Supporting Information

1 Experimental

1.1 Materials and Methods

Column chromatography was performed using 63–210 μm silica gel. All other commercially available reagents and solvents were of reagent grade and used without further purification. NMR spectra were recorded on Bruker DPS300, and JEOL JNM-ECA500 NMR spectrometers. Absorption spectra in solution and solid film were recorded on a microscope attached to ultraviolet-visible-near infrared spectrophotometer (JASCO MSV-370). Thin films were prepared by spin-coating solutions (10 mg mL^{-1}) of materials onto a glass substrate. Differential scanning calorimetry was performed on SII DSC6220. The HOMO levels were measured on photoelectron yield spectroscopy (MODEL AC-3, RIKEN KEIKI. Co.,Ltd) under an atmospheric pressure. Powder X-ray diffraction analysis was carried out with a Rigaku Rint-2200 X-ray diffractometer with monochromated CuKa radiation and temperature-controlled heating stage. AFM image was acquired under ambient conditions using Nanoscope V Dimension Icon (Bruker AXS) in tapping mode.

1.2 Fabrication of organic solar cells

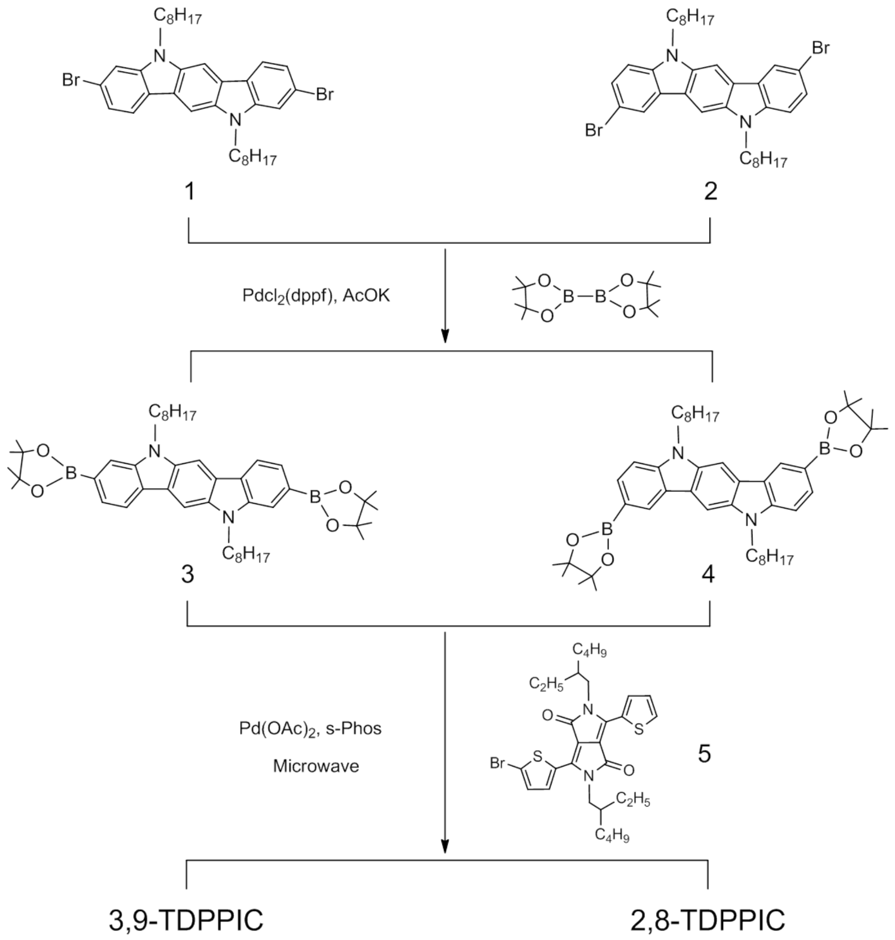
Bulk heterojunction solar cell devices were fabricated on indium-tin oxide (ITO) coated glass. The ITO glass substrates were subsequently cleaned with acetone and 2-propanol in ultrasonic bath. The resultant ITO substrates were then exposed to UV-ozone for 5 mins and coated with PEDOT:PSS [poly(3,4-ethylene dioxythiophene):poly(styrene sulfonate)](AI 4083, thickness: ca. 30 nm). The substrates were heated for 20 min at 120 °C to remove residual water. In a N_2 glove box, 0.5 mL of chloroform solutions containning PCBM (Luminescence Technology Corp., Taiwan Province) and TDPPICs were spin-coated onto the substrate. After drying the solvent, the substrates were annealed at individual temperatures for 10 min to give active layers with thicknesses ranging from 140 to 160 nm. The substrates were moved to a high-vacuum chamber (10^{-5} Pa), and the top electrode were evaporated through a mask (Ca:10 nm, Al:90 nm) to give solar cells with an active area of 0.04 cm^2. Finally, the devices were encapsulated by a glass lid in the nitrogen glove box system. The *J-V* characteristics of the solar cells were evaluated by using a Keithley 2400 source-measure unit under AM 1.5G illumination at an intensity of 100 mW cm^{-2}.

