Supporting Information

Fine structural design and configuration regulation of DPP-based organic small molecule photovoltaic donors

Xu Wang,‡ Chang Liu,‡ Lunxiang Yin,* Yaru Liu, Peiwen Jiang and Yanqin Li*

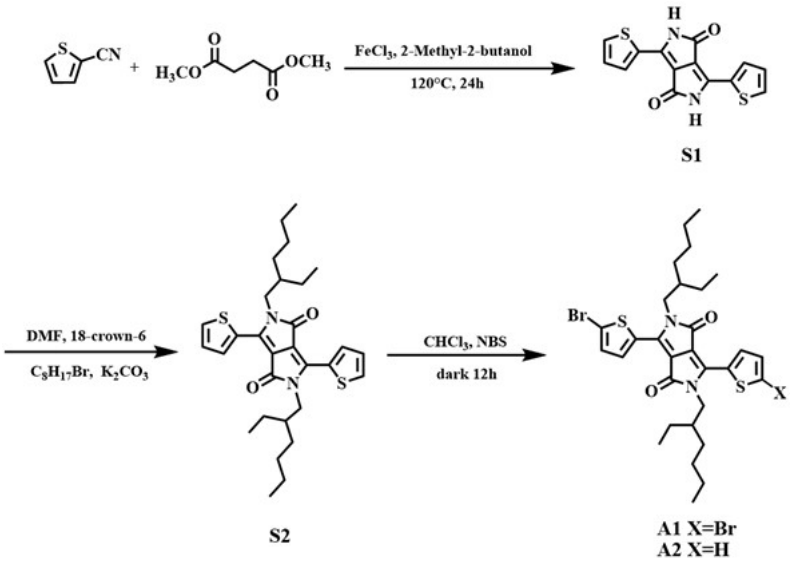
School of Chemistry, Dalian University of Technology, Linggong Road 2, Dalian, P. R. China.

**Corresponding author: E-mail: lxyin@dlut.edu.cn; liyanqin@dlut.edu.cn.Tel: 86-155-24572530.*

‡ These authors contributed equally to this work and should be regarded as co-first authors.

Table of Contents

1. Synthesis



Scheme S1 Synthetic routes of the diketopyrrolopyrrole (DPP) based compound **S1** and **S2**

Synthesis of 3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrol-1,4-dione (S1)
Compound **1** was synthesized according to the previously reported methods[1].

