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Electronic Supplementary Information

Diketopyrrolopyrrole-based low bandgap polymer with enhanced photovoltaic performances through backbone twisting

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Materials

All reactions and manipulations were carried out under Ar with the use of standard inert atmosphere. Common solvents were dried by standard procedures. Deuterated chloroform ($CDCl_3$), 1, 8-diiodooctane (DIO) and *o*-dichlorobenzene (*o*-DCB) were purchased from Sigma-Aldrich. All column chromatography was performed with the use of silica gel 200-300 mesh. 2,6-Bis(trimethyltin)-4,8-bis(5-ethylhexyl-2-thienyl)-benzo[1,2-b:4,5-b']dithiophene, monomers (**6a**, **6b**) and polymers were synthesized according to the literature methods.[1] Unless stated otherwise, other reagents were purchased from commercial sources, and used without further purification.

Instruments

^1H NMR and ^{13}C NMR spectra were performed in a Bruker AVANCE-III 600 MHz spectrometer using solutions in $CDCl_3$ and chemical shifts were recorded in ppm units with TMS as the internal standard. UV-vis spectra were recorded on a Lambda25 spectrophotometer. The electrochemical measurements were carried out under nitrogen on a deoxygenated solution of tetra-*n*-butylammonium hexafluorophosphate (0.1 M) in acetonitrile with a computer-controlled CHI660C electrochemical workstation, a Pt working electrode, a platinum-wire auxiliary electrode, and an SCE as the reference electrode. Potentials were referred to the ferrocenium/ferrocene (Fc/Fc^+) couple by using ferrocene as a standard. The HOMO levels of the polymers were determined using the oxidation onset value. TGA measurements were performed on STA-409 at a heating rate of 10 ^oC/min under N_2 atmosphere. All GPC analyses were made using THF as eluant and polystyrene standard as reference. Topographic images of the active layers were obtained through atomic force microscopy (AFM) in tapping mode under ambient conditions using an Agilent 5400 instrument. Bright field transmission electron microscopy (TEM) images were acquired using a HITACHI H-7650 electron microscope operating at an acceleration voltage of 100 kV. The structure of the films was analyzed using X-ray diffraction (Bruker D8 ADVANCE). The ground-state geometries of BDT-DTBT molecules were fully optimized with DFT method under B3LYP/6-31G(d, p) level.[2] The reliability of this method had already been verified by a similar previous study.[3]

Photovoltaic Device Fabrication and Characterization

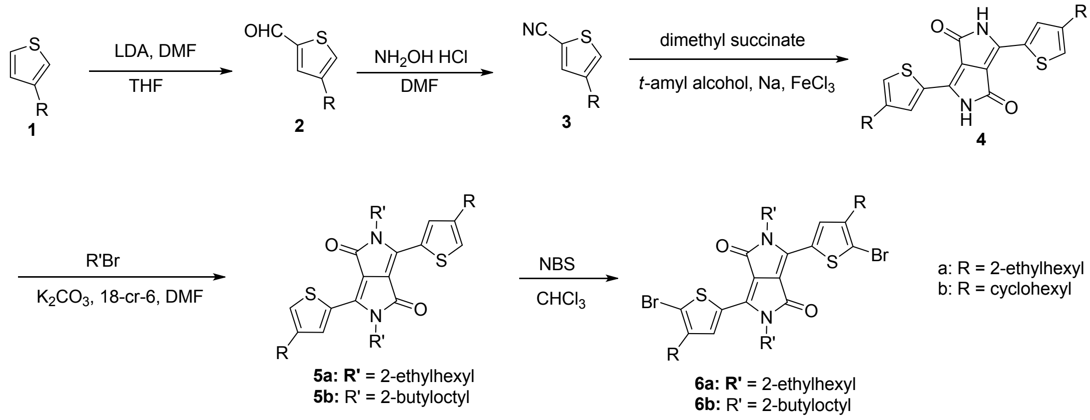
The PSCs were fabricated with a configuration of ITO/PEDOT:PSS/ polymers:$PC_{71}BM$/Ca/Al.[4] A thin layer of PEDOT:PSS (30 nm, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)) was spin-cast on pre-cleaned ITO-coated glass from a PEDOT:PSS aqueous solution (Baytron P VP AI 4083 from H. C. Starck) at 4000 rpm and dried subsequently at 150 °C for 30 min in air, then the device was transferred into glovebox, where the active layer (100 nm) of the blend of the polymer and $PC_{71}BM$ was spin coated on the PEDOT:PSS layer. Finally, a Ca (10 nm)/Al (100 nm) metal top electrode was thermal evaporated onto the active layer under about 2×10^{-4} Pa. The active area of the device was 0.1 cm^2 defined by shadow mask. The current density-voltage (*J-V*) characteristics were measured with a Keithley 2420 source measurement unit under simulated 100 mW/cm^2 (AM 1.5 G) irradiation from a Newport solar simulator. Light intensity was calibrated with a standard silicon solar cell. The external quantum efficiencies (EQE) of solar cells were analyzed using a certified Newport incident photon conversion efficiency (IPCE) measurement system.

