Supplementary Information of

Toward Green Solvent Processable Photovoltaic Materials for Polymer Solar Cells: The Role of Highly Polar Pendant Groups on Charge Carrier Transport and Photovoltaic Behavior

Chunhui Duan,[a] Wanzhu Cai,[a] Ben B.Y. Hsu,[b] Chengmei Zhong,[ab] Kai Zhang,[a] Chunchen Liu,[a] Zhicheng Hu,[a] Fei Huang,*[b] Guillermo C. Bazan,[ab] Alan J. Heeger,[b] Yong Cao*[a]

[†]Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, P. R. China

[‡]Center for Polymers and Organic Solids, University of California at Santa Barbara, Santa Barbara, California 93106-5090, USA

Experimental section

Instruments and Measurements. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AV-300 spectrometer operating at 300 or 75 MHz, respectively in appropriated deuterated solution at room temperature, unless specified otherwise. Chemical shifts were reported as δ values (ppm) relative to an internal tetramethylsilane (TMS) standard. Mass spectrometry (MS) data of C_{70} fullerene-derived compounds **11**, **12** and **PC$_{71}$BM-N** were collected with fast atom bombardment (FAB) MS on a MAT

95XP (Thermo). The remaining MS data were obtained on a Bruker Esquire HCT PLUS with atmospheric pressure chemical ionization resource (APCI). Number-average (M_n), weight-average molecular weights (M_w) and polydispersity index (PDI) of polymers were determined by gel permeation chromatography (GPC) using a series of mono-disperse polystyrene as standards in chloroform (with 0.25 v/v% triethylamine) on a Water system at room temperature. Differential scan calorimetry (DSC) analyses were performed on a Netzsch DSC 204. Glass transition temperatures (T_g) were measured at heating and cooling rates of 10 °C /min under a nitrogen flow. UV-vis absorption spectra were recorded on an HP 8453 spectrophotometer. Photoluminescent (PL) spectra were recorded on a Jobin Yvon Fluorolog-3 spectrophotometer. Cyclic voltammetry (CV) was performed on a CHI800C electrochemical workstation with a platinum working electrode and a platinum wire counter electrode at a scan rate of 30 mV s^{-1} against a Ag/Ag^+ (0.1 M of $AgNO_3$ in acetonitrile) reference electrode with an argon-saturated anhydrous solution of 0.1 mol L^{-1} tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in acetonitrile. The films of the samples for electrochemical measurements were coated from their dilute solution. Electrochemical onsets were determined at the position where the current starts to differ from the baseline.

Materials. All starting organic compounds and chemical reagents were purchased from Aladdin Reagent Inc, Alfa Aesar, Aldrich, or Acros Organics and used without further purification. Some solvents (tetrahydrofuran (THF), toluene, dichloromethane, acetonitrile, *N,N*-dimethylformamide (DMF) and pyridine) for reactions were purified by normal procedures prior to use. All reactions were carried out under argon at 1 atmosphere unless otherwise mentioned. Column chromatography was carried out on silica gel (200～300 mesh). 2,7-Dibromo-9-*H*-carbazole,[1] 4,7-di(2'-bromothien-5'-yl)-2,1,3-benzothiadiazole (**9**),[2] and 4-(*p*-cresoxylbutyl)-benzoyl *p*-tosylhydrazone (**10**)[3] were synthesized according the methods reported in literatures. All other compounds were synthesized following procedures described below.

*Synthesis of p-tolyoxyhexyl bromide (**2**).* In a three-necked 500 mL round-bottom flask, K_2CO_3 (60 g, 434 mmol) and tetrabutylammonium bromide (3.8 g, 11.8 mmol) were added into a mixture of *p*-cresol (20 g, 259 mmol) and 1,6-dibromohexane (220 mL) in acetone (150 mL) under an argon atmosphere. The reaction was heated to reflux for 48 hours with vigorous stirring. After cooling to room temperature, the solid were separated by filtration. The filtrate was concentrated in rotary evaporator, and then was distilled in vacuum to yield colorless oil (53.5 g, 197 mmol, 76%). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.09-7.06 (d, J=8.0 Hz, 2H), 6.81-6.78 (d, J=8.3 Hz, 2H), 3.96-3.92 (t, J=6.4 Hz, 2H), 3.45-3.41 (t, J=6.8 Hz, 2H), 2.29 (s, 3H), 1.92-1.85 (m, 2H), 1.81-1.75 (m, 2H), 1.50-1.49 (m, 4H). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 156.95, 129.85, 129.75, 114.40, 67.80, 33.73, 32.71, 29.16, 27.94, 25.32, 20.44. **MS (APCI)** *m/z*, calculated for $C_{13}H_{19}BrO$ (M^+): 271.19; found: 271.1.