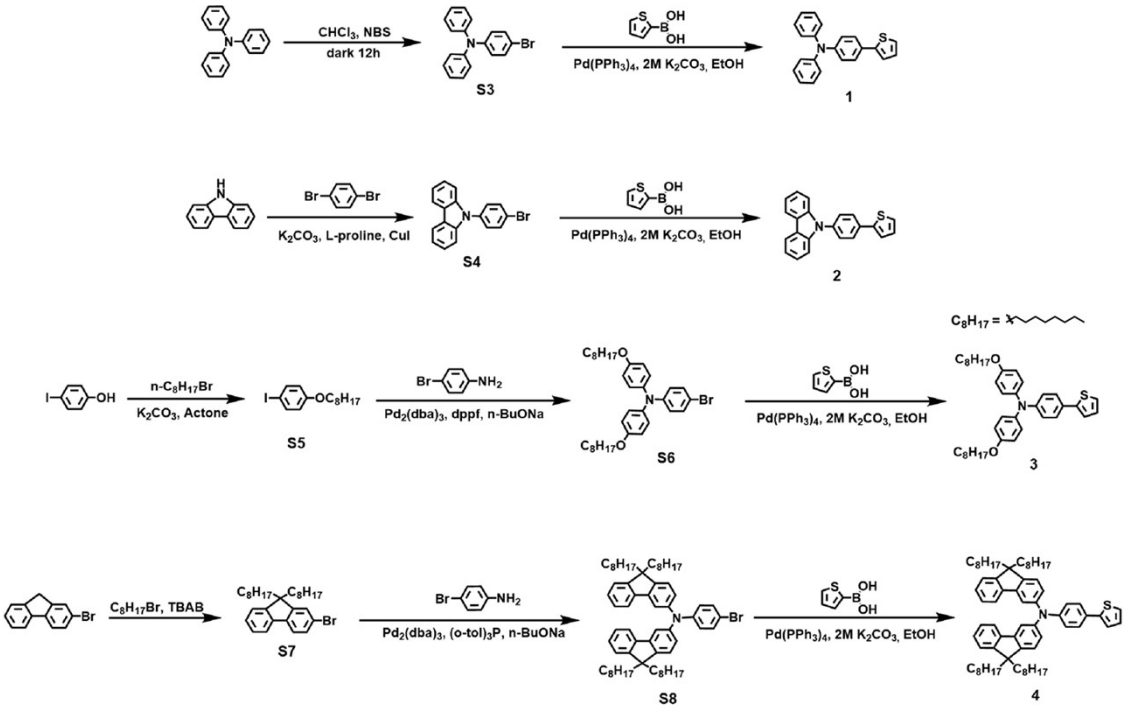
Synthesis of 2,5-bis(2-ethylhexyl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (S2)[2]
A mixture of compound **1** (1.80 g, 6.0 mmol), K_2CO_3 (3.31 g, 24 mmol), 18-crown-6 (0.79 g, 3.0 mmol), and 35 mL of N, N-dimethylformamide (DMF) was stirred at 120°C for 1 hour under nitrogen. Then 1-Bromo-2-ethyl hexane (1.73 g, 9.0 mmol) in DMF (15 mL) was dropped slowly into the reaction solution and heated at 130°C for 18 h under nitrogen. After cooling to room temperature, the mixture was poured into water (50 mL). The resulting mixture was extracted with CH_2Cl_2 (3 × 20 mL) and the combined organic phase was dried over anhydrous Na_2SO_4. After removing the solvent, the residue was purified by column chromatography on silica gel eluting with petroleum ether / CH_2Cl_2 (2:3, v/v) to give a red solid (0.72 g, 23%). M.p.: 102 - 104 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (dd, J_1 = 3.8 Hz, J_2 = 0.9 Hz, 2H), 7.62 (dd, J_1 = 5.0 Hz, J_2 = 0.9 Hz, 2H), 7.27 (d, J = 4.7 Hz, 2H), 4.08 - 3.97 (m, 4H), 1.91 - 1.81 (m, 2H), 1.40 - 1.21 (m,16H), 0.90 - 0.83 (m, 12H).

Synthesis of 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophene-2-yl)-2,5-dihydropyrr-olo[3,4-c]pyrrole-1,4-dione (compound A1)[3]
A mixture of compound **2** (0.84 g, 1.6 mmol) and $CHCl_3$ (40 mL) was stirred at 0°C for 20 min. A solution of NBS (0.12 g, 1.7 mmol) in $CHCl_3$ (10 mL) was added dropwise to the reaction solution at 0°C and the resulting mixture was stirred at room temperature overnight in dark. The reaction solution was poured into water (30 mL) and the solution was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phase was dried over anhydrous Na_2SO_4. After removing the solvent, the residue was purified by column chromatography on silica gel with petroleum ether / CH_2Cl_2 (2:3, v/v) as an eluent to afford a red solid. (0.61 g, 63%). M.p.: 125 - 127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 - 8.87 (m, 1H), 8.63 (d, J = 4.2 Hz, 1H), 7.69 - 7.58 (m, 1H), 7.28 (d, J = 4.3 Hz, 1H), 7.22 (d, J =

4.2 Hz, 1H), 4.04 - 3.87 (m, 4H), 1.91 - 1.81 (m, 2H), 1.38 - 1.21 (m, 16H), 0.92 - 0.83 (m, 12H).

Synthesis of 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-2,5-dihydropyrrolo[3,4-c] pyrrole-1,4-dione (compound A2)[3]

A mixture of compound **2** (0.84 g, 1.6 mmol) and $CHCl_3$ (40 mL) was stirred at 0°C for 20 min. A solution of NBS (0.24 g, 3.4 mmol) in $CHCl_3$ (10 mL) was added dropwise to the reaction solution at 0°C and the resulting mixture was stirred at room temperature overnight in dark. The reaction solution was poured into water (30 mL) and the resulting solution was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phase was dried over anhydrous Na_2SO_4. After removing the solvent, the residue was purified by column chromatography on silica gel with petroleum ether/CH_2Cl_2 (3:2, v/v) as the eluent to afford a red solid. (0.86 g, 78%). M.p.: 159-160 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) 8.64 (d, *J* = 4.0 Hz, 2H), 7.22 (d, *J* = 4.2 Hz, 2H), 3.99-3.87 (m, 4H), 1.89-1.78 (m, 2H), 1.37-1.23(m, 16H), 0.90-0.85 (m, 12H).