1.3 Fabrication of organic field-effect transistor

OFET devices were fabricated on SiO_2/Si substrates (SiO_2/Si, thickness: ca. 300 nm). The SiO_2/Si substrates were subsequently cleaned with acetone and 2-propanol in ultrasonic bath. Thin films of TDPPICs were prepared by spin-coating (1500 rpm) from the CHCl3 solutions. After drying the solvent, the substrates were annealed at individual temperatures for 10 min to give active layers with thicknesses ranging from 100 to 120 nm. Subsequently, top-contact gold electrodes (Au, thickness: ca. 70 nm) were deposited through shadow masks under vacuum to define channels with width and length of 5.5 mm and 50 μm, respectively. The OFET device measurements were performed using a semiconductor parameter analyzer (Agilent 4155C) at room temperature in a nitrogen glove box where the concentration of H_2O and O_2 was less than 1 ppm. The hole mobilities of TDPPICs were calculated in the saturation regime of transfer characteristics.

1.4 Synthesis and characterization

The 5,11-dioctyl-3,9-dibromo-3-indolo[3,2-b]carbazole (**1**), 5,11-dioctyl-2,8-dibromo-3-indolo [3,2-b]carbazole (**2**) and monobrominated diketopyrrolopyrrole compound (**5**) were prepared as described in the literature.[S1,S2]



Scheme S1 Synthetic route for 3,9-TDPPIC and 2,8-TDPPIC.

5,11-octyl-3,9-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-indolo[3,2-b]carbazole (3). The mixture of 5,11-dioctyl-3,9-dibromo-3-indolo[3,2-b]carbazole (1) (400 mg, 0.63 mmol), 4,4,4’,4’,5,5,5’,5’,-octamethyl-2,2’-bi-(1,3,2-dioxaborolane) (352 mg, 1.38 mmol), diphenylphosphineferrocene palladium dichloride (PdCl$_2$(dppf), 30 mg, 0.04 mmol), potassium acetate (124 mg, 1.26 mmol), and 1,4-dioxane (20 mL) was stirred at 80 °C for 12 h under N$_2$ atmosphere. The solution was cooled to room temperature, and poured into water to form precipitates. The precipitates were filtered off, and washed with methanol. The precipitates were dissolved in chloroform, and dried over Na$_2$SO$_4$. After the solvent was evaporated, purification by silica gel column chromatography (chloroform only) gave compound 3 as a yellow solid (180 mg, 40 %). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.40 (s, 2H), 8.10 (s, 2H), 8.00 (d, *J* = 9 Hz, 2H), 7.40 (d, *J* = 9 Hz, 2H), 4.38 (t, *J* = 6 Hz 4H), 1.93 (t, *J* = 6 Hz, 4H), 1.52−1.20 (m, 44H), 0.86 (t, *J* = 6 Hz, 6H).