*Synthesis of 1,13-bis(p-tolyoxy)tridecan-7-ol (**3**).* In a three-necked 100 mL round-bottom flask, magnesium chips (1.44 g, 60 mmol) was added into a solution of compound **2** (16.2 g, 60 mmol) in 60 mL of THF under an argon atmosphere. The reaction was initiated by slow heating. After stirring for 3 hours under reflux, the resulted *p*-tolyoxyhexylmagnesium bromide solution was cooled to room temperature. In another three-necked 250 mL round-bottom flask equipped with a pressure-equalizing dropping funnel, ethyl formate (1.48 g, 20 mmol) was added into 100 mL of THF and cooled to -78 °C under an argon atmosphere. The fresh *p*-tolyoxyhexylmagnesium bromide solution was transferred into the pressure-equalizing dropping funnel by a syringe and was then added dropwise into the reaction. After the completion of the addition, the reaction was allowed to warm to room temperature with stirring overnight. The reaction was quenched by the addition of methanol and saturated aqueous NH_4Cl. This mixture was extracted with dichloromethane. The combined organic phase was then washed with brine and dried over anhydrous $MgSO_4$. After removing the solvent under reduced pressure, the crude product was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 20/1) to afford a white solid (6.8 g, 16.4 mmol, 82%). ^{1}H-NMR (300 MHz, $CDCl_3$), δ(ppm): 7.09-7.06 (d, J=8.6 Hz, 4H), 6.82-6.79 (d, J=6.7 Hz, 4H), 3.95-3.91 (t, J=6.5 Hz, 4H), 3.60 (br, 1H), 2.29 (s, 6H), 1.80-1.73 (m, 4H), 1.50-1.38 (m, 16H). ^{13}C-NMR(75 MHz, $CDCl_3$), δ(ppm): 157.00, 129.84, 129.66, 114.40, 71.91, 68.00, 37.42, 29.44, 29.28, 26.05, 25.57, 20.43. **MS (APCI)** *m/z*, calculated for $C_{27}H_{40}O_3$ (M^+): 412.60; found: 413.5.

*Synthesis of 1,13-bis(p-tolyloxy)tridecan-7-yl-4-methylbenzenesulfonate (**4**).* To a stirred solution of compound **3** (6.0 g, 14.6 mmol), triethylamine (5 mL) and trimethylamine hydrochloride (1.38 g, 14.6 mmol) in dichloromethane (30 mL) in a three-necked 100 mL round-bottom flask under ice-water bath, *p*-toluenesulfonyl chloride (4.16 g, 21.8 mmol) solution in 30 mL of dichloromethane was added dropwise through a pressure-equalizing dropping funnel. After the addition, the reaction was allowed to warm to room temperature and stirred for 90 min. Then, water was added, and the mixture was extracted with dichloromethane for three times. The combined organic phase was washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated under rotary evaporator. The crude product was subjected to silica gel column and eluted with petroleum ether/dichloromethane (3/1) to give white solid (6.5 g, 11.5 mmol, 79%). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.81-7.78 (d, J=8.3 Hz, 2H), 7.33-7.30 (d, J=8.4 Hz, 2H), 7.10-7.07 (d, J=8.6 Hz, 4H), 6.81-6.78 (d, J=8.6 Hz, 4H), 4.57-4.53 (m, 1H), 3.92-3.90 (d, J=6.5 Hz, 4H), 2.42 (s, 3H), 2.29 (s, 6H), 1.75-1.66 (m, 4H), 1.61-1.57 (m, 4H), 1.38-1.26 (m, 12H). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 156.94, 144.40, 134.70, 129.87, 129.71, 129.67, 127.72, 114.32, 84.37, 67.85, 34.09, 29.16, 29.05, 25.86, 24.64, 21.61, 20.48. **MS (APCI)** *m/z*, calculated for $C_{34}H_{46}O_5S$ (M^+): 566.79; found: 567.4.

*Synthesis of N-7'-[(1',13'-bis(p-tolyoxy)tridecanyl)]-2,7-dibromocarbazole (**5**).* In a three-necked 250 mL round-bottom flask equipped with an pressure-equalizing dropping funnel was charged with 2,7-dibromo-9-*H*-carbazole (6.5 g, 20 mmol), 30 mL of dimethyl sulfoxide (DMSO), and freshly powdered potassium hydroxide (5.6 g, 100 mmol). After the complete dissolution of 2,7-dibromo-9-*H*-carbazole, a solution of compound **4** (17.0 g, 30.0 mmol) in 50 mL of DMSO was added dropwise over 1.5-2 hours at room temperature. After 6 hours, the reaction was poured into 300 mL of water, and the aqueous layer was extracted with dichloromethane for three times. The combined organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed under rotary evaporator. The crude product was subjected to silica gel column and eluted with petroleum ether to yield a colorless sticky oil (11.1 g, 15.4 mmol, 77%). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.90-7.85 (m, 2H), 7.69 (s, 1H), 7.52 (s, 1H), 7.32 (m, 2H),7.04-7.02 (d, J=8.6 Hz, 4H), 6.74-6.72 (d, J=8.6 Hz, 4H) 4.41-4.39 (m, 1H), 3.82-3.79 (t, J=6.5 Hz, 4H), 2.26 (s, 6H), 1.91-1.90 (m, 2H), 1.63-1.60 (m, 4H), 1.29-1.22 (m, 10H), 0.99 (m, 2H), 0.88-0.85 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 156.92, 129.81, 129.65, 122.44, 121.53, 121.29, 119.82, 119.23, 114.37, 112.08, 68.04, 67.81, 56.99, 33.44, 29.12, 29.04, 26.70, 25.78, 20.44. **MS (APCI)** *m/z*, calculated for $C_{39}H_{45}Br_2NO_2$ (M^+): 719.59; found: 720.4.