Scheme S2. Synthetic routes of compound **1,2,3** and **4**.

Synthesis of 4-bromo-N, N-diphenylaniline (S3)[4]

Dissolve a mixture of triphenylamine (2.45 g, 10 mmol) and NBS (1.95 g, 11 mmol) in $CHCl_3$ (45 mL) and reflux the solution under dark conditions for 12 hours. Filter the precipitated succinimide and evaporate the solvent from the solution. Recrystallize the remaining gray oily substance from ethanol to obtain white crystalline powder (2.48 g, 77%). M.p.: 113-114 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35-7.20 (m, 6H), 7.11-6.99 (m, 6H), 6.97-6.90 (m, 2H).

Synthesis of N, N-diphenyl-4-(thiophen-2-yl) aniline (1)[5]

Compound **1** was synthesized according to the previously reported methods. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60-7.55 (m, 2H), 7.40-7.35 (m, 2H), 7.35-7.29 (m, 4H), 7.12–7.02 (m, 9H).

Synthesis of 9-(4-bromophenyl)-9H-carbazole (S4)[6]

Compound **S4** was synthesized according to the previously reported methods. M.p.: 143–146 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0Hz, 2H), 7.42-7.34 (m, 6H), 7.29-7.26 (m, 2H).

Synthesis of 9-(4-(thiophen-2-yl)phenyl)-9H-carbazole (2)[7]

Compound **2** was synthesized according to the previously reported methods.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J*=7.7 Hz, 2H), 7.84 (d, *J*=8.4 Hz,2H), 7.59 (d, *J*=8.4 Hz, 2H), 7.39-7.49 (m, 5H), 7.29-7.37 (m, 3H), 7.15 (dd, *J*=4.7 Hz, 1H).

Synthesis of 1-Iodo-4-(octyloxy)benzene (S5)[8]

Compound **S5** was synthesized according to the previously reported methods. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.8 Hz,2H), 6.65 (d, *J* = 8.8 Hz, 2H), 3.88 (t, *J* = 6.5 Hz, 2H), 1.90-1.78 (m, 2H), 1.41(s, 2H), 1.27 (s, 8H), 0.87 (t, *J* = 6.3 Hz, 3H).

Synthesis of 4-bromo-N, N-bis(4-(octyloxy)phenyl)aniline (S6)[9]

Under nitrogen atmosphere, 4-bromoaniline (10 mmol, 1.72 g), t-BuONa (40 mmol, 3.84 g), $Pd_2(dba)_3$ (0.05 mmol, 0.046 g), and dppf (0.20 mmol, 0.11 g) were dissolved in 50 mL dry toluene, and then 4-isooctyloxyiodobenzene (21 mmol, 6.97 g) was added to the reaction system. The reaction mixture was refluxed at 110 °C for 48 h. After being cooled to the room temperature, the mixture was poured into 15 mL water and extracted with ethyl acetate (4 × 15 mL) and organic layers were collected and dried over anhydrous Na_2SO_4. After removing organic solvent under the reduced pressure, the residue was purified by silica column chroma tography, eluting with petroleum ether / CH_2Cl_2 (3:1, v/v) to obtain **S6** as a light orange oily liquid of 4.574 g, in a yield of 79%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 4H), 6.83-6.76 (m, 6H), 3.80 (d, *J* = 5.7 Hz, 4H), 1.76-1.66 (m, 2H), 1.57-1.37 (m, 8H), 1.35-1.29 (d, *J* = 5.5 Hz, 8H), 0.93 (t, *J* = 7.5 Hz, 6H), 0.90 (t, *J* = 7.0 Hz, 6H).