5,11-octyl-2,8-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-indolo[3,2-b]carbazole (4). This compound was obtained from 5,11-dioctyl-3,9-dibromo-3-indolo[3,2-b]carbazole (2) (400 mg, 0.63 mmol) according to the same procedure for 3 as a yellow solid (190 mg, 50 %). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 8.69 (s, 2H), 8.08 (s, 2H), 7.93 (d, *J* = 9 Hz, 2H), 7.40 (d, *J* = 9 Hz, 2H), 4.38 (t, *J* = 6 Hz, 4H), 1.92 (t, *J* = 6 Hz, 4H), 1.52−1.20 (m, 44H), 0.86 (t, *J* = 6Hz, 6H).

3,9-TDPPIC. A 20-mL of microwave reactor vessel was charged with 3 (160 mg, 0.22 mmol), 5 (330 mg, 0.55 mmol), palladium acetate (8 mg, 0.04 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (28 mg, 0.16 mmol), K_3PO_4 (800 mg, 3.76 mmol) and THF/H_2O (10 mL/4 mL), and the vessel was placed into a microwave reactor. The reaction temperature and period was set to 130 °C and 30 min, respectively. After the reaction, the mixture was diluted with chlorofrom and washed twice with water, and the organic layer was dried with Na_2SO_4. After the solvent was removed under vacuum, purification by silica gel column chromatography (chloroform only), give the product as a black solid in 60 % yield (160 mg). This compound was further purified by preparative GPC (eluent: $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 60°C, δ): 9.00 (d, *J* = 5 Hz, 2H), 8.83 (d, *J* = 5 Hz, 2H), 8.19 (d, *J* = 10 Hz, 2H), 8.00 (s, 2H), 7.63−7.56 (m, 8H), 7.29−7.27 (m, 4H), 4.50−4.42 (m, 4H), 4.12−4.04 (m, 8H), 2.05−1.85 (m, 8H), 1.50−1.20 (m, 56H), 0.96−0.82 (m, 30H); Analysis calculated for $C_{94}H_{120}N_6O_4S_4$: C 73.97, H 7.92, N 5.51; found: C 74,12, H 7.94, N 5.58. MS analysis could not be performed because of low solubility.

2,8-TDPPIC. This compound was obtained from 4 (160 mg, 0.22 mmol) according to the same procedure for 3,9-TDPPIC as a black solid (130 mg, 48%). 2,8-TDPPIC was further purified by preparative GPC (eluent: $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 60°C, δ): 9.04 (d, *J* = 3 Hz, 2H), 8.88 (d, *J* = 3 Hz, 2H), 8.44 (s, 2H), 8.03 (s, 2H), 7.84 (dd, *J* = 12 Hz, 2H), 7.61 (d, *J* = 3 Hz, 2H), 7.56 (d, *J* = 6 Hz, 2H), 7.45 (d, *J* = 9 Hz, 2H), 7.29−7.27 (m, 4H), 4.50−4.40 (m, 4H), 4.10−3.90 (m, 8H), 2.05−1.85 (m, 8H), 1.55−1.18 (m, 56H), 0.98−0.81 (m, 30H); HRMS (ESI, *m/z*): $[M + H]^+$ calculated for $C_{94}H_{120}N_6O_4S_4$, 1525.8254; found, 1525.8327. Analysis calculated for $C_{94}H_{120}N_6O_4S_4$: C 73.97, H 7.92, N 5.51; found: C 73.96, H 7.91, N 5.56.

