Supporting Information

Enhanced Solar Cell Performance by Replacing Benzodithiophene with Naphthodithiophene in Diketopyrrolopyrrole-Based Copolymers

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Synthetic Details:

Materials and Instruments:

All reagents were purchased from Aladdin Co., Alfa Aesar Co. and Aldrich Chemical Co. without further purification, unless stated otherwise. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance-400 spectrometer with d-chloroform as solvent and tetramethylsilane as internal standard. MALDI-TOF MS were obtained with a Bruker Autoflex spectrometer by using laser of 337 nm and potassium chloride or sodium chloride and 1,8,9-trihydroxyanthracene as ionizing and matrix reagents, respectively. High-resolution (HR) EI mass spectrum was recorded on Finnigan TSQ 7000 triple stage quadrupole mass spectrometer. Elemental analysis was performed by a Carlo Erba 116 Elemental Analyzer. Molecular weights of the copolymers were determined using Waters 1515 GPC analysis with THF as eluent and polystyrene as standard. UV-vis-NIR spectra were obtained on a Carry 5000 spectrophotometer. Thermogravimetric analysis (TGA) and Differential scanning calorimetry (DSC) measurements were conducted on a TA Instrument Model SDT Q600 simultaneous TGA/DSC analyzer at a heating rate of 10 ^{o}C min^{-1} and under a N_2 flow rate of 90 mL min^{-1}.

2,6-dibromo-1,5-didodecyloxynaphthalene (1): Under an argon atmosphere, a mixture of 2,6-dibromo-1,5-dihydroxynaphthalene (2.48 g, 7.86 mmol), 1-bromododecane (4.29 g, 17.29 mmol), K_2CO_3 (3.28 g, 23.8 mol), and 20 mL DMF was heated at 100 °C overnight. The mixture was filtered, and DMF was removed under a reduced pressure. The residue was then extracted with methylene chloride, and the solvent was evaporated. The crude product was purified by recrystallization from acetone to give compound 1 as a white crystal (4.45 g, 86.8%). ^{1}H NMR ($CDCl_3$, 400Hz, δ/ppm): 7.74 (d, 2H), 7.60 (d, 2H), 4.07 (t, 4H), 1.98-1.86 (m, 4H), 1.63-1.50 (m, 4H), 1.38- 1.24 (m, 32H), 0.88 (t, 6H). ^{13}C NMR ($CDCl_3$, 100MHz, δ/ppm): 152.9, 131.2, 130.3, 119.5, 113.9, 74.7, 32.1, 30.5, 29.9, 29.8, 29.8, 29.8, 29.7, 29.5, 26.2, 22.9, 14.3. HRMS calcd. for $C_{34}H_{54}Br_2O_2$ 652.2491; Found 652.2496.

2,6-bis(1',1'-diethoxy-2'-ethylthio)-1,5-didodecyloxynaphthalene (2): Under an argon atmosphere, the solution of compound 1 (4.24 g, 6.5 mmol) in 100 mL dry THF was cooled to -78 ^{o}C, and n-butyllithium (6.6 mL, 16.5mmol, 2.5M in hexane) was added. The mixture was then stirred at -78 ^{o}C for 2 h and then bis(2,2-diethoxyethyl) disulfide (5.25 g, 17.6 mmol) was added slowly by dropwise addition. After stirring for another 30 min, the reaction mixture was allowed to warm up to room temperature and stirred overnight. The reaction was subsequently quenched with water and extracted with ether. The combined organic layers were dried over $MgSO_4$ and evaporated. The residue was purified by column chromatography on silica gel eluting with ethyl acetate:hexane (1:49) to give compound 2 as a yellow oil (3.85 g, 75%). ^{1}H NMR ($CDCl_3$, 400Hz, δ/ppm): 7.78 (d, 2H), 7.48 (d, 2H), 4.66 (t, 2H), 3.98-3.52 (m, 12H), 3.22 (d, 4H), 1.78-1.18 (m, 52H) , 0.94 (t, 6H). ^{13}C NMR ($CDCl_3$, 100MHz, δ/ppm): 153.6, 128.2, 128.5, 125.2, 118.0, 102.3, 76.5, 62.4, 40.4, 36.6, 30.5, 29.1, 23.4, 23.3, 22.1, 15.6, 14.4, 13.6, 11.6, 10.7. HRMS calcd. for $C_{46}H_{80}O_6S_2$ 792.5396; Found 792.5401.