Synthesis of 4-(octyloxy)-N-(4-(octyloxy)phenyl)-N-(4-(thiophen-2-yl)phenyl)aniline (3)

Under nitrogen atmosphere, compound **S6** (1.16 g, 2 mmol), thiophene boric acid (0.38 g, 3 mmol), $Pd(PPh_3)_4$ (0.023 g, 0.02 mmol), and K_2CO_3 (2.76 g, 20 mmol) were dissolved in 30 mL dry toluene. Ethanol (5 ml) and H_2O (10 ml) were added to the mixture and refluxed 110 °C for 48 h. After being cooled to the room temperature, the mixture was poured into 15 mL water and extracted with chloroform (3 × 15 mL) and organic layers were collected and dried over anhydrous Na_2SO_4. After removing organic solvent under the reduced pressure, the residue was purified by silica column chromatography, eluting with petroleum ether/CH_2Cl_2 (3:1, v/v) to obtain **3** as a yellow oily liquid of 0.68 g, in a yield of 58%. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.7 Hz, 2H), 7.06 (d, *J* = 4.1 Hz, 2H), 6.96 (d, *J* = 8.9 Hz, 4H), 6.92 (dd, J_1 = 4.8 Hz, J_2 = 3.9 Hz, 1H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.73 (d, *J* = 9.0 Hz, 4H), 3.72 (dd, J_1 = 5.7 Hz, J_2 = 1.1 Hz, 4H), 1.67 – 1.58 (m, 2H), 1.47 – 1.28 (m, 8H), 1.26 – 1.21 (m, 8H), 0.85 (t, *J* = 7.5 Hz, 6H), 0.82 (t, *J* = 7.0 Hz, 6H).

Synthesis of 2-bromo-9,9-dioctyl-9H-fluorene (S7)[10]

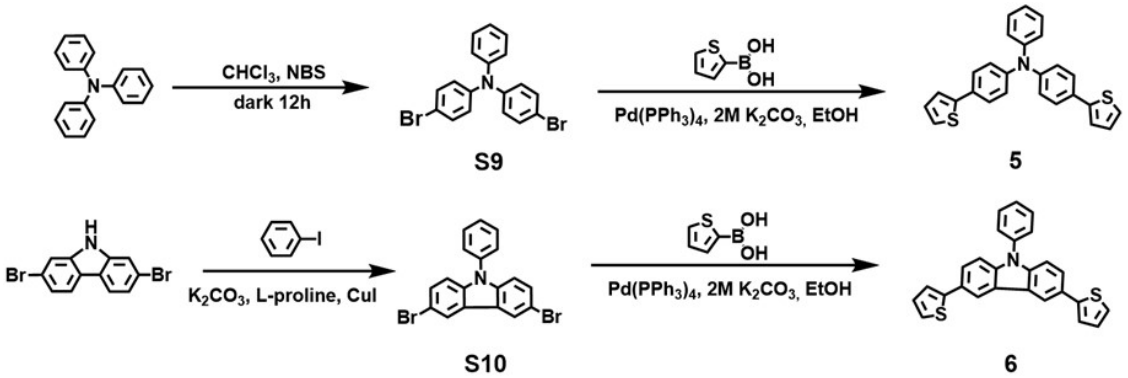
Under nitrogen atmosphere, 2-bromofluorene (10 mmol, 2.45 g), TBAB (1.0 mmol, 0.33 g), and KOH (20 mmol, 1.12 g) were dissolved in 30 mL acetone, 3.6 mL of bromo-n-octane was added to the mixture and refluxed at 60 °C for 12 hours. After removing organic solvent under the reduced pressure, the residue was purified by silica column chromatography, eluting with petroleum ether to obtain **S7** as a light yellow oily liquid of 4.12 g, in a yield of 88%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68-7.64 (m, 1H), 7.56-7.53 (m, 1H), 7.47-7.42 (m, 2H), 7.32 (dd, J_1 = 6.8 Hz, J_2 = 3.2 Hz, 3H), 1.98-1.88 (m, 4H), 1.23-1.17 (m, 4H), 1.16-1.02 (m, 16H), 0.82 (t, *J* = 7.2 Hz, 6H), 0.59 (s, 4H).

