Electronic Supplementary Material (ESI)

Non-Fullerene Polymer Solar Cells with V_{OC} > 1 V Based on Fluorinated Quinoxaline Unit Conjugated Polymers

Baitian He, [a †] Qingwu Yin, [a †] Xiye Yang, [a] Liqian Liu, [a] Xiao-Fang Jiang, [a] Jie Zhang, [a] * Fei Huang, [a] * and Yong Cao [a]

[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

† These authors contributed equally to this work.

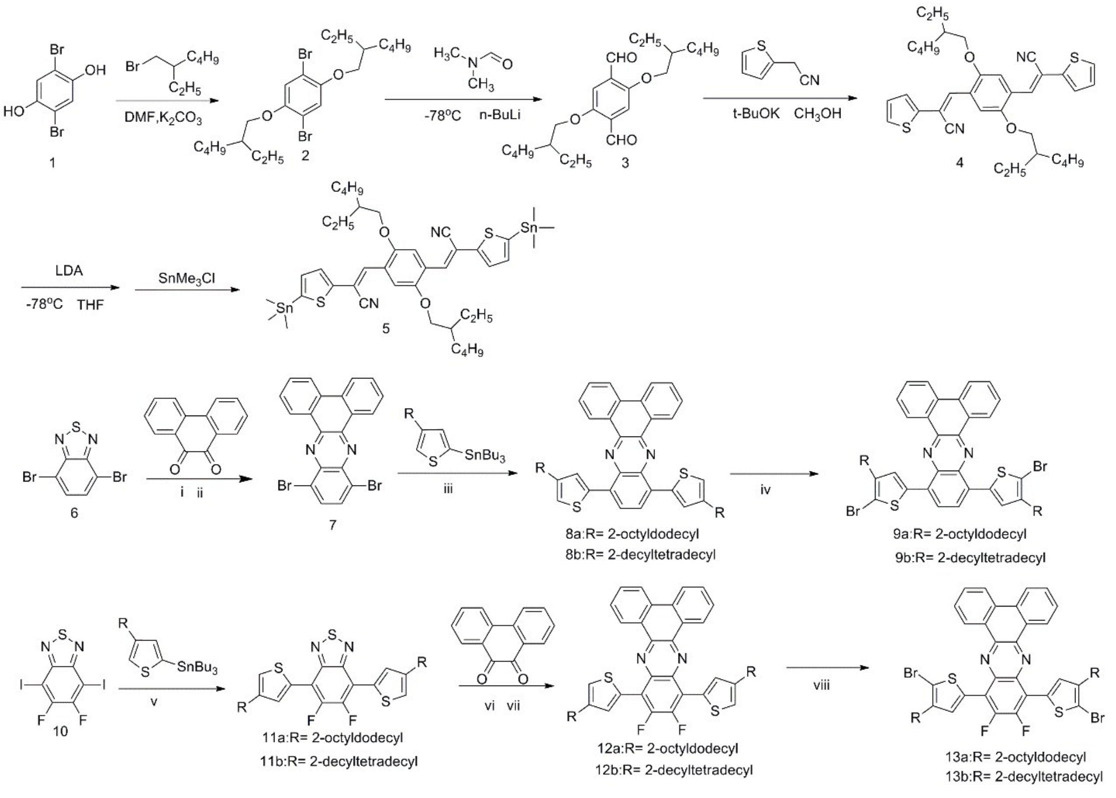
Experimental Section

Materials: All solvents and reagents were purchased from commercial sources and used without further purification unless stated otherwise. All reactions were carried out under the nitrogen atmosphere. Tetrahydrofuran (THF) was distilled over sodium/benzophenone before use to ensure an anhydrous state. Anhydrous N,N-Dimethylformamide (DMF) and chlorobenzene (CB) were purchased from Sigma-Aldrich and used as received. 2,5-dibromo-1,4-benzenediol (1),[1] 2-(tri-n-butylstannyl)-4-(2-octyldodecyl)thiophene, 2-(tri-n-butylstannyl)-4-2-decyltetradecyl)thiophene,[2] 4,7-dibromo-2,1,3-benzothiadiazole (6),[3] and 4,7-diiodo-5,6-difluoro-2,1,3-benzothiadiazole (10)[4] were prepared according to the previously reported literature.

Measurements: Molecular weights of the copolymers were determined using an Agilent Technologies PL-GPC 220 high-temperature chromatograph in 150 °C and 1,2,4-trichlorobenzene using a calibration curve of polystyrene standards. Thermogravimetric (TGA) measurements were carried out with a NETZSCH (TG209F3) apparatus at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis was performed on a NETZSCH (DSC200F3) apparatus at a heating or cooling rate of 10 °C min^{-1} under a nitrogen atmosphere. UV-vis absorption spectra were recorded on a SHIMADZU UV-3600 spectrophotometer. Photoluminescence was measured with a SHIMADZU RF-5301PC fluorimeter. Cyclic voltammetry (CV) was carried out on a CHI660A electrochemical workstation with platinum electrodes at a scan rate of 50 mV s^{-1} against an Ag/Ag$^+$ reference electrode with nitrogen-saturated solution of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile. Potentials were referenced to the 2 ferrocenium/ferrocene couple by using ferrocene as an internal standard. The deposition of a copolymer on the electrode was done by the evaporation of a chlorobenzene solution. Tapping-mode atomic force microscopy (AFM) images were obtained using a NanoScope NS3A system (Digital Instrument). Transmission electron microscopy (TEM) images were obtained using a JEM-2100F instrument. The transient photocurrent of devices was measured by applying 580 nm laser pulses with a pulse width of 120 fs and a low pulse energy to the short circuited devices in dark. The laser pulses were generated from optical parametric amplifier (TOPAS-Prime) pumped by a mode-locked Ti:sapphire oscillator seeded regenerative amplifier with a pulse energy of 1.3 mJ at 800 nm and a repetition rate of 1 kHz (SpectraPhysics Spitfire Ace).