*Synthesis of N-7'-(1',13'-dibromo)tridecanyl-2,7-dibromocarbazole (**6**).* To a three-necked 250 mL round-bottom flask, compound **5** (11 g, 15.2 mmol), hydrobromic acid (60 mL, 47%) and glacial acetic acid (180 mL) were added under an argon atmosphere. The mixture was heated to refluxing and stirred for 48 hours. After cooling to room temperature, the reaction was poured into 300 mL of water, and extracted with dichloromethane for three times. The combined organic fractions were washed with water and then aqueous potassium carbonate, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using petroleum ether as eluent to give a white solid (7.7 g, 11.6 mmol, 76%). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.93-7.88 (t, J= 8.6 Hz, 2H), 7.68 (s, 1H), 7.53 (s, 1H), 7.35-7.33 (br, 2H), 4.44-4.40 (m, 1H), 3.33-3.28 (t, J=6.8 Hz, 4H), 2.25-2.18 (m, 2H), 1.97-1.87 (m, 2H), 1.76-1.66 (m, 4H), 1.31-1.19 (m, 10H), 1.04-0.93 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 142.85, 122.50, 121.59, 121.34, 120.86, 119.86, 119.26, 114.42, 112.04, 56.83, 33.79, 33.33, 32.49, 28.37, 27.79, 26.52. (Multiple carbon peaks are due to the phenomenon of atropisomerism).[4-7] **MS (APCI)** *m/z*, calculated for $C_{25}H_{31}Br_4N$ (M^+): 665.14; found: 666.2.

Synthesis of N-7'-[(1',13'-bis(N,N-diethylamino)tridecanyl]-2,7-dibromocarbazole (7). To a stirred mixture of compound **6** (15 g, 22.6 mmol) in 100 mL of DMF under an argon atmosphere, 20 mL of diethylamine was added in one portion. The reaction was refluxed with vigorous stirring for 6 hours. After cooling to room temperature, the reaction was poured into ice water, extracted with dichloromethane for three times. The combined organic fractions were washed with water and brine, dried over anhydrous $MgSO_4$, concentrated under reduced pressure. The crude product was purified by silica gel column chromatography using petroleum ether/triethylamine as eluent to afford a light yellow sticky oil (12.5 g, 19.2 mmol, 86%). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.92-7.86 (t, J=8.7 Hz, 2H), 7.68 (s, 1H), 7.52 (s, 1H), 7.33-7.31 (br, 2H), 4.42-4.39 (m, 1H), 2.49-2.42 (q, J=7.2 Hz, 8H), 2.32-2.28 (t, J= 7.5 Hz, 4H), 2.27-2.15 (m, 2H), 1.93-1.85 (m, 2H), 1.35-1.07 (m, 14 H), 0.99-0.92 (t, J=6.4 Hz, 14 H). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 142.87, 139.40, 122.36, 121.48, 121.24, 120.85, 119.78, 119.19, 114.48, 112.11, 56.95, 52.78, 46.81, 33.45, 29.23, 27.36, 26.76, 26.71, 11.57. (Multiple carbon peaks are due to the phenomenon of atropisomerism).[4-7] **MS (APCI)** *m/z*, calculated for $C_{33}H_{51}Br_2N_3$ (M^+): 649.59; found: 650.5.