Synthesis of N-(4-bromophenyl)-N-(9,9-dioctyl-9H-fluoren-3-yl)-9,9-dioctyl-9H-fluoren-3-amine (S8)

Under nitrogen atmosphere, compound **S7** (1.16 g, 2.5 mmol), p-bromoaniline (0.17 g, 1.0 mmol), $Pd_2(dba)_3$ (0.018 g, 0.02 mmol), $(o\text{-tolyl})_3P$ (0.054 g, 0.08 mmol), and sodium tert butanol (0.77 g, 8.0 mmol) were dissolved in 30 mL dry toluene. The mixture was stirred at room temperature for 0.5 hours and refluxed at 120 °C for 24 hours. After being cooled to the room temperature, the mixture was poured into 15 mL water and extracted with chloroform (3 × 15 mL) and organic layers were collected and dried over anhydrous Na_2SO_4. After removing organic solvent under the reduced pressure, the residue was purified by silica column chromatography, eluting with petroleum ether/CH_2Cl_2 (6:1, v/v) to obtain **S8** as a yellow oily liquid of 0.63 g, in a yield of 76%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.1 Hz, 1H), 7.58-7.55 (m, 2H), 7.53 (d, *J* = 7.4 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 4H), 7.39-7.34 (m, 4H), 7.15 (s, 1H), 7.07 (s, 1H), 6.93 (d, *J* = 8.2 Hz, 3H), 1.84 (dd, *J* = 10.6, 4.3 Hz, 8H), 0.96 (s, 20H), 0.74 (t, *J* = 7.5 Hz, 12H), 0.53 (d, *J* = 6.0 Hz, 8H).

Synthesis of N-(9,9-dioctyl-9H-fluoren-3-yl)-9,9-dioctyl-N-(4-(thiophen-2-yl)phenyl)-9H-fluoren-3-amine (4)

Under nitrogen atmosphere, compound **S8** (0.94 g, 1.0 mmol), thiophene boric acid (0.26 g, 2 mmol), $Pd(PPh_3)_4$ (0.012 g, 0.01 mmol), and K_2CO_3 (1.38 g, 10 mmol) were dissolve in 30 ml dry toluene. Ethanol (2.5 ml) and water (5.0 ml) were added sequentially, the mixture was refluxed at 120 °C for 24 h. After being cooled to the room temperature, the mixture was poured into 15 mL water and extracted with chloroform (3 × 15 mL) and organic layers were collected and dried over anhydrous Na_2SO_4. After removing organic solvent under the reduced pressure, the residue was purified by silica column chromatography, eluting with petroleum ether/CH_2Cl_2 (6:1, v/v) to obtain **4** as a yellow oily liquid of 0.51 g, in a yield of 54%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.29 (s, 3H), 7.23 (s, 2H), 7.19 (s, 1H), 7.14-7.09 (m, 4H), 7.08-7.03 (m, 4H), 1.87 (d, *J* = 5.6 Hz, 8H), 1.56 (s, 4H), 1.43 (s, 4H), 1.33 (s, 4H), 1.25 (d, *J* = 7.1 Hz, 8H), 1.06 (s, 20H), 0.83 (t, *J* = 6.7 Hz, 12H), 0.67 (s, 8H).



Scheme S3. Synthetic routes of compound **5** and **6**.

Synthesis of 4-Bromo-N-(4-bromophenyl)-N-phenylaniline (S9).[4]

A mixture of triphenylamine (2.45 g, 10 mmol) and NBS (3.90 g, 22 mmol) in $CHCl_3$ (45 mL) were refluxed at room temperature for 12 hours under dark. The precipitated succinimide was filtered. After removing organic solvent under the reduced pressure, the remaining grey coloured oil was recrystallized from ethanol to obtain white crystalline powder (2.48 g, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.31 (m, 4H), 7.25-7.22 (m, 2H), 7.08-7.05 (m, 3H), 6.94-6.91 (m, 4H).

Synthesis of N-phenyl-4-(thiophen-2-yl)-N-(4-(thiophen-2-yl)phenyl)aniline (5).