Fabrication of polymer solar cells and Characterization: The indium tin oxide (ITO) glass substrates were cleaned sequentially under sonication for 30 min with acetone, detergent, deionized water and isopropyl alcohol and then dried at 80 °C in baking oven overnight, followed by a plasma treatment for 4 min. The pre-cleaned ITO substrate were coated with PEDOT:PSS (filtered through a 0.45 μm PES filter) by spin-coating (3000 rpm. for 30 s, thickness of ∼40 nm) and then baked at 150 °C for 15 min in air. Then, the substrates were transferred into a nitrogen (N_2) protected glovebox. For fullerene system, the device structure is ITO/PEDOT:PSS/copolymer: $PC_{71}BM$/Ca/Al the active layers were spin coated from the warm (70 °C) CB:ODCB (1:1) +0.5% DIO solutions containing Donor:$PC_{71}BM$ (weight ratio 1:2) to obtain thicknesses of ~110 nm. While for non-fullerene system, the device configuration was ITO/PEDOT:PSS/copolymer:ITIC/PFN-Br/Ag. The active layers spin coated from CB+0.25% DIO solution containing Donor:ITIC (weight ratio 1:1) to obtain thicknesses of ~100 nm. Thermal annealing of the blend films was carried out by placing them onto a hot plate with 140 °C for 20 minutes in a nitrogen atmosphere. A 5 nm PFN-Br layer was then spin-coated from methanol solution onto the active layer. The thin films were transferred into a vacuum evaporator connected to the glove box, and Ag (90 nm) was deposited sequentially through a shadow mask under 10^{-7} Pa, with an active area of the cells of 0.04 cm^2.

The current–voltage (*J*–*V*) curves were measured on a computer-controlled Keithley 2400 sourcemeter under 1 sun, AM 1.5 G spectra from a class solar simulator (Taiwan, Enlitech), and the light intensity was 100 mW cm^{-2} as calibrated by a China General Certification Center certified reference monocrystal silicon cell (Enlitech). Before the *J*–*V* test, a physical mask of an aperture with a precise area of 0.04 cm^2 was used to define the device area. The EQE data were recorded with a QE-R3011 test system from Enli technology company (Taiwan).



Scheme S1. Synthetic routes of monomers.

Synthesis of the monomers

1,4-dibromo-2,5-ethylhexyloxybenzene (2). Obtained as white oil. ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.08 (s, 2H), 3.83 (dd, J = 5.6, 0.9 Hz, 4H), 1.78~1.70 (m, 2H), 1.55~1.39 (m, 8H), 1.36~1.28 (m, 8H), 0.91 (t, J =6.5 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 147.6, 120.5, 110.9, 74.2, 40.3, 30.9, 29.6, 23.8, 23.0, 14.1, 11.9.

2,5-Diethylhexyloxy-1,4-dicarboxylaldehyde (3)[5]**.** Under N_2 protection, compound **2** (13.6 g, 31.17 mmol) was dissolved in anhydrous THF (150 ml) and cooled to -78 °C for 30 min. n-Butyl lithium (2.5 M in hexanes, 30 ml, 74.80 mmol.) was injected into the solution. After the reaction was stirred at -78°C for 1 hour, the reaction temperature was increased to 0°C for another 1 hour. Then the reaction cooled to -78°C and DMF (7.2 mL, 93.51 mmol) was added into the reaction. After 30 min, the solution was allowed to warm to room temperature overnight, the reaction was then poured in NH_4Cl solution, extracted with DCM, the organic phase was dried over magnesium sulfate and the solvent removed under reduced pressure. Finally, the residue was purified by column chromatography on silica gel (PE:DCM = 3:1) to get the product as yellow solid (6 g, yield 65%). ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 10.53 (s, 2H), 7.45 (s, 2H), 3.99 (d, *J* = 5.1 Hz, 4H), 1.82~1.76 (m, 2H), 1.55~1.39 (m, 8H), 1.36~1.28 (m, 8H), 0.91 (t, J = 6.5 Hz, 12H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 191.11, 150.58, 130.61, 115.94, 74.2, 40.3, 30.9, 29.6, 23.8, 23.0, 14.1, 11.9.

(2E, 2'E)-3,3'-(2,5-bis(2-ethylhexyloxy)-1,4-phenylene)bis(2-(thiophen-2-yl)acrylonitrile) (4)[6]**.** Compound **3** (3.4 g, 10 mmol) and 2-thiopheneacetonitrile (2.9 g, 24 mmol) were dissolved in methanol (25 mL). The mixture was added with a catalytic amount of potassium tert-butoxide solution in methanol with gentle stirring and allowed to react for 2 days at room temperature. The product was obtained as a precipitate, which was collected by filtration and washed with methanol. The solid was then recrystallized from acetonitrile to get the product as red solid (3.8 g, yield 70%). ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.90 (s, 2H), 7.87 (s, 2H), 7.39 (dd, J = 3.7, 1.1 Hz, 2H), 7.32 (dd, J = 5.1, 1.1 Hz, 2H), 7.08 (dd, J = 5.1, 3.7 Hz, 2H), 4.02 (d, J = 5.3 Hz, 4H), 1.84~1.76 (m, 2H), 1.61~1.43 (m, 8H), 1.40~1.29 (m, 8H), 0.98 (t, J = 7.5 Hz, 6H), 0.93~0.86 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 151.68, 139.98, 133.15, 128.16, 127.21, 126.46, 125.45, 117.22, 110.73, 105.98, 71.65, 39.54, 30.91, 29.18, 24.24, 23.08, 14.09, 11.35.