5,10-bis(dodecyloxy)naphtho[2,3-b:6,7-b']dithiophene (3): Under an argon atmosphere, a mixture of compound 2 (2.84 g, 3.59 mmol) in 500 mL dry methylene chloride was added dropwise into a refluxing solution of $BF_3{\cdot}OEt_2$ (1.0 mL, 8 mmol) in 1000 mL dry methylene chloride. The mixture was then refluxed overnight and poured into 800 mL saturated aqueous $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted with methylene chloride for three times. The combined organic layers were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography on silica gel eluting with ethyl acetate:hexane (1:199) to give compound 3 as a yellow solid (0.328 g, 15%). ^{1}H NMR ($CDCl_3$, 400Hz, δ/ppm): 8.49 (s, 2H), 7.48-7.39

(m, 4H), 4.12 (d, 4H), 1.88-1.16 (m, 40H), 0.92 (t, 6H). ^{13}C NMR ($CDCl_3$, 100MHz, δ/ppm): 150.2, 139.9, 128.2, 127.0, 124.6, 124.4, 111.3, 75.7, 40.6, 30.5, 29.2, 23.8, 23.2, 15.9, 14.3, 13.5, 11.4, 10.4. HRMS calcd. for $C_{38}H_{56}O_2S_2$ 608.3722; Found 608.3727.

2,7-di(tributyltin)-5,10-bis(dodecyloxy)naphtho[2,3-b:6,7-b']dithiophene (4): Under an argon atmosphere, compound 3 (3.36 g, 5.52 mmol) was dissolved in 15 mL dry THF was cooled to -78 ^{o}C, and n-butyllithium (5.54 mL, 13.84 mmol, 2.5M in hexane) was added by dropwise addition. The reaction mixture was stirred at -78 ^{o}C for 1 h and then brought to room temperature. The stirring was continued for another 20 min and the reaction mixture was cooled to -78 ^{o}C again. A solution of trimethyltin chloride (3.32 g, 16.62 mmol) was added by dropwise addition. The mixture was slowly brought to room temperature and stirred overnight. Water was subsequently added to the reaction mixture and the aqueous phase was extracted with dichloromethane for three times. The combined organic layers were dried over $MgSO_4$ and concentrated. The crude product was purified by recrystallization in ethanol to give monomer 4 as a yellow solid (3.77 g, 73%). ^{1}H NMR($CDCl_3$, 400Hz, δ/ppm): 8.46 (s, 2H), 7.53 (s, 2H), 4.28 (d, 4H), 1.86-1.38 (m, 40H), 0.95 (t, 6H), 0.50 (s, 18H). ^{13}C NMR ($CDCl_3$, 100MHz, δ/ppm): 149.7, 142.5, 141.3, 132.8, 130.2, 124.5, 109.8, 75.5, 40.6, 30.6, 29.3, 23.9, 23.2, 15.7, 14.2, 13.6, 11.4, 10.3. HRMS calcd. for $C_{44}H_{72}O_2S_2Sn_2$ 936.3018; Found 936.3011.

PBDTDPP: 3,6-bis(5-bromothiophen-2-yl)-2,5-dihexadecylpyrrolo[3,4-c]pyrrole-1,4-dione (271.3 mg, 0.3 mmol) and 2,6-di(trimethyltin)-4,8-bis(dodecyloxy)benzo[1,2-b:4,5-b′]dithiophene (265.9 mg, 0.3 mmol) were dissolved in 15 mL of toluene. The solution was flushed with argon for 10 min, and then Pd_2dba_3 (9.2 mg, 2 mol%) and P(o-tolyl)$_3$ (16.36 mg, 8%) were added into the flask. The flask was purged three times with successive vacuum and argon filling cycles. The polymerization reactant solution was heated to 110 °C, and the mixture was stirred for 48 h. 2-Trimethylstannyl thiophene (20 μL) was added to the reaction solution. After two hours, 2-bromothiophene (6.3 μL) was then added. The reactant was stirred overnight to complete the end-capping reaction. The mixture was cooled to room temperature and poured slowly in 350 mL of methanol. The precipitate was filtered and washed with methanol and hexane in a Soxhlet extraction apparatus to remove the oligomers and catalyst residues. Finally, the polymer was extracted with chloroform. The solution was concentrated by evaporation and precipitated into methanol again. The resulting polymer was collected as a dark purplish solid (421.5 mg, 92%). ^{1}H NMR ($CDCl_3$, 400Hz, δ/ppm): 8.99 (br, 2H), 7.72-7.18 (br, 4H), 4.22 (br, 4H), 3.75 (br, 4H), 1.97-0.72 (br, 108H). Anal. Calcd for $(C_{80}H_{122}N_2O_4S_4)_n$: C, 73.68; H, 9.43; N, 2.15. Found: C, 73.02; H, 9.56; N, 2.24. M_n = 45.2 kDa; PDI = 2.89.