Under nitrogen atmosphere, compound **S9** (0.40 g, 1.0 mmol), thiophene boric acid (0.26 g, 2 mmol), $Pd(PPh_3)_4$ (0.012 g, 0.01 mmol), and K_2CO_3 (1.38 g, 10 mmol) were dissolve in 20 ml dry toluene. Ethanol (2.5 ml) and water (5.0 ml) were added sequentially, the mixture was refluxed at 120 °C for 24 h. After being cooled to the room temperature, the mixture was poured into 15 mL water and extracted with chloroform (3 × 15 mL) and organic layers were collected and dried over anhydrous Na_2SO_4. After removing organic solvent under the reduced pressure, the residue was purified by silica column chromatography, eluting with petroleum ether/CH_2Cl_2 (6:1, v/v) to obtain **5** as a yellow green oily liquid of 0.24 g, in a yield of 54%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.7 Hz, 4H), 7.31-7.26 (m, 2H), 7.23-7.21 (m, 4H), 7.17-7.13 (m, 2H), 7.10 (d, *J* = 8.7 Hz, 4H), 7.08-7.04 (m, 3H).

Synthesis of 3,6-dibromo-9-phenyl-9H-carbazole (S10).[11]

Under nitrogen atmosphere, compound 2,7-Dibromocarbazole (0.65 g, 2.0 mmol), iodobenzene (0.41 g, 2.0 mmol), CuI (0.056 g, 0.4 mmol), 1,10-Phenanthroline (0.08 g, 0.4 mmol) and K_2CO_3 (0.83 g, 6.0 mmol) in 20 mL DMF were refluxed at 160 °C for 24 hours. After evaporating organic solvent under the reduced pressure, the residue was purified by silica column chromatography, eluting with with petroleum ether / CH_2Cl_2 (6:1, v/v) to afford compound **S10** as a light yellow oily liquid of 0.47 g in a yield of 59%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 2H), 7.54-7.47(m, 5H), 7.40 (t, *J* = 8.2 Hz, 2H).

Synthesis of 9-phenyl-3,6-di(thiophen-2-yl)-9H-carbazole (6).

Under nitrogen atmosphere, compound **S10** (0.40 g, 1.0 mmol), thiophene boric acid (0.33 g, 2.6 mmol), $Pd(PPh_3)_4$ (0.012 g, 0.01 mmol), and K_2CO_3 (1.38 g, 10 mmol) were dissolve in 20 mL THF and 5 mL H_2O. The mixture was refluxed at 120 °C for 24 h. After being cooled to the room temperature, the mixture was poured into 30 mL water and extracted with chloroform (3 × 30 mL) and organic layers were collected and dried over anhydrous Na_2SO_4. After removing organic solvent under the reduced pressure, the residue was purified by silica column chromatography, eluting with petroleum ether/CH_2Cl_2 (3:1, v/v) to obtain **6** as a red solid of 0.26 g, in a yield of 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.61 – 7.56 (m, 2H), 7.53 (d, *J* = 7.0 Hz, 2H), 7.49 (d, *J* = 6.3 Hz, 4H), 7.25 (s, 2H), 7.18 (d, *J* = 5.1 Hz, 3H), 6.99 (s, 2H).

2. Device fabrication and characterization

The device consists of ITO/PEDOT:PSS/organic active layer/Al was used to prepare solution-treated BHJ OSCs (ITO is indium tin oxide; PEDOT:PSS means poly(3,4-ethylenedioxy-thiophene): poly(styrene sulfonate); organic active layer consist of oligomer donor and acceptor materials). Before manufacturing the device, ITO glass substrates should be cleaned by ultrasonic for 30 minutes in deionized water, methanol, acetone, toluene and isopropanol in proper sequence. Those cleaned glass substrates should be cleaned in proper sequence were dried in an infrared oven for 20 minutes. Subsequently, PEDOT:PSS was spin-coated on the substrate at a rate of 4000 rpm for 1 minute and thermal annealed at 140 °C for 20 minutes. Then, the mixed solution of oligomer materials and $PC_{71}BM$ in chloroform (9 mg/mL) was spin-coated on ITO/PEDOT:PSS substrate at a rate of 1000 r pm for 1 minute. Finally, after thin layer of aluminum (80 nm) was deposited on the active layer under a vacuum of 10^{-4} Pa, an effective area of 5.0 mm device was

obtained. The above device structure was also used to measure the hole mobility (μ_h), except that the anode was replaced with gold, and electron mobility (μ_e) is measured by replacing PEDOT:PSS with ZnO. The hole mobility (μ_h) and electron mobility (μ_e) are estimated by the Mott - Gurney law: $J = (9/8)\ \varepsilon_0\ \varepsilon_r\ \mu_{h/e}\ (V^2/L^3)$ J is current density, ε_0 is the permittivity of free space, ε_r is the relative permittivity and assumed as approximately 3.0, $\mu_{h/e}$ is the hole mobility and electron mobility, V is the effective voltage, and L is the thickness of the active layer.

