymer films. To obtain the oxidation potentials of the polymer films, the reference electrode was calibrated against ferrocene/ferrocenium (Fc/Fc⁺), which has a redox potential with an absolute energy level of -4.80 eV in vacuum; the potential of this external standard under the experimental conditions was 0.092 eV. Accordingly, the HOMO energy values (E_{HOMO}) were calculated using the following equation: $E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}} + 4.708)$ eV, where $E_{\text{ox}}^{\text{onset}}$ is the onset oxidation potential versus Ag/Ag⁺.

◆ Two-dimensional grazing incidence X-ray scattering (2D-GIXS) experiments

2D-GIXS measurements were performed on beamline 9A at the Pohang Accelerator Laboratory (South Korea). X-Rays with wavelengths of 1.1010 Å were used. The chosen incidence angle (~0.15°) allowed complete penetration of the X-rays into the polymer film. A thin layer (40–50 nm) of PEDOT:PSS was spin-coated onto silicon substrates, followed by spin-coating of a layer of the polymer thin films.

◆ Fabrication of field-effect transistor devices

Organic thin-film field-effect transistors (OTFTs) were fabricated using a bottom-contact geometry (channel length, L , of 12 μm and width, W , of 120 μm). The source and drain

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contacts were composed of gold (100 nm), and the dielectric comprised a 300 nm thick layer of silicon oxide (SiO₂). The SiO₂ surface was cleaned, dried, and pretreated with a solution of 10.0 mM octyltrichlorosilane (OTS-8) in toluene at room temperature for 2 h under a N₂ atmosphere to produce smooth, non-polar surfaces onto which the polymers were spin-coated. The polymers were dissolved in chlorobenzene at a concentration of 0.5 wt%. Films of the organic semiconductors were spin-coated at 1000 rpm for 50 s to form 60 nm thick layers. All device fabrication procedures and measurements were carried out in air at room temperature. The resultant TFTs exhibited typical p-channel TFT characteristics. The TFT mobilities were calculated in the saturation region using the following equation:

$$I_{ds} = (WC_i/2L)\mu(V_G - V_T)^2,$$

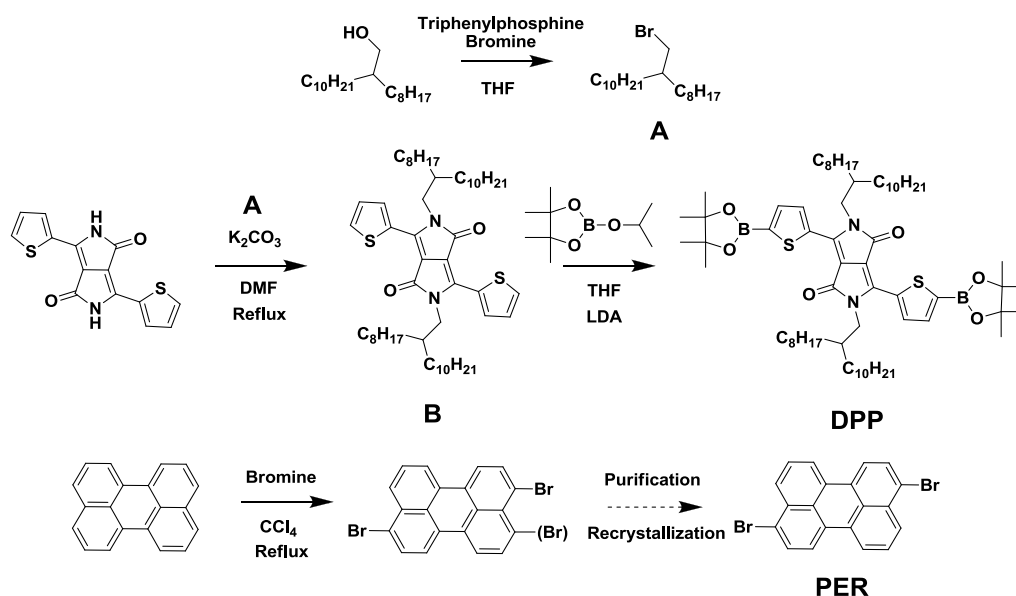
where I_{ds} is the drain-source current in the saturated region, W and L are the channel width (120 μm) and length (12 μm), respectively, μ is the field-effect mobility, C_i is the capacitance per unit area of the insulation layer (SiO₂, 300 nm), and V_G and V_T are the gate and threshold voltages, respectively.