2 Supporting Figures

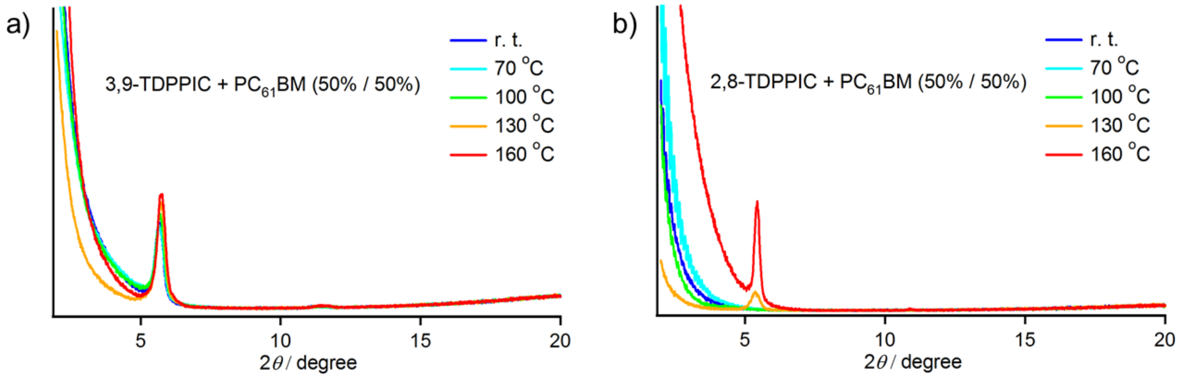


Fig. S1 XRD diffraction patterns of thin films of a) 3,9-TDPPIC:PCBM (5:5) and b) 2,8-TDPPIC:PCBM (5:5). The diffraction patterns of thermally annealed films with various annealing temperatures (as-cast, 70, 100, 130, and 160 °C) are also show by color curves. The films were prepared by drop-cast of their chloroform solutions onto glass substrate.

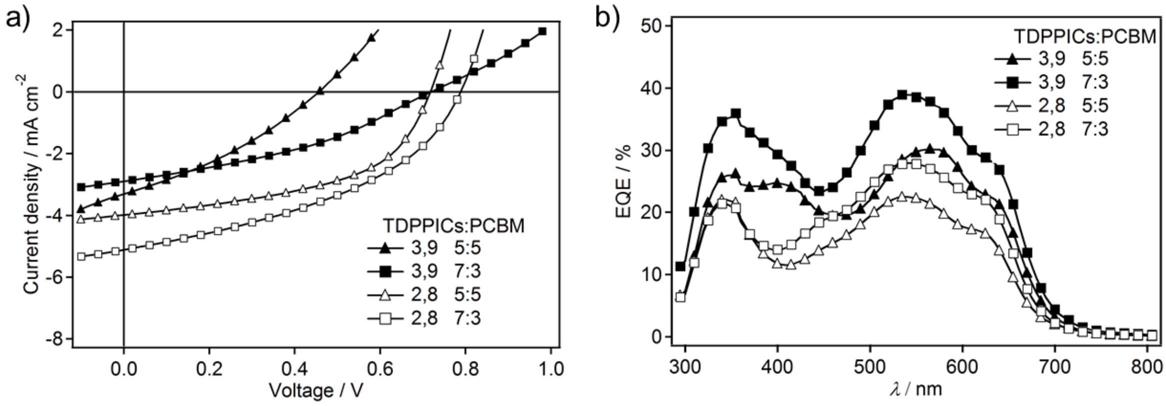


Fig. S2 a) *J-V* response and b) EQE spectra of annealed (130 °C) TDPPICs:PCBM devices using different blend ratio: (▲) 5:5 of 3,9-TDPPIC:PCBM; (■) 7:3 of 3,9-TDPPIC:PCBM; (△) 5:5 of 2,8-TDPPIC:PCBM; (□) 7:3 of 2,8-TDPPIC:PCBM.

3 References

S1: (a) Y. Wu, Y. Li, S. Gardner and B. S. Ong, *J. Am. Chem. Soc.*, 2005, **127**, 614; (b) P.-L. T. Boudreault, S. Wakim, N, Blouin, M. Simard, C. Tessier, Y. Tao and M. Leclerc, *J. Am. Chem. Soc.*, 2007, **129**, 9125.

S2: S. Loser, C. J. Bruns, H. Miyauchi, R. P. Ortiz, A. Facchetti, S. I. Stupp and T. J. Marks, *J. Am. Chem. Soc.*, 2011, **133**, 8142.