(2E, 2'E)-3,3'-(2,5-bis(2-ethylhexyloxy)-1,4-phenylene)bis(2-(5-(trimethylstannyl)thiophen-2-yl)acrylonitrile) (5). Under N_2 atmosphere, compound 4 (3 g, 5.5 mmol) was dissolved in anhydrous THF (60 mL) and cooled to -78 °C for 30 min. Next, 1.0 M lithium diisopropylamide (12.1 mL, 12.1 mmol) was added to the resulting mixture, which was stirred for 2 hour in -78 °C. Then, trimethyltin chloride (13.2 mL in 1 M hexane solution, 13.2 mmol) was added to the resulting reaction mixture, which was stirred for 30 min and then warmed to RT. After the solvent was removed, the solid was then recrystallized from acetonitrile to get the product as deep red solid (3.5 g, yield 75%). ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.91 (s, 2H), 7.87 (s, 2H), 7.46 (d, J = 2.7 Hz, 2H), 7.15 (d, J = 3.4 Hz, 2H), 4.03~3.99 (d, 4H), 1.84~1.76 (m, 2H), 1.61~1.43 (m, 8H), 1.40~1.29 (m, 8H), 0.98 (t, J = 7.5 Hz, 6H), 0.93~0.86 (m, 6H), 0.49~0.32 (m, 18H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm) 151.69, 145.91, 140.81, 136.94, 132.99, 128.89, 125.57, 117.54, 110.70, 105.65, 71.85, 39.58, 30.93, 29.27, 24.16, 23.13, 14.14, 11.38. FT-IR (cm^{-1}): 3035 (aromatic), 2933~2861 (aliphatic, C-H), 2204 (-CN), 1502–1431 (C=C), 1200 (C-O).

10,13-dibromodibenzo[a,c]phenazine (7). To a suspension of compound **6** (8.82 g, 30 mmol) in EtOH (250 mL), $NaBH_4$ (20.42 g, 540 mmol) was added portionwise at 0°C, and the mixture was stirred for 20 h at r.t. After evaporation in vacuo, H_2O (100 mL) was added, and the mixture was extracted with DCM. Evaporation in vacuo gave white solid. Then adding phenanthrene-9,10-dione (5.09 g, 24.44 mmol) and acetic acid (200 mL), the mixture was refluxed overnight. The reaction mixture was cooled to the room temperature and poured into water, the precipitated solid was filtered out and washed with water and methanol. The crude product was purified by re-crystallization to give a yellow solid (6.5 g, yield=60%). ^1H NMR (500 MHz, $CDCl_3$), δ (ppm): 9.48 (dd, J_1 = 7.9 Hz, J_2 = 1.3Hz, 2H), 8.58 (d, J = 8.0 Hz, 2H), 8.03 (s, 2H), 7.90~7.73 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 140.83, 135.57, 132.56, 129.41, 127.80, 127.37, 124.32, 123.93, 117.75.

10,13-bis(4-(2-octyldodecyl)thiophen-2-yl)dibenzo[a,c]phenazine (8a). 2-(tri-n-butylstannyl)-4-(2-octyldodecyl)thiophene (11.77 g, 18 mmol), compound 7 (2.64 g, 6 mmol), $Pd(pph_3)_4$ (500 mg) were put into 250 mL three-neck flask and then purged with nitrogen. Subsequently, anhydrous DMF (80 mL) was added. The mixture was heated to reflux overnight. Then the solvent was removed and the residue was purified by column chromatography on silica gel (PE) to afford the product as red solid (2.5 g, yield 55%). ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 9.56-9.49 (m, 2H), 8.54 (dd, J_1 = 7.1Hz, J_2 = 2.1 Hz, 2H), 8.17(s, 2H), 7.80-7.74 (m, 4H),7.74 (d, J = 1.3 Hz, 2H), 7.20 (d, J = 1.0 Hz, 2H), 2.68 (d, J = 6.8 Hz, 4H), 1.77 (s, 2H), 1.42-1.14 (m, 64H), 0.97-0.84 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 141.30, 141.07, 136.76, 135.65, 133.59, 132.17, 130.44, 129.41, 128.09, 127.80, 127.37, 124.32, 123.93, 38.52, 37.10, 34.71, 31.73, 29.39, 28.93, 27.56, 23.16, 14.00.

10,13-bis(4-(2-decyltetradecyl)thiophen-2-yl)dibenzo[a,c]phenazine (8b). Compound 8b was synthesized similarly as described for compound 8a. Red solid (1.8 g, yield 50%). ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 9.57-9.53 (m, 2H), 8.56 (dd, J_1 = 7.2 Hz, J_2 = 2.2 Hz, 2H), 8.19 (s, 2H), 7.82-7.76 (m, 4H), 7.75 (d, J = 1.4 Hz, 2H), 7.20 (d, J = 1.0 Hz, 2H), 2.68 (d, J = 6.8 Hz, 4H), 1.77 (s, 2H), 1.42-1.14 (m, 80H), 0.97-0.84 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 141.30, 141.07, 136.76, 135.65, 133.59, 132.17, 130.44, 129.41, 128.09, 127.80, 127.37, 124.32, 123.93, 38.52, 37.10, 34.71, 31.73, 29.39, 28.93, 27.56, 23.16, 14.00.

10,13-bis(5-bromo-4-(2-octyldodecyl)thiophen-2-yl)dibenzo[a,c]phenazine (9a). N-Bromosuccinimide (587 mg, 3.3 mmol) was added to a mixture of **3a** (1.51 mg, 1.5 mmol) in 30mL THF at 0^{o}C. The reaction mixture was warmed to r.t. and stirred overnight. 50 mL water was added and the mixture was extracted with dichloromethane for three times. The organic phase was dried with Mg_2SO_4 and the solvent was evaporated. The residue was purified with flash column chromatography (PE) to afford the product as dark red solid (1.42 g, yield 80%). ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 9.18 (dd, J_1 = 7.7, J_2 = 1.5 Hz, 2H), 8.33 (d, J = 7.5 Hz, 2H), 7.81 (s, 2H), 7.64-7.55 (m, 4H), 7.33 (s, 2H), 2.55 (d, J = 7.1 Hz, 4H), 1.74 (d, J = 33.7 Hz, 2H), 1.42-1.14 (m, 64H), 0.97-0.84 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 141.58, 140.28, 137.66, 137.32, 132.17, 130.28, 130.01, 127.94, 127.77, 126.73, 125.20, 122.64, 114.68, 38.76, 34.25, 33.45, 31.97, 31.94, 29.76, 29.73, 29.71, 29.42, 29.39, 26.67, 22.71, 14.14. MALDI-TOF MS: Calculated for C68H94Br2N2S2: 1163.43. Found: 1163.41.