◆ Fabrication of photovoltaic devices

BHJ OPVs devices with ITO/PEDOT:PSS/polymer:PC₇₁BM/Ca/Al structures were fabricated. The ITO surface was cleaned via sonication and rinsing in distilled water, methanol, and acetone. The hole-transporting PEDOT:PSS layer (45 nm) was spin-coated onto each ITO anode from a solution purchased from Heraeus (CleviosTM P VP AI4083), followed by spin-coating of a layer of polymer:PC₇₁BM; the polymer solution for spin-coating was prepared

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by dissolving the polymer (10 mg/mL) in chlorobenzene or a 97% chlorobenzene/3% 1,8-diodooctane (DIO) mixture. Calcium and aluminum contacts were formed by vacuum deposition at pressures below 3×10^{-6} Torr, providing an active area of 9 mm^2 . The thickness of the active layer was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of ± 1 nm. The current-density–voltage (J – V) characteristics of the polymer photovoltaic cells were determined by illuminating the cells with simulated solar light (AM 1.5G) at an intensity of 100 mW/cm^2 using an Oriel 1000 W solar simulator. Electronic data were recorded using a Keithley 236 source-measure unit, and all characterizations were carried out under ambient conditions. The illumination intensity was calibrated by employing a standard Si photodiode detector from PV Measurements Inc., which was calibrated at the National Renewable Energy Laboratory (NREL). The external quantum efficiency (EQE) was measured as a function of the wavelength in the range 360–800 nm using a halogen lamp as the light source; calibration was performed using a silicon reference photodiode. The measurements were carried out after masking all but the active cell area of the fabricated device. All characterization was performed under ambient conditions.



Scheme S1. Synthetic routes to DPP and PER and their chemical structures.

◆ Synthesis of monomers and polymers

Synthesis of 3,6-bis-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl)-*N,N'*-bis((octyldodecyl)-1,4-dioxo-pyrrolo[3,4-c]pyrrole (DPP)

LDA (2 M in hexane/THF, 2.6 mL, 5.2 mmol) was dropwise added to a solution of compound **B** (1.5 g, 1.74 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxoborolane (1.3 g, 6.98 mmol) in THF (30 mL) under N₂ at -20 °C over 10 minutes. The resulting solution was stirred for 1 h at 0 °C and then quenched with 1 M HCl. The product was extracted by DCM, washed with water, and dried over MgSO₄. After evaporation of the solvent, the residue was dissolved in a small amount of DCM and then slowly added to 200 mL of acetone with vigorous stirring. The precipitate was collected by filtration, washed with acetone, and dried under vacuum to afford 0.85 g of powder (44%). ¹H NMR (300 MHz, CDCl₃, ppm): δ 8.90 (d, 2H), 7.70 (d, 2H), 4.04 (d, 4H), 1.89 (m, 2H), 1.36 (m, 24H), 1.24 (br, 64H), 0.85 (m, 12H); ¹³C NMR (75 MHz, CDCl₃, ppm): δ 161.76, 140.53, 137.66,

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136.13, 135.68, 108.75, 84.59, 46.28, 37.79, 31.93, 31.88, 31.31, 31.29, 30.03, 30.02, 29.64, 29.59, 29.53, 29.35, 29.29, 26.36, 26.34, 24.78, 22.69, 22.67, 14.12, 14.12.