Hole mobility was measured using the space charge limited current (SCLC) model,[5] using a device configuration of ITO/PEDOT:PSS/polymer/Au by taking current-voltage in the range of 0-5 V and fitting the results to a space charge limited current for hole-only device. In the presence of carrier traps in the active layer, a trap-filled-limit (TFL) region exists between the ohmic and trap-free SCLC regions. The SCLC behavior in the trap-free region can be characterized by using the Mott-Gurney square law,

$$J = \frac{9\varepsilon\mu V^2}{8L^3}$$

where ε is the static dielectric constant of the medium and μ is the carrier mobility, V is the voltage drop across the device, and L is the polymer thickness.

Synthesis



Scheme S1. Synthetic routes of DPP-based monomers.

4-(2-ethylhexyl)thiophene-2-carbaldehyde (2a)

In a Schlenk flask, 21 mL *n*-butyllithium (2.4 M) is added dropwise to 7.9 mL diisopropylamine in 40 mL dry tetrahydrofuran at 0 °C. After the addition, the reaction mixture is stirred at 0 °C for 1h. Then the reaction mixture is cooled to -78 °C and compound **1a** (10 g) is added dropwise and stirred for an additional hour at -78 °C. Then 5.9 mL dry dimethylformamide is added and stirred for 1h. The reaction is stopped by heating to room temperature and the addition of water. The organic layer is extracted with ether, dried over sodium sulphate and concentrated under reduced pressure. The product is purified by column chromatography on silica gel to give **2a** as colorless oil (8.3 g, 73%). ^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm): 9.88 (s, 1H), 7.58 (s, 1H), 7.35 (s, 1H), 2.58 (d, *J* = 6 Hz, 2H), 1.57-1.55 (m, 1H), 1.32-1.22 (m, 8H), 0.90-0.87 (m, 6H).[6]

4-cyclohexylthiophene-2-carbaldehyde (2b)

Yield 42%. ^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm): 9.87 (s, 1H), 7.66 (s, 1H), 7.39 (s, 1H), 2.64-2.61 (m, 1H), 1.98-1.97 (m, 1H), 1.85-1.82 (m, 1H), 1.76-1.73 (m, 1H), 1.41-1.34 (m, 4H), 1.27-1.23 (m, 1H). ^{13}C NMR (150 MHz, CDCl$_3$) δ (ppm): 183.08, 150.49, 143.55, 135.97, 129.03, 39.38, 34.09, 26.40, 25.94.