*Synthesis of 2,7-bis(4',4',5',5'-tetramethyl-1',3',2'-dioxaborolan-2'-yl)-N-7"-[(1",13"-bis(N",N"-diethylamino)tridecanyl]-carbazole (**8**)*. To a solution of compound **7** (3.25 g, 5 mmol) in 50 mL of anhydrous THF at -78 °C under argon, 5 mL (12.5 mmol) of *n*-butyllithium (2.5 M in hexane) was added dropwise and the mixture was stirred at -78 °C for 2 hours. Subsequently, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5 mL, 20 mmol) was added to the solution in one shot. The reaction was allowed to warm to room temperature and was stirred overnight. The mixture was poured into water and extracted with petroleum ether for three times. The combined organic extract was washed with water and brine, dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by recrystallization from acetonitrile several times to afford colorless needles (2.7 g, 3.7 mmol, 73%). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 8.14-8.09 (t, J=8.1 Hz, 2H), 8.01 (s, 1H), 7.87 (s, 1H), 7.67-7.65 (d, J= 7.6 Hz, 2H), 4.70-4.66 (m, 1H), 2.47-2.40 (q, J=7.2 Hz, 8H), 2.35-2.25 (m, 6H), 1.99-1.90 (m, 2H), 1.39 (s, 24H), 1.34-1.24 (m, 10H), 1.16-1.08 (m, 4H), 0.98-0.94 (t, J=6.4 Hz, 14H). ^{13}C-NMR (75 MHz, $CDCl_3$), δ (ppm): 141.97, 126.08, 124.66, 120.00, 119.71, 118.02, 115.36, 83.69, 56.47, 52.78, 46.81, 33.82, 29.40, 27.38, 26.79, 26.65, 24.94, 11.52. **MS (APCI)** *m/z*, calculated for $C_{45}H_{75}B_2N_3O_4$ (M^+): 743.72; found: 744.7.

Synthesis of

*poly{N-7'-[(1',13'-bis(N',N'-diethylamino)tridecanyl]-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)} (**PCDTBT-N**).* In a two-necked 25 mL round-bottom flask, diboronic ester monomer 8 (371.5 mg, 0.5 mmol), dibromide monomer 4,7-di(2'-bromothien-5-yl)-2,1,3-benzothiadiazole (229 mg, 0.5 mmol), 5 mg of $Pd(PPh_3)_4$, and three drops of Aliquat 336 were dissolved in 10 mL of degassed toluene and 2 mL of aqueous sodium carbonate (2.0 M). The reaction was vigorously stirred at 90-95 °C. After about 2 hours, the mixture became very viscous and 3 mL of anhydrous THF was added. After another 4 hours, 1 mL of phenylboronic acid solution (0.5 M in anhydrous THF) was added to the reaction then 2 hours later, 0.5 mL of bromobenzene was added and the reaction refluxed for another 2 hours to complete the end-capping reaction. After cooling to room temperature, the resulting mixture was precipitated in methanol. The precipitated material was collected by filtration through a funnel. The resulting material was washed on a Soxhlet apparatus with acetone, dichloromethane and chloroform, successively. The chloroform fraction was concentrated to about 30 mL under reduced pressure, then filtered through 0.45 μm PTFE filter, and precipitated from methanol, collected and finally dried overnight to yield a purple solid (327 mg, 83%). ^{1}H-NMR (300 MHz, $CDCl_3$), δ (ppm): 7.88-7.51 (m, 12H), 4.70 (br, 1H), 2.47-2.34 (m, 12H), 1.25-0.83 (m, 32H). GPC (chloroform, polystyrene standard): $M_n = 18$ kg mol^{-1}, PDI = 2.5.

*Synthesis of 5-phenyl-5-[(6',6')-C_{71}-pentyl] p-tolyl ether (**11**).* To a 100 mL two-necked round-bottom flask, compound **10** (700 mg, 1.6 mmol), sodium methoxide (90 mg, 1.67 mmol), and anhydrous pyridine (10 mL) were added under an argon atmosphere. The mixture was stirred at room temperature for 30 min. To the mixture, a solution of C_{70} (1.26 g, 1.5 mmol) in *o*-DCB (50 mL) was added, and the reaction was stirred at 75 °C under argon overnight. Afterward, the reaction was further heated, and the reaction was allowed to be stirred for 24 hour under refluxing. After cooling to room temperature, the reaction was mixture was precipitated from methanol. The resulting precipitates were dissolved in toluene and reabsorbed on silica gel. The unreacted C_{70} and (6,6)-phenyl-C_{71}-pentyl *p*-tolyl ether were separated by column chromatography (silica gel, petroleum ether/toluene (5/1)). The title compound 11 was precipitated from methanol, centrifuged, and decanted. The product was treated with the same manner for several times to afford a brown solid (573 mg, 0.525 mmol, 35%). ^{1}H-NMR ($CDCl_3$, 300 MHz), δ (ppm): 7.92-7.78 (m, 2H), 7.56-7.41 (m, 3H), 7.06-7.01 (m, 2H), 6.82-6.73 (m, 2H), 4.02-3.90 (m, 2H), 2.48-2.36 (m, 2H), 2.31-2.23 (m, 3H), 2.00-1.92 (m, 4H). **MS (FAB)** *m/z*, calculated for $C_{88}H_{20}O$ (M^+): 1093.10; found: 1092.