Synthesis of 3,9-dibromoperylene (PER). Bromine (8.81 g, 7.92 mmol) was added to a stirred solution of perylene (5 g, 19.81 mmol) in carbon tetrachloride (200 mL) in the dark. The mixture was stirred at 110 °C for 12 h and 2 M HCl was added to the mixture. The product was extracted with chloroform and the organic phase was successively washed with 10% sodium bisulfate, 2 M HCl, and water before being dried over MgSO₄. The solvent was removed to afford dark-red crystals (2.81 g, 63%) that were recrystallized from hot hexane. ¹H NMR (300 MHz, CDCl₃, ppm): δ 8.25 (d, 2H), 8.13 (d, 2H), 7.96 (d, 2H), 7.78 (t, 2H), 7.60 (d, 2H) ¹³C NMR (75 MHz, CDCl₃, ppm): δ 135.8, 130.1, 128.9, 128.2, 127.1, 126.9, 125.9, 124.1, 121.3, 118.0. Anal. Calcd for C₂₀H₁₀Br₂: C, 58.55; H, 2.42; Br, 38.94. Found: C, 58.30; H, 2.30.

Synthesis of poly[perylene-*alt*-3,6-dithiophene-2-yl-2,5-di(2-octyldecyl)pyrrolo[3,4-c]pyrrole-1,4-dione-5',5"-diyl] (PDPP-PER).

3,6-Di(2-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)thien-5-yl)-2,5-di(2-octyl-1dodecyl)-pyrrolo[3,4-c]pyrrole-1,4-dione (**DPP**) (400 mg, 0.36 mmol) was mixed with 3,9-dibromoperylene (**PER**) (146.6 mg, 0.36 mmol, 1 equiv.), potassium phosphate (K₃PO₄; 1 mL, 2 M aqueous solution), and 3 drops of Aliquit 336 in anhydrous toluene (5 mL) in a Schlenk flask. The solution was purged with argon for 30 min, then *tris*(dibenzylideneacetone)dipalladium (0.2 mg, 2.6 μmol) and *tris*-*o*-tolylphosphine (1.0 mg, 10.4 μmol) were added. The reaction was stirred at 90 °C for two days. Phenylboronic acid

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and bromobenzene were added consecutively, and the resultant mixture was stirred overnight. For purification, the reaction mixture was cooled to approximately 50 °C and 200 mL of methanol was added slowly with vigorous stirring. The polymer fibers were collected via filtration and reprecipitation from methanol and acetone. The polymers were further purified by washing with acetone for two days in a Soxhlet apparatus to remove oligomers and catalyst residues. Column chromatography using a chloroform solution was performed on the polymer. The reprecipitation procedure in chloroform/methanol was repeated several times. The resulting polymers were soluble in common organic solvents. Anal. Calcd for: C, 80.09; H, 9.02; N, 2.46; S, 5.63. Found: C, 74.34; H, 8.57; N, 3.00; S, 4.93. M_w/M_n (GPC) = 49 000/20 000, polydispersity index (PDI) = 2.4.

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Table S1. Average molecular weights and thermal properties of the synthesized polymers.

Polymer	M_n^a	M_w^a	PDI ^a	T_d^b	T_{cr}
	(g/mol)	(g/mol)		(°C)	(°C)
PDPP-PER	20,000	49,000	2.4	411	176.8

^a M_n , M_w , and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards in CHCl_3 . ^b Temperature at 5% weight loss with a heating rate of 10 °C/min under nitrogen.