4-(2-ethylhexyl)thiophene-2-carbonitrile (3a)

A mixture of 7.33 g of **2a** and 2.73 g hydroxylamine hydrochloride in 30 mL of DMF is heated to 145 °C for 3 hours. After cooling to room temperature, water is added to the reaction mixture and extracted with ether. The organic layer is washed with water, dried and concentrated. The crude product is purified by column chromatography affording the desired nitrile **3a** (4.07 g, 56%). ^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.42 (s, 1H), 7.16 (s, 1H), 2.56 (d, *J* = 6 Hz, 2H), 1.55-1.53 (m, 1H), 1.30-1.25 (m, 8H), 0.89-0.86 (m, 6H).[6]

4-cyclohexylthiophene-2-carbonitrile (3b)

Yield 71%. ^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm): 7.49 (s, 1H), 7.19 (s, 1H), 2.62-2.58 (m, 1H), 1.95-1.94 (m, 1H), 1.84-1.83 (m, 1H), 1.75-1.73 (m, 1H), 1.39-

1.32 (m, 4H), 1.24-1.20 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 149.85, 137.21, 126.10, 114.67, 109.31, 39.28, 34.04, 26.34, 25.86.

3,6-bis(4-(2-ethylhexyl)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (4a)

Sodium (1.11 g, 48.2 mmol) and iron (III) chloride (13 mg) were added into 2-methyl-2-butanol (13 mL) and the mixture was heated to 95 ^{o}C for 2 h until the sodium dissolved. After the solution was cooled to 75 ^{o}C, compound (**3a**) (4.27 g, 19.3 mmol) was added and the mixture was heated to reflux. Diethyl succinate (1.97 g, 13.5 mmol) in 2-methyl-2-butanol (13 mL) was added dropwise in 30 min. After stirring for 3 h, the reaction was cooled to 50 ^{o}C, and methanol (13 mL) and glacial acetic acid (13 mL) were added. The mixture was then refluxed for 30 min, cooled to room temperature, and poured into methanol (100 mL). The precipitate was filtered and washed with water and methanol to afford **4a** as dark red solid (2.9 g, 57%), which was used for the next step without further purification.

3,6-bis(4-cyclohexylthiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**4b**) was synthesized according to the procedure of **4a** with the yield of 60%.

2,5-bis(2-ethylhexyl)-3,6-bis(4-(2-ethylhexyl)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (5a). To a solution of **4a** (1.21 g, 2.30 mmol), potassium carbonate (1.11 g, 8.09 mmol) and 18-crown-6 (11 mg) in DMF (15 mL) was added 2-ethylhexyl bromide (1.33 g, 6.91 mmol). The reaction mixture was stirred at 120 ^{o}C for 20 h and then cooled to room temperature. Diethyl ether and water were added and the layers were separated. The organic layer was washed with brine and the solvent was evaporated. The resulting solid was subjected to column chromatography on silica gel to afford **5a** (597 mg, 34%) as red solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.62 (s, 2H), 7.19 (s, 2H), 4.00 (m, 4H), 2.64 (d, J = 6 Hz, 4H), 1.87-1.85 (m, 2H), 1.67−1.60 (m, 2H), 1.34-1.26 (m, 32 H), 0.91-0.84 (m, 24H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 161.77, 143.53, 143.51, 140.24, 136.52, 129.45, 126.50, 107.78, 45.77, 40.19, 40.16, 39.01, 34.38, 32.42, 32.40, 30.20, 30.18, 29.72, 28.83, 28.81, 28.35, 26.93, 25.60, 25.58, 23.57, 23.07, 14.14, 14.03, 10.77, 10.56.

2,5-bis(2-butyloctyl)-3,6-bis(4-cyclohexylthiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (5b). Yield: 21%. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.75 (s, 2H), 7.23 (s, 2H), 4.00 (d, J = 6 Hz, 4H), 2.72-2.68 (m, 2H), 2.06-2.05 (m, 4H), 1.93-1.92 (m, 2H), 1.85-1.83 (m, 4H), 1.75−1.73 (m, 2H), 1.43-1.20 (m, 42 H), 0.88-0.83 (m, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 161.82, 150.44, 140.39, 135.21, 129.45, 124.30, 107.73, 46.03, 39.42, 37.69, 34.05, 31.79, 31.09, 30.84, 29.72, 28.43, 26.53, 26.16, 26.01, 23.12, 22.66, 14.10, 14.05.