Synthesis of 5-phenyl-5-[(6',6')-C_{71}-pentyl] bromide ***(12)***. To a solution of compound **11** (500 mg, 0.458 mmol) in *o*-DCB (40 mL) at 0 °C was added BBr_3 (3 mL) dropwise under argon atmosphere. The reaction mixture was slowly warmed to room temperature and kept stirred for 4 h. Then, water was added to quench the reaction. After washing with water for several times, the separated organic phase was precipitated from methanol. The collected precipitate was purified using column chromatography (silica gel, petroleum ether/toluene (5/1)). The solution of pure title compound **12** was concentrated and precipitated from methanol to yield a brown solid

(473 mg, 97%). ^{1}H-NMR (CDCl$_3$, 300 MHz), δ (ppm): 7.92-7.77 (m, 2H), 7.61-7.40 (m, 3H), 3.51-3.20 (m, 2H), 2.46-2.36 (m, 2H), 2.11-1.96 (m, 4H). **MS (FAB)** *m/z*, calculated for $C_{81}H_{13}Br$ (M^+): 1065.87; found: 1066.

*Synthesis of N,N-diethyl-5-phenyl-5-[(6',6')-C$_{71}$-pentyl]-1-amine (**PC$_{71}$BM-N**).* To a stirred mixture of compound **12** (200 mg, 0.188 mmol) in 15 mL of *o*-DCB under an argon atmosphere, 3 mL of diethylamine was added in one portion. The reaction was stirred at 110 °C overnight. After cooling to room temperature, the mixture was precipitated from petroleum ether. The resulting precipitates were dissolved in toluene and reabsorbed on silica gel. The title compound was separated by column chromatography (silica gel, toluene/triethylamine (20/1)) to afford a brown solid (145 mg, 0.137 mmol, 73%). ^{1}H-NMR (CDCl$_3$, 300 MHz), δ (ppm): 7.88-7.75 (m, 2H), 7.50-7.43 (m, 3H), 2.71 (m, 6H), 2.43 (m, 2H), 1.99 (m, 4H), 1.11-1.02 (m, 6H). **MS (FAB)** *m/z*, calculated for $C_{85}H_{23}N$ (M^+): 1058.10; found: 1058.

Polymer Solar Cells Fabrication and Characterization. Poly[*N*-9'-heptadecanyl-2,7-carbazole-*alt*-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) was purchased from 1-material Chemscitech Inc. PC$_{71}$BM was purchased from Sigma-Aldrich. They were all used as received. Tin-doped indium oxide (ITO) coated glass substrates (15 Ω per square) were cleaned by sonication in acetone, detergent, de-ionized water and isopropyl alcohol. Subsequently, the substrate were dried under 80 °C in baking oven, followed by a 5 minutes oxygen plasma treatment. The device structure was ITO/poly(3,4-ethylenedioxythiophene): poly(styrene sulfonate) (PEDOT:PSS)(40nm)/photoactive layer/aluminum (Al). The

PCDTBT-N:$PC_{71}BM$-N (1:4) active layer with thickness of ~80 nm was spin-cast from *n*-butanol:acetic acid and 1,2-dichlorobenzene:chlorobenzene (3:1), respectively. The polymer concentration in *n*-butanol is 3.5 mg mL^{-1}, whereas it is 5.6 mg mL^{-1} in 1,2-dichlorobenzene:chlorobenzene solution. The PCDTBT:$PC_{71}BM$(1:4) film was spin-cast from a mixture of a 1,2-dichlorobenzene:chlorobenzene (3:1) with polymer concentration of 5.6 mg mL^{-1}. Thickness of PCDTBT:$PC_{71}BM$ film was also ~80 nm. And the doped films were processed under the identical conditions as PCDTBT:$PC_{71}BM$ film. The concentration of PCDTBT-N was defined as the ratio of PCDTBT-N mass to total donor mass, the concentration of $PC_{71}BM$-N is the ratio of $PC_{71}BM$-N mass to total acceptor mass. When PCDTBT-N and $PC_{71}BM$-N were used as interlayer material, they were dissolved in methanol and *n*-butanol, respectively, under the presence of a trace amount of acetic acid. The concentration of PCDTBT-N and $PC_{71}BM$-N were 0.5 and 0.25 mg mL^{-1}, respectively. Then solutions were spin-cast on top of BHJ layer at 2 000 rpm for 30 seconds. Control devices to probe the solvent effect were washed with methanol and *n*-butanol, respectively, under the existence of acetic acid by spin-coating at the same spin rate. Finally, the Al cathode (100 nm) was deposited by thermal evaporation under a vacuum of about 2×10^{-6} mbar. The active area of the device was 0.16 cm^2 defined by a shadow mask. Current density–voltage (*J–V*) measurements on solar cells were carried out with a Keithley 2400 source meter. For evaluating the photovoltaic performance of devices, the photocurrent was measured under AM 1.5G illumination at 100mW cm^{-2} with a solar simulator (Oriel model 91192). The light intensity was calibrated using an National

Renewable Energy Laboratory (NREL) calibrated silicon photodiode with a KG5 filter.