PNDTDPP: PNDTDPP was synthesized from 3,6-bis(5-bromothiophen-2-yl)-2,5-dihexadecylpyrrolo[3,4-c]pyrrole-1,4-dione and monomers 4 as a dark purplish solid with a yield of 86% according to the method of PBDTDPP described above. ^{1}H NMR ($CDCl_3$, 400Hz, δ/ppm): 8.98 (br, 2H), 7.70-7.21 (br, 6H), 4.28 (br, 4H), 3.92 (br, 4H), 2.01-0.76 (br, 108H). Anal. Calcd for $(C_{84}H_{124}N_2O_4S_4)_n$: C, 74.39; H, 9.36; N, 2.07. Found: C, 73.71; H, 9.48; N, 2.13. M_n = 31.6 kDa; PDI = 2.55.

Cyclic Voltammetry (CV):

Cyclic voltammetry (CV) measurements were carried out on the CHI660 potentiostat/galvanostat electrochemical workstation at a scan rate of 50 mV s^{-1}, with a platinum wire counter electrode and an Ag/AgCl reference electrode in anhydrous nitrogen-saturated 0.1 mol L^{-1} acetonitrile (CH_3CN) solution of tetrabutylammonium perchlorate (Bu_4NClO_4). A Pt plate coated with thin film of the studied copolymer, a Pt wire and and an Ag/AgCl (0.1 M) were used as the work electrode, counter electrode and reference electrode, respectively. The energy level of the Ag/AgCl reference electrode was calibrated against the Fc/Fc^+ system to be 4.40 eV according to the previous methods.[1]

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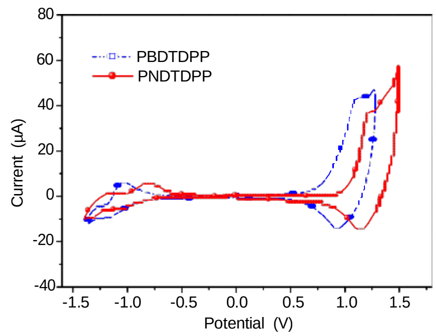

Figure S1. Cyclic voltammogram of PBDTDPP and PNDTDPP film in Bu_4NClO_4/CH_3CN solution.

X-ray Diffraction:

X-ray diffraction patterns of the polymers are recorded in Philips X-ray diffroctometer operated in reflection geometry at 30 mA, 40 kV with Cu-Kα radiation. The polymer films were spin-coated on silicon wafers from the 1,2-diclorobenzene solutions, followed by drying under vacuum.

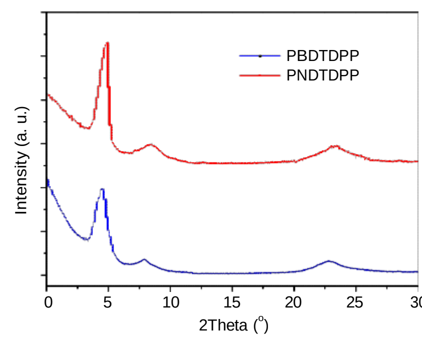

Figure S2. X-ray diffraction patterns of PBDTDPP and PNDTDPP films on silicon wafers.

Hole Mobility Measure (SCLC):

Hole-only devices, with a structure of ITO/PEDOT/polymer/MoO_3/Au, were fabricated to determine the hole mobilities using the space charge limited current (SCLC) method reported previously.[2] The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by the following equation:

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

where J is the current, μ_h is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the substrate's series resistance from the applied voltage (V_{appl}), $V=V_{appl} - V_{bi} - V_s$. The hole mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.