3,6-bis(5-bromo-4-(2-ethylhexyl)thiophen-2-yl)-2,5-bis(2-ethylhexyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (6a). To a degassed solution of **5a** (395 mg, 0.527 mmol) in chloroform (20 mL) at 0 ^{o}C, *N*-bromosuccinimide (192 mg, 2 mmol) was added in portions, and the reaction mixture was stirred for 2 h at room temperature. Then, the mixture was diluted with chloroform, washed with water and brine, and evaporated. The crude product was purified by column chromatography to yield **6a** (410 mg, 85%) as a purple solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm)): 8.47 (s, 2H), 3.92 (m, 4H), 2.59 (d, J = 6 Hz, 4H), 1.84 (m, 2H), 1.72 (m, 2H), 1.36-1.22

(m, 32 H), 0.92-0.85 (m, 24H). ^{13}C NMR (150 MHz, CDCl$_3$) δ (ppm): 161.44, 143.08, 139.28, 135.89, 129.18, 116.72, 107.93, 45.89, 39.75, 39.06, 33.72, 32.46, 32.43, 31.95, 30.14, 29.68, 29.38, 28.73, 28.30, 25.69, 23.58, 23.06, 22.71, 14.14, 14.03, 10.78, 10.54. HRMS (APCI) calcd for C46H70Br2N2O2S2 $[M+H]^+$: 905.3318, found: 905.3318.

3,6-bis(5-bromo-4-cyclohexylthiophen-2-yl)-2,5-bis(2-butyloctyl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (6b). Yield: 83%. ^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm): 8.59 (s, 2H), 3.93 (d, J = 6 Hz, 4H), 2.74 (m, 2H), 1.91-1.86 (m, 10H), 1.77-1.75 (m, 2H), 1.57-1.22 (m, 42 H), 0.89-0.83 (m, 12H). ^{13}C NMR (150 MHz, CDCl$_3$) δ (ppm): 161.50, 148.58, 139.39, 133.57, 129.58, 115.14, 107.88, 46.03, 39.14, 37.71, 33.02, 31.79, 30.97, 30.71, 29.70, 28.30, 26.57, 26.08, 25.77, 23.10, 22.66, 14.10, 14.05. HRMS (APCI) calcd for C50H74Br2N2O2S2 $[M+H]^+$: 957.3631, found: 957.3620.

General procedure for the synthesis of polymers.

BDT (0.2 mmol), monomer **6** (0.2 mmol), $Pd_2(dba)_3$ (1.8 mg, 0.002 mmol) and $P(o\text{-tol})_3$ (3.6 mg, 0.012 mmol) were dissolved into 6 mL toluene in a 25 mL round bottom flask protected by argon. The flask was purged three times with successive vacuum and argon filling cycles. The oil bath was heated to 110 °C gradually, and the reaction mixture was stirred for 18 h at 110 °C under argon atmosphere. After cooling, the mixture was cooled to room temperature and precipitated in 200 mL methanol. The precipitate was filtered and washed with methanol and hexane successively in a soxhlet apparatus to remove oligomers and catalyst residue. Finally, the polymer was extracted with chloroform. The chloroform fraction was concentrated and precipitated in methanol. The precipitate was filtered and dried in vacuum at 40 °C overnight.

PDPP-EH, GPC: Mn= 158.7 kg mol^{-1}, PDI = 3.25, Td = 423 °C. ^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm): 9.11-8.80 (br, 2H), 7.80-6.92 (br, 6H), 4.03 (br, 4H), 2.87 (br, 8H), 1.80-0.79 (br, 90H).