10,13-bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)dibenzo[a,c]phenazine (9b). Compound 9b was synthesized similarly as described for compound 9a. Dark red solid (1.2 g, yield 73%). ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 9.34 (dd, J_1 = 7.8, J_2 = 1.6 Hz, 2H), 8.46 (d, J = 7.6 Hz, 2H)， 7.97 (s, 2H), 7.78~7.69 (m, 4H), 7.44 (s, 2H), 2.59 (d, *J* = 7.1 Hz, 4H), 1.79 (s, 2H), 1.42-1.14 (m, 80H), 0.97-0.84 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm) 141.62, 140.33, 137.72, 137.36, 132.21, 130.31, 130.05, 127.96, 127.79, 126.78, 125.25, 122.66, 114.66, 38.75, 34.28, 33.46, 31.93, 29.75, 29.71, 29.68, 29.39, 29.38, 26.67, 22.69, 14.11. MALDI-TOF MS: Calculated for C76H110Br2N2S2: 1275.64. Found: 1275.61.

5,6-difluoro-4,7-bis(4-(2-octyldodecyl)thiophen-2-yl)benzo[c][1,2,5]thiadiazole (11a). Under a nitrogen atmosphere, A mixture of compound **10** (4 g, 9.43 mmol), 2-(tri-n-butylstannyl)-4-(2-octyldodecyl)thiophene (18.5 g, 28.7 mmmol), $Pd(pph_3)_4$ (544.9 mg, 0.47 mmol) and anhydrous THF (120 mL) was stirred and heated to reflux overnight. The reaction mixture was then cooled to r.t. and the solvent was evaporated. The residue was purified by flash column chromatography (PE) to afford the product as yellow solid (4.23 g, yield 50%). ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.11 (s, 2H), 7.19 (s, 2H), 2.66 (d, *J* = 6.7 Hz, 4H), 1.77 (s, 2H), 1.42~1.14 (m, 64H), 0.97~0.84 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 156.77, 156.72, 156.70, 156.67, 155.37, 155.21, 153.36, 153.19, 135.26, 135.20, 135.17, 132.11, 110.48, 110.42, 110.32, 110.26, 38.52, 37.10, 34.71, 31.73, 29.28, 29.15, 29.04, 27.56, 23.16, 14.00.

4,7-bis(4-(2-decyltetradecyl)thiophen-2-yl)-5,6-difluorobenzo[c][1,2,5]thiadiazole (11b). Compound 11b was synthesized similarly as described for compound 11a. Yellow solid, (4.05 g, yield 40%). ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.09 (s, 2H), 7.17 (s, 2H), 2.72 (d, J = 6.9 Hz, 4H), 1.69 (s, 2H), 1.42–1.14 (m, 80H), 0.97-0.84 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 151.61, 151.34, 148.99, 148.94, 148.88, 148.17, 147.90, 142.35, 132.86, 132.81, 131.01, 124.83, 111.78, 111.66, 111.60, 38.97, 34.89, 33.37, 31.94, 30.04, 29.71, 29.68, 29.37, 26.66, 22.70, 14.11.

11,12-difluoro-10,13-bis(4-(2-octyldodecyl)thiophen-2-yl)dibenzo[a,c]phenazine (12a). Under a nitrogen atmosphere, Compound **11a** (2 g, 2.23 mmol), zinc dust (3.48 g, 53.48 mmol) and acetic acid (60 mL) were put into a 250 mL two-neck round-bottom flask. The mixture was stirred overnight at 80^{o}C and the excess zinc was removed by filtration. Subsequently, phenanthrene-9,10-dione (510 mg, 2.45 mmol) was put into the filtrate and the mixture was stirred at 60 ^{o}C for 8 hours. After cooling to room temperature, the reactant was poured into 100 mL water and extracted with dichloromethane for three times. After removal of the solvent by vacuum evaporation, the residue was purified by column chromatography on silica gel (PE), followed by re-crystallization from ethanol to give product as orange red solid (1.5 g, yield 65%).^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 9.43 (dd, J_1 = 7.8, J_2 = 1.6 Hz, 2H), 8.51 (d, J = 7.6 Hz, 2H), 7.86 (s, 2H), 7.75 (m, 4H), 7.31 (s, 2H), 2.71 (d, J = 6.8 Hz, 4H), 1.76 (s, 2H), 1.42~1.14 (m, 64H), 0.97~0.84 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 155.26, 155.11, 153.25, 153.09, 141.30, 139.07, 135.91, 135.88, 135.85, 135.82, 133.52, 133.50, 133.45, 133.43, 130.44, 129.41, 127.83, 127.76, 127.37, 124.32, 123.93, 115.35, 115.28, 115.19, 115.12, 38.52, 37.10, 34.71, 31.73, 29.28, 29.15, 29.04, 27.56, 23.16, 14.00.

10,13-bis(4-(2-decyltetradecyl)thiophen-2-yl)-11,12-difluorodibenzo[a,c]phenazine (12b). Compound 12b was synthesized similarly as described for compound 12a. Orange red solid, (1.3 g, yield 58%). ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 9.46 (dd, J_1 = 7.8, J_2 = 1.6 Hz, 2H), 8.53 (d, J = 7.5 Hz, 2H), 7.87 (s, 2H), 7.76 (m, 4H), 7.32 (s, 2H), 2.71 (d, J = 6.8 Hz, 4H), 1.76 (s, 2H), 1.42–1.14 (m, 80H), 0.97-0.84 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 155.26, 155.11, 153.25, 153.09, 141.30, 139.07, 135.91, 135.88, 135.85, 135.82, 133.52, 133.50, 133.45, 133.43, 130.44, 129.41, 127.83, 127.76, 127.37, 124.32, 123.93, 115.35, 115.28, 115.19, 115.12, 38.52, 37.10, 34.71, 31.73, 29.28, 29.15, 29.04, 27.56, 23.16, 14.00.