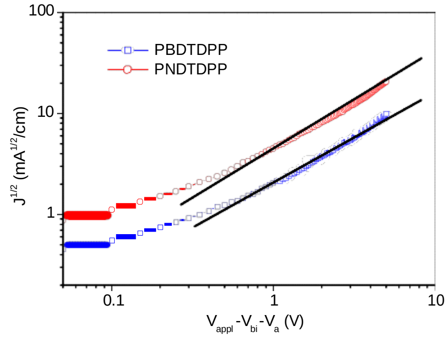

Figure S3. $J^{1/2}$-V characteristics of PBDTDPP and PNDTDPP hole-only devices measured at ambient temperature.

Atomic Force Microscopy (AFM):

The surface morphology of blended films of copolymer:$PC_{71}BM$ was studied by atom force microscopy (AFM) performed on a Nanoscope IIIa (Digital Instruments, CA) multimode AFM in the tapping mode.

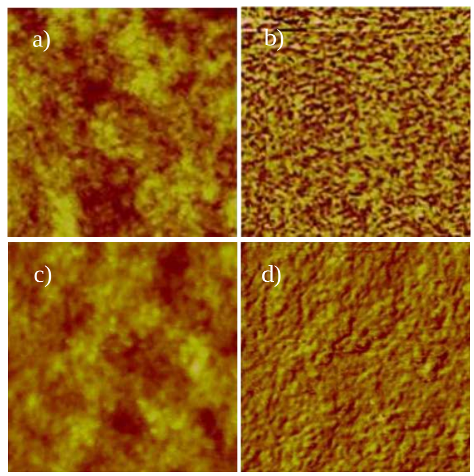

Figure S4. AFM height and phase topographic images of the PBDTDPP (a, b) and PNDTDPP (c, d) blend films (copolymer:$PC_{71}BM$ = 1:1.5, w/w). Image size: 2 µm × 2 µm.

Device fabrication:

Conventional polymer solar cells were fabricated with ITO glass as an anode, Ca/Al as a cathode, and blend film of the copolymer and $PC_{71}BM$ as a photosensitive layer. After spin-coating a 30 nm layer of PEDOT:PSS onto the pre-cleaned ITO substrate, the photosensitive layer (thickness for PDBTDPP: 90 nm; for PNBTDPP: 95 nm) was subsequently prepared by spin-coating a blend solution of the copolymer and $PC_{71}BM$ (w/w) in 1,2-dichlorobenzene on the ITO/PEDOT:PSS electrode with a typical concentration of 10 mg mL^{-1}. For the inverted devices, an about 40 nm ZnO thin film was deposited on the surface of ITO glass. The ZnO layer was pretreated with UV-ozone for 10 minutes and the conjugated polyelectrolyte of poly[(9,9-bis(3'-(N,N-dimethylamino)propyl)-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene)] dibromide (PNFBr) was spin-coated on the top of ZnO layer. The photoactive layer of PNDTDPP:$PC_{71}BM$ composite (1:1.5; 120 nm) was then spin-coated on the top of above layer from 1,2-dichlorobenzene solution. The photoactive layer was then thermally annealed at 110 ^{o}C for 10 minutes. Subsequently, about 10 nm MoO_3 and 100 nm Ag were deposited in turn through shadow masks by thermal evaporation. The device area was 0.09 cm^2. The current–voltage (I–V) characterization of the devices was carried out on a computer-controlled Keithley 236 Source Measurement system. A solar simulator

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was used as the light source, and the light intensity was monitored by a standard Si solar cell. The thickness of films was measured using a Dektak 6 M surface profilometer.

Table S1. Photovoltaic properties of PBDTDPP and PNDTDPP-based solar cell devices with copolymer/ $PC_{71}BM$ (1:1.5, w/w) blends.

Polymer	Device	Thickness [nm]	J_{sc} [$mAcm^{-2}$]	V_{oc} [V]	FF	PCE_{max} [%]	J_{sc} (calc.) [$mAcm^{-2}$]
PBDTDPP	Conventional	90	8.63	0.67	0.50	2.91	8.49
PNDTDPP	Conventional	95	11.89	0.77	0.59	5.37	11.55
PNDTDPP	Inverted	120	13.34	0.76	0.68	6.92	12.86

References:

1 Y. F. Li, Y. Cao, J. Gao, D. L. Wang, G. Yu, A. J. Heeger, Synth. Met. 1999, 99, 243.

2 V. Shrotriya, Y. Yao, G. Li, Y. Yang, Appl. Phys. Lett. 2006, 89, 063505.