PDPP-CH, GPC: Mn= 148.2 kg mol^{-1}, PDI = 2.62, Td = 403 °C. ^{1}H NMR (600 MHz, CDCl$_3$) δ (ppm): 8.94 (br, 2H), 7.80-6.93 (br, 6H), 4.04 (br, 4H), 3.13 (br, 4H), 2.88 (br, 4H), 1.88-0.71 (br, 94H).

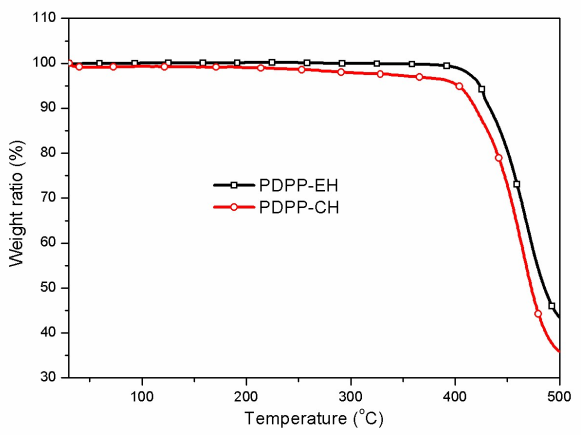
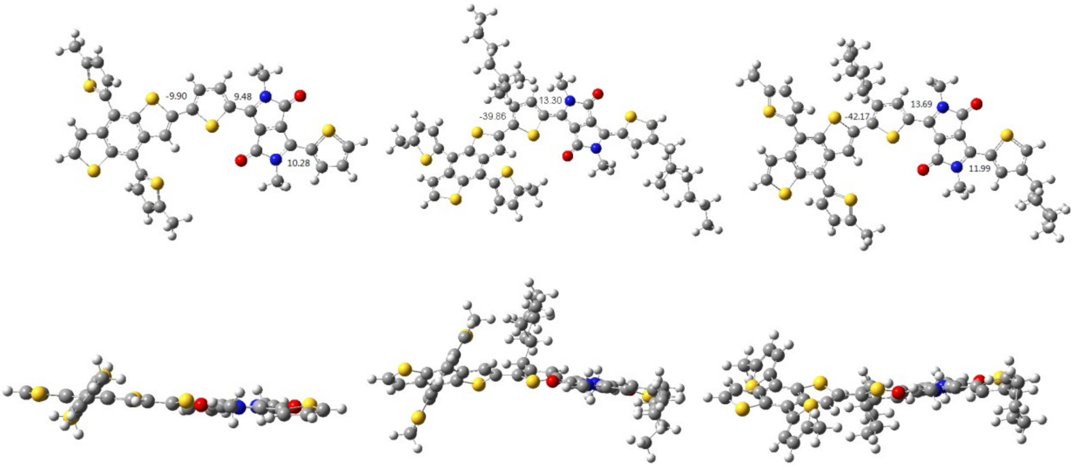


Figure S1. TGA curves of polymers PDPP-EH and PDPP-CH at a heating rate of 10 °C min^{-1} under nitrogen.



PBDTT-DPP PDPP-EH PDPP-CH

Figure S2. Gaussian-predicted (B3LYP/6-31G(d) Level) conformations of PBDTT-DPP, PDPP-EH and PDPP-CH in front view (top) and side view (bottom).