10,13-bis(5-bromo-4-(2-octyldodecyl)thiophen-2-yl)-11,12-difluorodibenzo[a,c]phenazine (13a). In a 100mL single-neck round bottom flask, N-Bromosuccinimide (427.2 mg, 2.4 mmol) was added to a mixture of **12a** (1.04 g, 1 mmol) in 20ml THF at 0^{o}C. The reaction mixture was warmed to r.t. and stirred overnight. 50mL water was added and the mixture was extracted with dichloromethane for three times. The organic phase was dried with Mg_2SO_4 and the solvent was evaporated. The residue was purified with flash column chromatography (PE) to afford the product as red solid (0.96 g, yield 80%). ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 9.02 (dd, J_1 = 7.9, J_2 =1.0 Hz, 2H), 8.27 (d, J = 8.0 Hz, 2H), 7.65~7.59 (m, 2H), 7.56 (s, 2H), 7.55-7.52 (m， 2H), 2.59 (d, J = 7.1 Hz, 4H), 1.78 (s, 2H), 1.42~1.14 (m, 64H), 0.97~0.84 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 150.42, 150.29, 150.25, 150.15, 148.33, 148.24, 148.16, 148.11, 140.79, 140.34, 134.98, 132.24, 131.31, 130.18, 130.08, 130.01, 129.16, 127.70, 122.35, 116.52, 116.35, 38.70, 34.17, 33.45, 31.96, 30.16, 29.78, 29.74, 29.72, 29.44, 29.41, 26.66, 22.72, 14.13. MALDI-TOF MS: Calculated for C68H92Br2F2N2S2: 1199.41. Found: 1199.40.

10,13-bis(5-bromo-4-(2-decyltetradecyl)thiophen-2-yl)-11,12-difluorodibenzo[a,c]phenazine (13b). Compound 13b was synthesized similarly as described for compound 13a. Red solid (0.8 g, yield 75%). ^{1}H NMR (500

MHz, $CDCl_3$), δ (ppm): 8.99 (dd, J_1 = 7.9, J_2 = 1.1 Hz, 2H), 8.25 (d, J = 8.1 Hz, 2H), 7.64~7.57 (m, 2H), 7.55 (s, 2H), 7.52 (dd, J = 11.3, 4.3 Hz, 2H), 2.59 (d, J = 7.1 Hz, 4H), 1.78 (s, 2H),1.42–1.14 (m, 80H), 0.97-0.84 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$), δ (ppm): 150.41, 150.30, 150.23, 150.18, 148.32, 148.25, 148.15, 148.11, 140.79, 140.34, 134.98, 132.25, 131.41, 130.18, 130.10, 129.15, 127.70, 122.34, 116.53, 116.35, 38.70, 34.19, 33.45, 31.95, 30.16, 29.78, 29.73, 29.71, 29.42, 29.40, 26.67, 22.71, 14.12. MALDI-TOF MS: Calculated for C76H108Br2F2N2S2: 1311.62. Found: 1311.61.

Synthesis of the copolymers

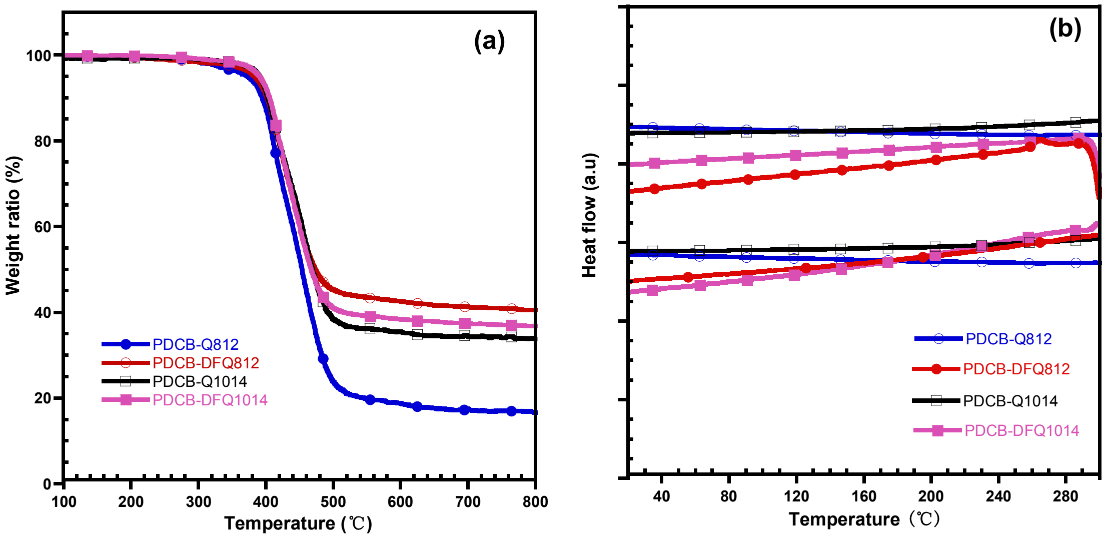
PDCB-Q812. To a mixture of monomer **5** (92.6 mg, 0.1 mmol), monomer **9a** (121.9 mg, 0.1 mmol) and 3 mL chlorobenzene were added to a 35 mL flask protected with N_2. The mixture was purged with argon for 15 min. Then catalyst $Pd_2(dba)_3$ (2.5 mg) and $P(o\text{-}tol)_3$ (5 mg) was quickly added under a stream of argon, and the mixture was purged with argon for another 15 min. Subsequently, the reaction mixture was then sealed and heated at 160 °C for 2 days. After cooling to room temperature, the reaction mixture was poured into a mixture of methanol (100 mL), the solid was collected by filtration and loaded into an extraction thimble and washed successively with methanol, acetone, hexane and chlorobenzene. The chlorobenzene solution was then concentrated by evaporation, precipitated into methanol. The solid was collected by filtration and dried in vacuo to get the polymer as a black solid (140 mg, 88.8%). Mn= 31.8 kDa, Mw= 50.8 kDa, PDI= 1.60

PDCB-Q1014, PDCB-DFQ812, PDCB-DFQ1014 were synthesized according to the similar procedures for **P-DCB-Q812** from corresponding monomers.