Hole/Electron-only Devices Fabrication and Mobility Measurement. Hole only current has been tested in device with a structure of ITO/PEDOT:PSS/active layer/MoO_3 (10nm)/Al. The processing condition of active layer was identical with those of solar cells. MoO_3 film was thermally evaporated onto active layer at a rate of 0.1 Å s^{-1} under a pressure of 3×10^{-6} mbar. Electron only current has been tested in device with a structure of ITO/Al (30nm)/active layer/Ca (5nm)/Al. The mobilities of pristine material were determined by fitting the *J-V* curve of hole/electron-only devices to the model of trap-free space charge-limited conduction, which described as[8,9]

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_0\frac{V^2}{L^3}$$

where J is the current density, μ_0 is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, L is the thickness of the active layer, and V is the effective voltage. The effective voltage was achieved by subtracting the built-in voltage (V_{bi}) and the voltage dropped on series resistance (V_{rs}) from applied voltage. For hole-only device, V_{bi} is 0.1V, whereas for electron-only device, V_{bi} takes the value of 0.0. The substrate's series resistance is ~10 Ω for hole-only device, and 0.1 Ω for electron-only device. In every simulation, ε_r was assumed to be 3, which is a typical value for organic materials. The thickness of devices equaled to 80 nm.

Organic Field-Effect Transistor Fabrications and Characterization

A bottom-gate top-contact architecture was applied for OFET measurements. The substrates were heavily doped n-type silicon wafers with 200 nm thermally grown SiO_2. A 30-nm-thick polypropylene-co-1-butene (PPCB) polymer layer was spun on the SiO_2 dielectric by 6000 rpm for 30 sec to passivate the electron traps. The active layer was spin-cast on top of the PPCB layer at 2000 rpm for 50 sec. Silver (Ag) source/drain electrodes were deposited by thermal evaporation through a silicon shadow mask. The channel length and width are 20 μm and 1 mm. FETs were tested in inner nitrogen environment with oxygen level less than 2 ppm. All the FET data were obtained by a Keithley 4200 system.

The transfer characteristics of the pristine materials are shown in Figure S3. Gate voltage (V_G) was swept from 0 to -100 V with constant source-drain voltage (V_{DS}) = -100 V for p-type operation and V_G was scanned from 0 to 100 V with V_{DS}= 100 V for n-type operation. The *I-V* profiles show obvious hole-dominated transport in the PCDTBT but holes are totally suppressed in the PCDTBT-N and only small electron transport is sustained in both PCDTBT and PCDTBT-N. $PC_{71}BM$ demonstrates much higher electron current than $PC_{71}BM$-N.

In the BHJ blends, the amino groups decrease not only hole current about two orders of magnitude but electron current about one order of magnitude as shown in Figure S4. The film quality in the BHJ blends with amino groups was generally poor, showing no obvious hole transport and very limited electron current.

Ultraviolet Photoelectron Spectroscopy (UPS) Measurements. The UPS measurements were taken on a Kratos Axis Ultra X-ray Photoelectron Spectroscopy system (Kratos Analytical Ltd, UK) using a He I UV light source (21.2 eV) with a maximum energy resolution of 0.025 eV. 10 V of bias voltage was applied on the samples during the UPS measurement. The absolute value of kinetic energy of the photoelectrons was calibrated by measuring the Fermi edge of a silver thin-film whose surface is dry-etched by Ar ion beam.

Numerical Simulations of Polymer Solar Cell (PSC) Device Performance. The simulations of PSC device photo current density-voltage (*J-V*) curves were done by first getting the one dimensional spatial distribution of electron density (n), hole density (p) and electric potential (u) inside the active layer under different bias voltages (*V*) and light intensities (*G*) through numerically solving the coupled partial differential equation set consisting of electron/hole drift-diffusion equations and the Poisson's equation:

$$k_B T\mu_n \frac{\partial^2}{\partial x^2} n(x) + q\mu_n \frac{\partial}{\partial x} n(x) \frac{\partial}{\partial x} u(x) + G - \gamma[n(x)p(x) - n_i^{\,2}] = 0$$

$$k_B T\mu_p \frac{\partial^2}{\partial x^2} p(x) + q\mu_p \frac{\partial}{\partial x} p(x) \frac{\partial}{\partial x} u(x) + G - \gamma[n(x)p(x) - n_i^{\,2}] = 0.$$

$$\frac{\partial^2}{\partial x^2} u(x) = \frac{q}{\varepsilon_0 \varepsilon_r}[n(x) - P_t(x) - p(x)]$$