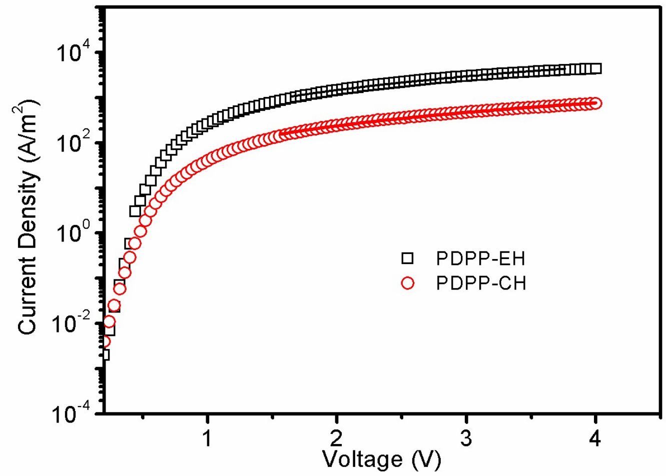


Figure S3. *J-V* curves of hole only devices with the structure of

ITO/PEDOT:PSS/polymr:PC$_{71}$BM/Au (the symbols are experimental data for transport of hole, and the lines are fitted according to the space-charge-limited-current model).

Table S1. Photovoltaic Parameters for Conventional Configuration Solar Cells with **PDPP-EH**:PC$_{71}$BM and **PDPP-CH**:PC$_{71}$BM as active layer.

polymer	PC$_{71}$BM *w/w ratio*	DIO	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)[a]
PDPP-EH	1:1	---	0.78	10.3	0.55	4.42 (4.27)
	1:2	---	0.75	15.1	0.64	7.25 (7.09)
	1:3	---	0.73	15.3	0.57	6.36 (6.20)
	1:2	1%	0.74	13.4	0.63	6.24 (6.13)
PDPP-CH	1:1	---	0.81	8.9	0.41	2.96 (2.85)
	1:2	---	0.76	14.6	0.60	6.66 (6.48)
	1:3	---	0.75	13.7	0.62	6.37 (6.16)
	1:2	0.5%	0.76	14.2	0.64	6.91 (6.73)
	1:2	1%	0.76	17.5	0.61	8.11 (8.01)
	1:2	2%	0.76	16.1	0.59	7.27 (7.13)
	1:2	3%	0.75	16.2	0.58	7.09 (6.92)

[a] Values in parentheses are average data from over 10 devices.

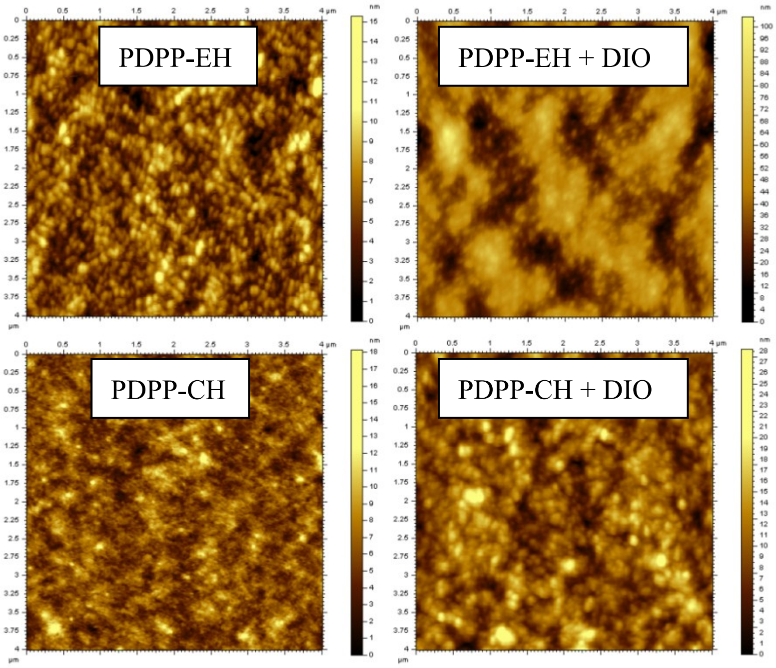


Figure S4. AFM topography images (4 × 4 μm) of blend films (polymer:PC$_{71}$BM in 1:2 weight ratio cast from *o*-dichlorobenzene solution) for PDPP-EH (top) and PDPP-

CH (bottom) without (left) and with (right) 1% DIO.

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