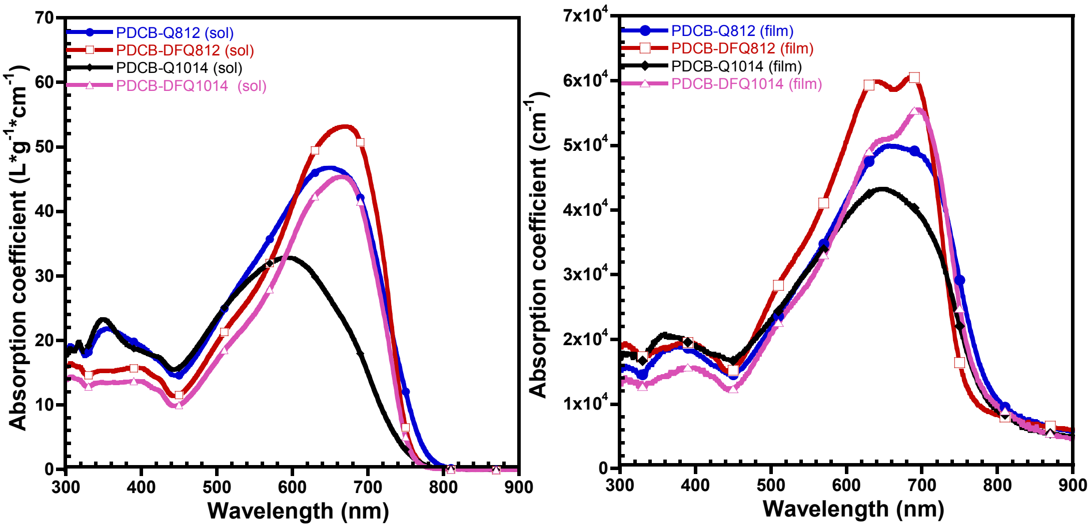
PDCB-Q1014: Yield (78%) GPC: Mn= 20.91 kDa, Mw= 39.3 kDa, PDI= 1.88

PDCB-DFQ812: Yield (86%) GPC: Mn= 40.9 kDa, Mw= 74.4 kDa, PDI= 1.82

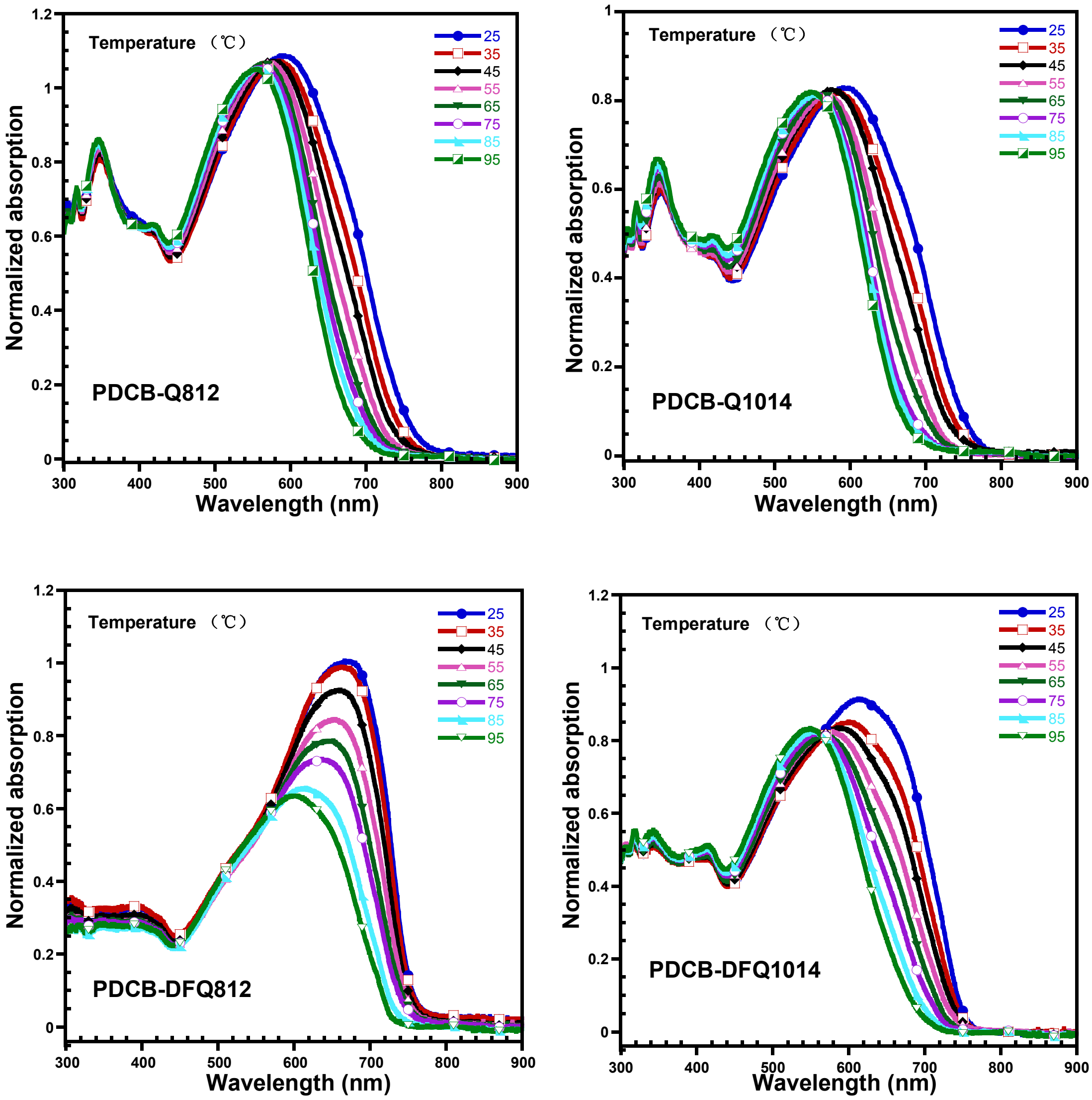
PDCB-DFQ1014: Yield (85%) GPC: Mn= 37.6 kDa, Mw= 66.5 kDa, PDI= 1.77