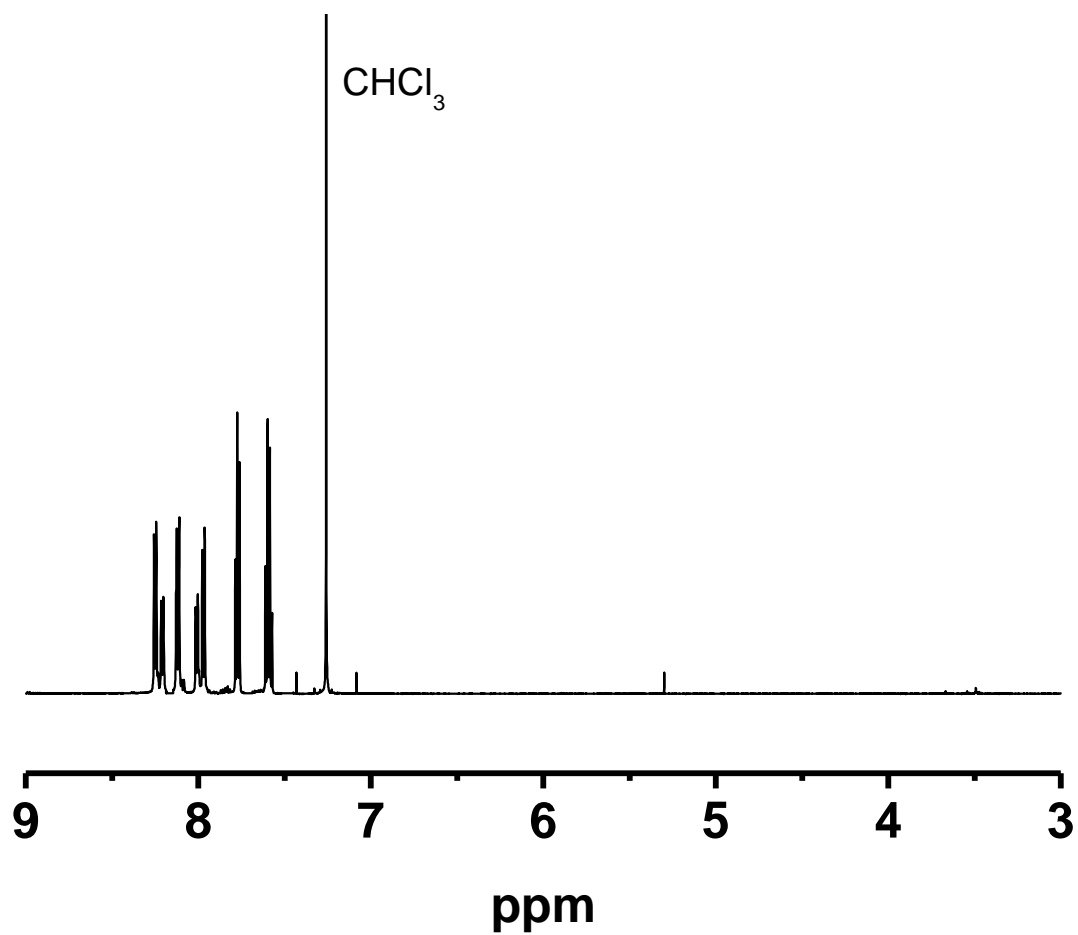
Table S2. Optical and electrochemical properties of the synthesized polymers.

Polymer	Solution^a	Film^b		E_g^{opt}	HOMO	LUMO
	$\lambda_{\text{max, abs}}$	$\lambda_{\text{max, abs}}$	λ_{edge}	(eV) ^c	(eV)	(eV)
	(nm)	(nm)	(nm)			
PDPP-PER	460, 611	466, 634	850	1.45	-5.44	-3.99

^a 1×10^{-5} M in anhydrous chloroform. ^b Polymer film on a quartz plate by spin-casting from a solution in chloroform at 1500 rpm for 30 s. ^c Calculated from the absorption band edge of the copolymer films.

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Figure S1. $^1\text{H-NMR}$ spectra of 3,9-dibromoperylene



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Figure S2. (a) Electrochemical measurements of PDPP-PER. (b) Energy-band diagram for PC₇₁BM and the synthesized polymers.