The boundary conditions for the equation set is:

$$n(x=0) = n_0; n(x=d) = \frac{n_i^{\,2}}{p_0}$$

$$p(x=0) = \frac{n_i^{\,2}}{p_0}; n(x=d) = p_0$$

$$u(x=0) = V_{bi} - V; u(x=d) = 0$$

k_B is the Boltzmann constant, ε_0 is the vacuum permittivity and q is the elemental charge. The meaning of the other symbols in the equation set and the values used in the simulations are listed in Table S1. P_t is the hole trap concentration distribution inside the active layer. The hole traps are considered as immobile holes inside the device. Once the n,p and u are solved, the output current J of the PSC device can then be calculated using the following equations for a given V:

$$J = J_n(x=0) - J_p(x=0)$$

$$J_n(x) = k_B T \mu_n \frac{\partial}{\partial x} n(x) + q\mu_n n(x) \frac{\partial}{\partial x} u(x)$$

$$J_p(x) = k_B T \mu_p \frac{\partial}{\partial x} p(x) + q\mu_p p(x) \frac{\partial}{\partial x} u(x)$$

Table S1. Input parameters for the *J–V* characteristics simulation of the OPV devices

Relative dielectric constant ε_r	3.4
Electron/Hole mobility μ_n/μ_p ($cm^2V^{-1}s^{-1}$)	1×10^{-4}/ 1×10^{-4}
Intrinsic electron/hole density n_i (m^{-3})	5.6×10^{15}
Active layer thickness d (nm)	80
Electron/Hole Concentration at Cathode/Anode n_0/p_0 (m^{-3})	1×10^{23} / 1×10^{23}
Charge pair generation rate G (m^{-3} s^{-1})	8×10^{27}
Built-in voltage V_{bi} (V)	1.1
Bimolecular recombination rate γ ($m^{-3}s^{-1}$)	$q\ (\mu_n+\ \mu_p)/(\varepsilon_0\varepsilon_r)$
Temperature T (K)	300

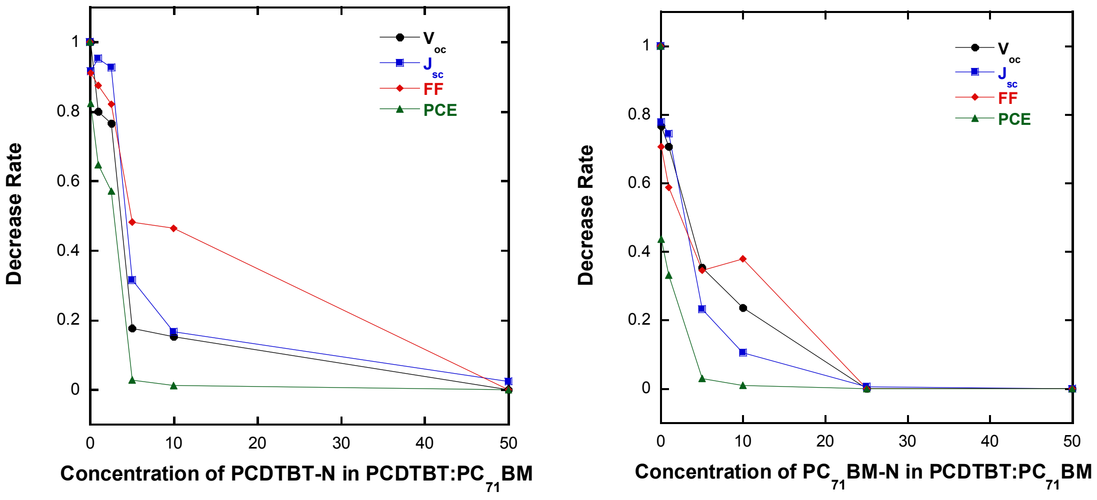

Figure S1. Photovoltaic parameters of devices based on PCDTBT:PC$_{71}$BM with different dopant concentrations from 0.1% to 50 %. Dopant is PCDTBT-N (a) and $PC_{71}BM$-N (b), respectively.

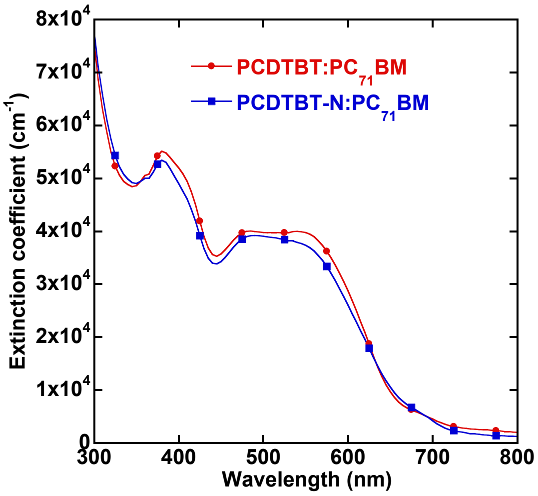

Figure S2. Film absorption spectra comparison of PCDTBT:$PC_{71}BM$ (1:4) and PCDTBT-N:$PC_{71}BM$ (1:4).