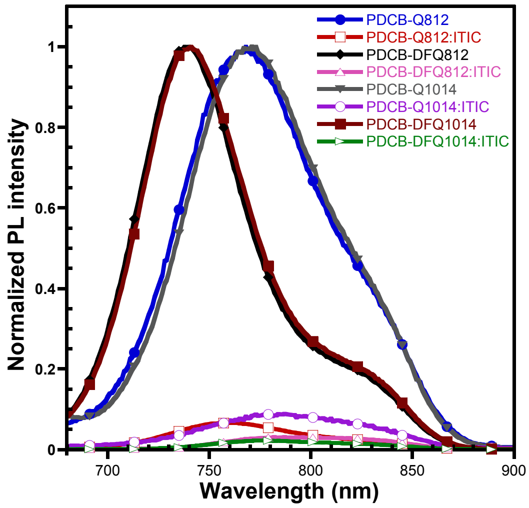
FigureS1. (a)TGA plot of polymers at a heating rate of 20 °C/min under a nitrogen atmosphere. (b) DSC plot of polymers at a heating or cooling rate of 10 °C /min under a nitrogen atmosphere.



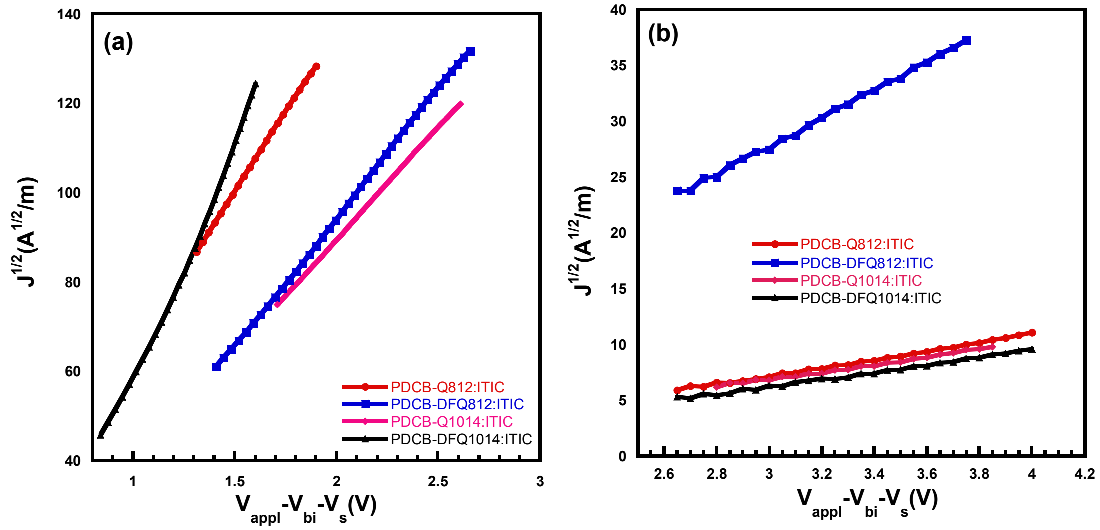
FigureS2. Solution and thin films absorption coefficient spectra of copolymers.



FigureS3. UV-Vis absorption spectra of copolymers at elevated temperatures in CB solution.



FigureS4. Photoluminescence spectra of pure copolymers and blends in as-cast films under optimized conditions.



FigureS5. $J^{1/2}$~V characteristics. (a) hole-only and (b) electron only devices of copolymers:ITIC under optimized conditions.

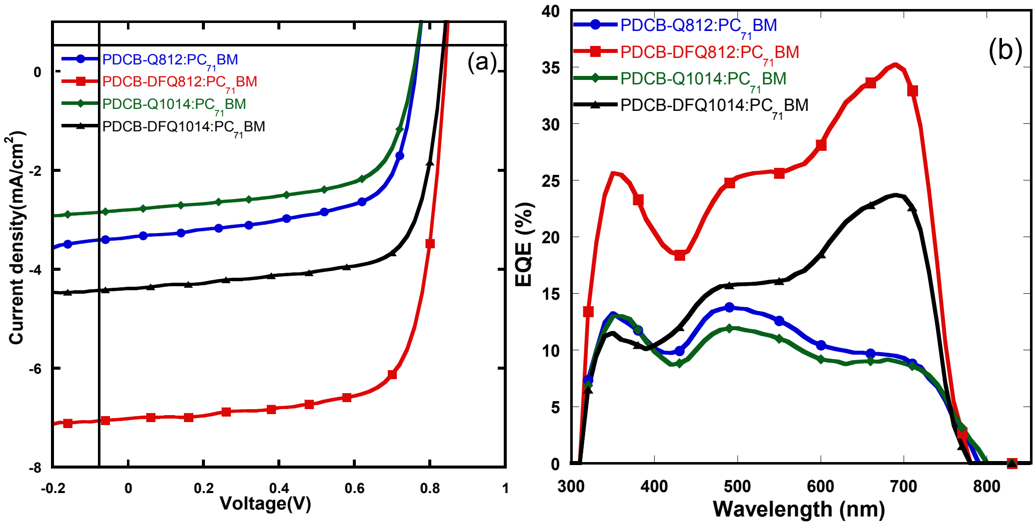


Figure S6. (a) Current−voltage characteristics of polymer solar cells for each copolymer under simulated AM1.5G illumination (100 mW cm^{-2}). (b) External quantum efficiency curves of the devices for each copolymer.