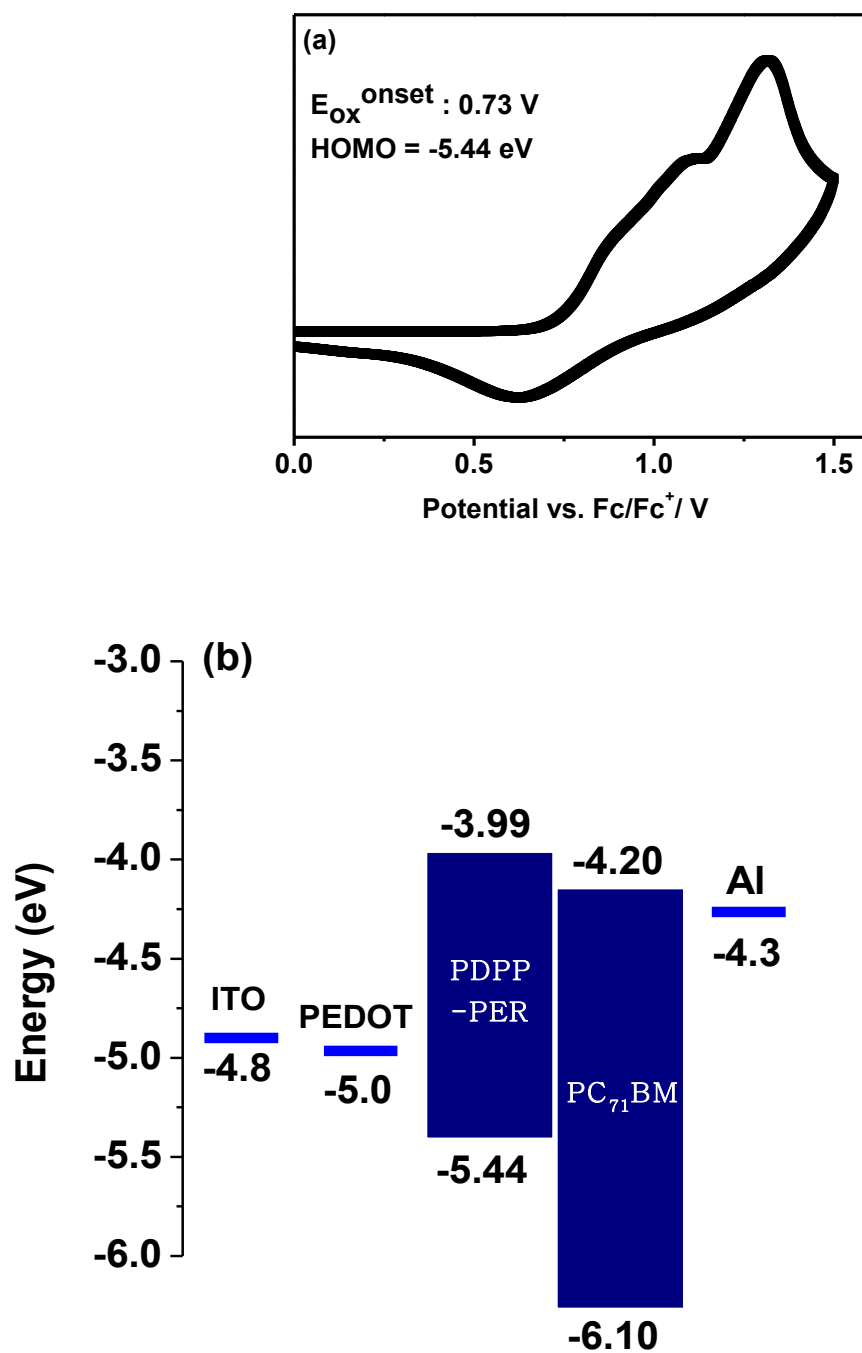


Figure S3. Schematic illustration of PDPP-PER crystals in a thin film.