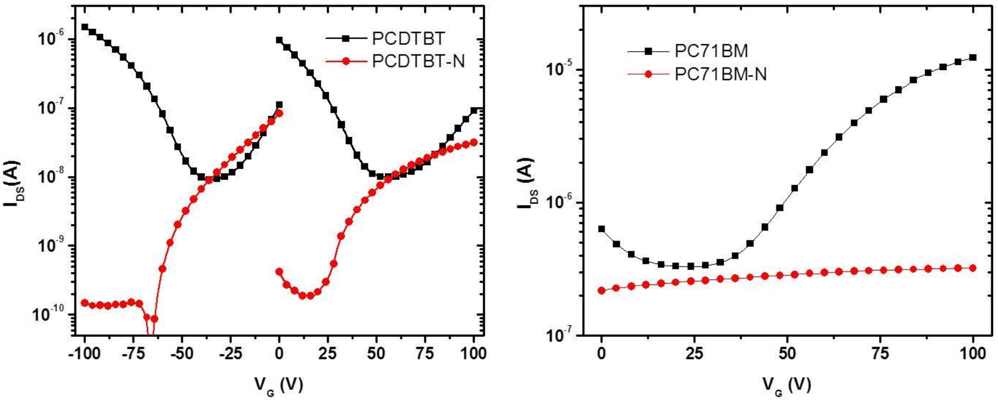

Figure S3. The *I-V* characteristics of PCDTBT and PCDTBT-N (left), and $PC_{71}BM$ and $PC_{71}BM$-N (right).

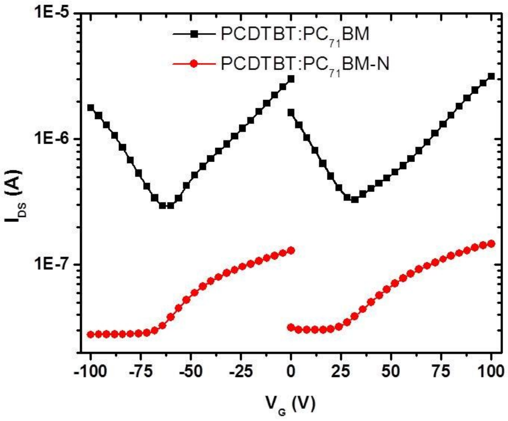

Figure S4. The *I-V* characteristics of PCDTBT:PC_{71}BM and PCDTBT:PC_{71}BM-N BHJ blends.

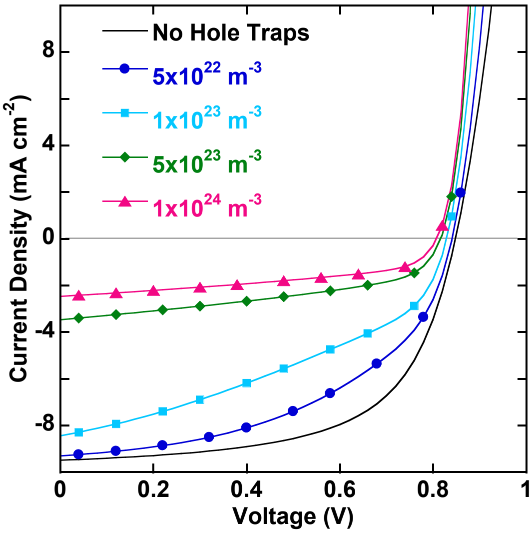

Figure S5. Simulated *J-V* characteristics of OPV devices with different hole trap densities inside active layer. The hole traps are uniformly distributed in space for all five devices.

References

(1) Freeman, A. W.; Urvoy, M.; Criswell, M. E. *J. Org. Chem.* **2005**, *70*, 5014-5019.

(2) Hou, Q.; Xu, Y. S.; Yang, W.; Yuan, M.; Peng, J. B.; Cao, Y. *J. Mater. Chem.*

2002, *12*, 2887-2892.

(3) Duan, C. H.; Zhong, C. M.; Liu, C. C.; Huang, F.; Cao, Y. *Chem. Mater.* **2012**, *24*, 1682-1689.

(4) Grosu, I.; Plé, G.; Mager, S.; Mesaros, E.; Dulau, A.; Gego, C. *Tetrahedron* **1998**, *54*, 2905-2916.

(5) Cammidge, A. N.; Crépy, K. V. L. *J. Org. Chem.* **2003**, *68*, 6832-6835.

(6) Clayden, J. *Tetrahedron* **2004**, *60*, 4335.

(7) Blouin, N.; Michaud, A.; Leclerc, M. *Adv. Mater.* **2007**, *19*, 2295-2300.

(8) Lampert, M. A.; Mark, P. *Current Injection in Solids*; Academic, New York, 1970.

(9) Sze, S. M.; Ng, K. K. *Physics of Semiconductor Devices, 2nd Edition*; John Wiley & Sons, Canada, 1981.