Table S1. Device performance of the PSCs based on PDCB-DFQ812:ITIC with different D/A ratios.

polymer	D/A (wt/wt)	V_{oc}(V)	J_{sc}(mA/cm^2)	FF(%)	PCE(%)
PDCB-DFQ812	1.3:1	0.984±0.008	11.15±0.17	54.53±1.23	5.98±0.02
	1:1	0.993±0.009	10.90±0.12	57.33±0.14	6.01±0.02
	1:1.3	0.970±0.022	9.39±0.33	56.61±0.55	5.16±0.34

Table S2. Device performance of the PSCs based on PDCB-DFQ812:ITIC with different thermal annealing temperature.

polymer	Temperature (°C)	V_{OC}(V)	J_{SC}(mA/cm^2)	FF(%)	PCE(%)
PDCB-DFQ812	100	1.052±0.003	9.52±0.06	59.88±0.76	5.99±0.13
	120	1.049±0.002	9.79±0.16	61.09±0.57	6.28±0.10
	140	1.024±0.003	12.50±0.04	59.04±0.37	7.56±0.06
	160	1.033±0.004	10.69±0.20	57.84±1.35	6.29±0.19

Table S3. Device performance of the PSCs based on PDCB-DFQ812:ITIC with different additive.

materials		V_{OC}(V)	J_{SC}(mA/cm^2)	FF(%)	PCE(%)	PCE$_{max}$(%)
DIO	0.1%	1.036±0.002	12.66±0.15	59.32±0.67	7.78±0.08	7.86
	0.25%	1.033±0.001	13.44±0.54	58.90±0.29	8.17±0.20	8.37
	0.5%	1.027±0.010	6.75±1.00	48.96±1.04	3.40±0.52	3.99
CN	0.25%	1.018±0.004	10.94±0.15	55.53±2.34	6.19±0.30	6.42
	0.5%	1.020±0.009	10.43±0.58	61.28±2.53	6.51±0.08	6.57
	1%	1.037±0.004	8.59±0.06	60.93±0.82	5.43±0.05	5.46

Table S4. Device performance of the PSCs based on PDCB-DFQ812:PCBM with different D/A ratios and solvent (ITO/PEDOT:PSS/PDCB-DFQ812:PC71BM/Ca/Al).

Solvent	D:A ratio (w/w)	Voc(V)	Jsc(mA/cm2)	FF(%)	PCE(%)
CB	1:2	0.789±0.016	1.75±0.11	66.98±2.51	0.92±0.05
CB:ODCB (1:1)	1.5:1	0.718±0.008	3.72±0.09	72.27±0.46	1.93±0.02
	1:1	0.719±0.016	4.25±0.12	72.40±0.09	2.21±0.01
	1:1.5	0.737±0.008	5.25±0.42	68.62±1.02	2.65±0.19
	1:2	0.726±0.004	5.96±0.25	71.61±0.33	3.10±0.12
	1:3	0.748±0.019	5.21±0.20	71.23±0.49	2.77±0.06

Table S5. Device performance of the PSCs based on PDCB-DFQ812:PC71BM with different additive ratio (ITO/PEDOT:PSS/PDCB-DFQ812:PC71BM/Ca/Al).

materials	ratio	Voc(V)	Jsc(mA/cm2)	FF(%)	PCE(%)
DIO	w/o	0.726±0.004	5.96±0.25	71.61±0.33	3.10±0.12
	0.5%	0.837±0.005	6.88±0.12	72.60±0.29	4.18±0.10
	1%	0.818±0.010	6.79±0.13	72.42±0.87	4.02±0.06

Table S6. Photovoltaic performances of copolymer:$PC_{71}BM$ devices with optimized conditions under the illumination of AM 1.5 G, 100 mW cm^{-2} (ITO/PEDOT:PSS/copolymer:$PC_{71}BM$/Ca/Al).

copolymer	D/A ratio (w/w)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)[a]
PDCB-Q812	1:2	0.764	3.30	65.10	1.64
PDCB-DFQ812	1:2	0.837	6.88	72.60	4.18
PDCB-Q1014	1:2	0.757	2.73	63.08	1.30
PDCB-DFQ1014	1:2	0.828	4.32	71.09	2.55

[a] Above were average values and the corresponding standard deviations were calculated over ten devices.

Table S7. Device performance of the PSCs based on copolymer:ITIC under the illumination of AM 1.5 G, 100 mW cm−2. (ITO/PEDOT:PSS/Copolymer:ITIC/Ca/Al).

copolymer	ratio(w/w)	Voc(V)	Jsc(mA/cm2)	FF(%)	PCE(%)	PCE $_{max}$ (%)
PDCB-Q812	1:1	0.903±0.002	8.36±0.04	56.53±1.20	4.27±0.10	4.37
PDCB-DFQ812	1:1	0.990±0.003	11.91±0.01	57.57±0.18	6.79±0.01	6.79
PDCB-Q1014	1:1	0.890±0.013	7.10±0.29	50.75±1.94	3.20±0.03	3.23
PDCB-DFQ1014	1:1	0.974±0.002	9.47±0.03	56.82±0.20	5.24±0.01	5.25

Reference

1. T. K. Prasad and M. P. Suh, *Chem. Asian J.*, 2015, **10**, 514-528.
2. Q. Hou, Q. Zhou, Y. Zhang, W. Yang, R. Yang and Y. Cao., *Macromolecules*, 2004, **37**, 6299-6305.
3. A. Gadisa, W. Mammo, L. M. Andersson, S. Admassie, F. Zhang, M. R. Andersson and O. Inganäs, *Adv. Funct. Mater.*, 2007, **17**, 3836-3842.
4. N. Cho, K. Song, J. K. Lee and J. Ko, *Chem. Eur. J.*, 2012, **18**, 11433-11439.
5. Ananda M. Sarker, L. Ding, Paul M. Lahti and Frank E. Karasz, *Macromolecules*, 2002, **35**, 223-230.
6. S. B. and M. Leclerc, *Macromolecules*, 2003, **36**, 8986-8991.