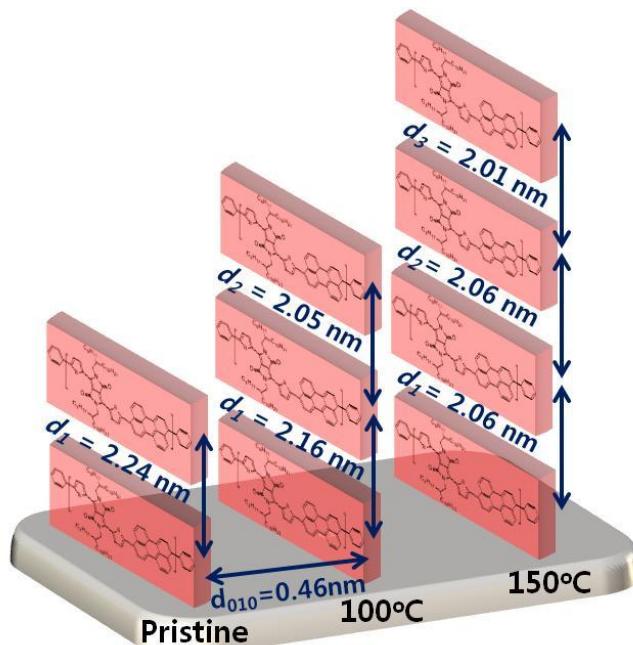
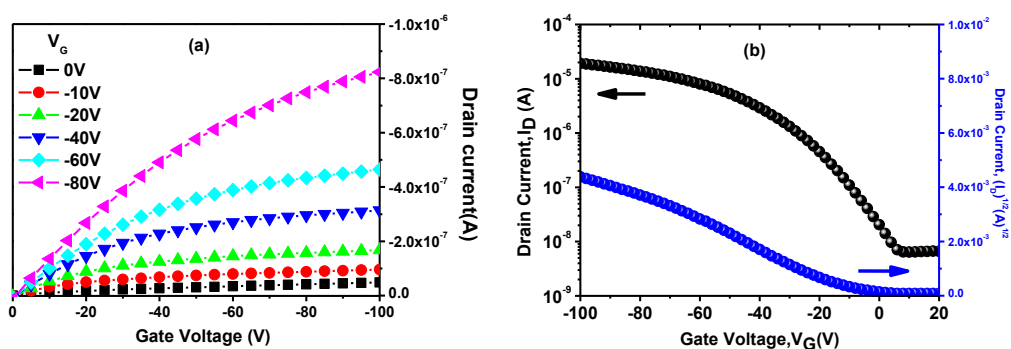


Figure S4. (a) Output and (b) transfer characteristics of OTFTs based on a PDPP-PER thin film.



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Figure S5. J - V curve of ITO/PEDOT:PSS/PDPP-PER+PC₇₁BM:(without DIO)/Ca/Al with different weight ratios.

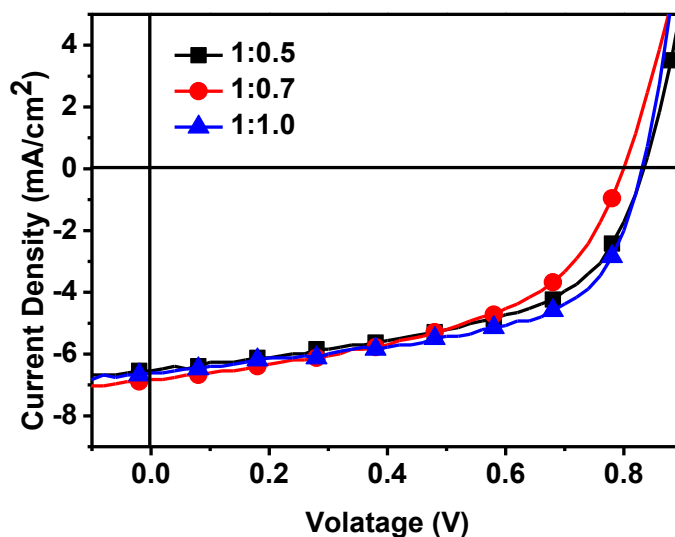


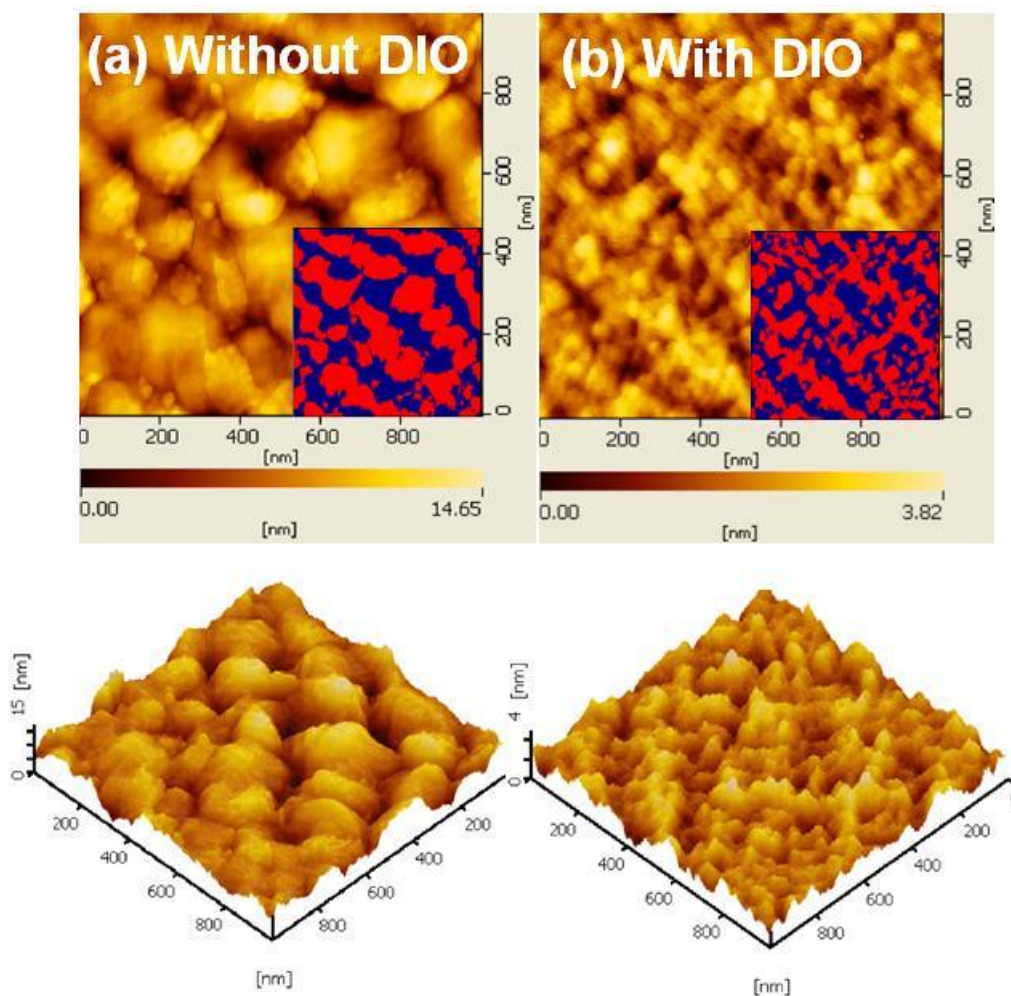
Table S3. Comparison of the photovoltaic properties of OPVs based on PDPP-PER/PC₇₁BM (without DIO) with different weight ratios under AM 1.5G illumination at 100 mW cm⁻².

Polymer	Ratio	V_{oc}^a	J_{sc}^a	FF ^a	PCE ^a
		(V)	(mA/cm ²)		(%)
PDPP-PER	1:0.5	0.83	6.54	0.53	2.89
	1:0.7	0.80	6.82	0.50	2.74
	1:1	0.83	6.61	0.58	3.17

^a Photovoltaic properties of copolymers/PC₇₁BM-based devices spin-coated from a chlorobenzene solution for polymers. (without DIO)

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Figure S6. AFM images of films spin-coated from (a) PDPP-PER/PC₇₁BM (1:1) without DIO and (b) PDPP-PER/PC₇₁BM (1:1) with DIO. The scanned area is 1 $\mu\text{m} \times 1 \mu\text{m}$.



[1] J. Lee, S. Cho, J. H. Seo, P. Anant, J. Jacob, C. Yang, *J. Mater. Chem.*, 2012, **22**, 1504–1510.