3. Spectra of ^{1}H NMR, ^{13}C NMR, and MALDI-TOF HRMS

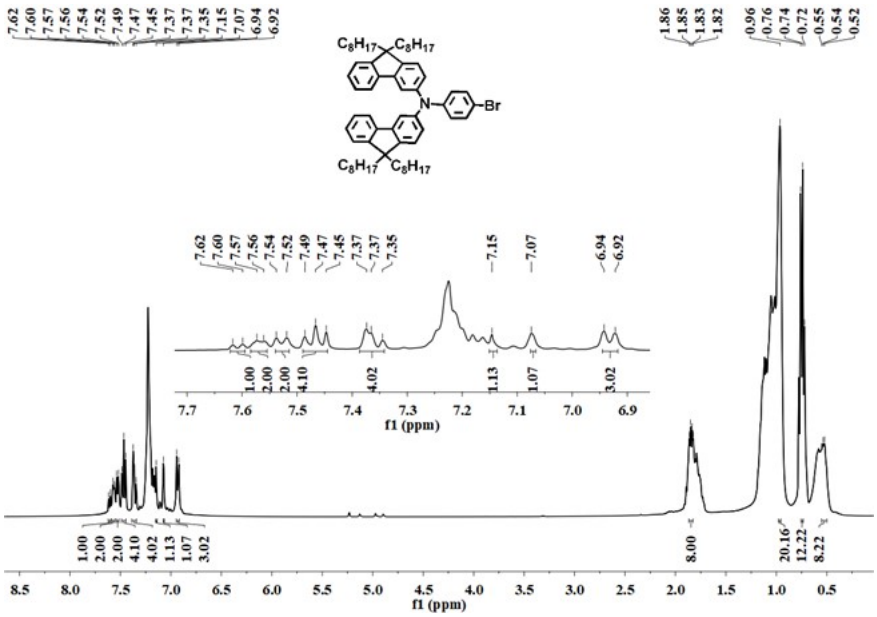


Figure S1 ^{1}H NMR spectrum of **compound S8**

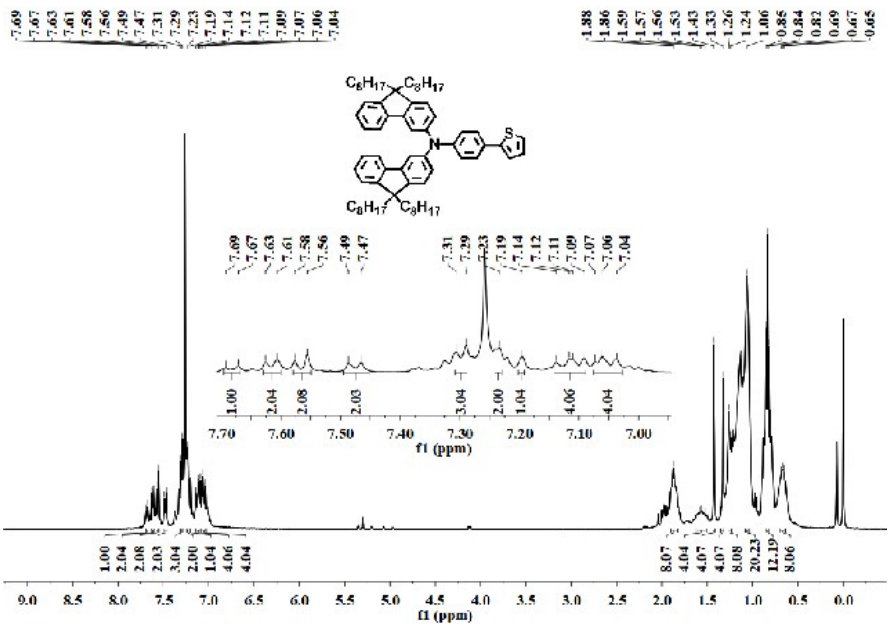


Figure S2 ^{1}H NMR spectrum of **compound 4**

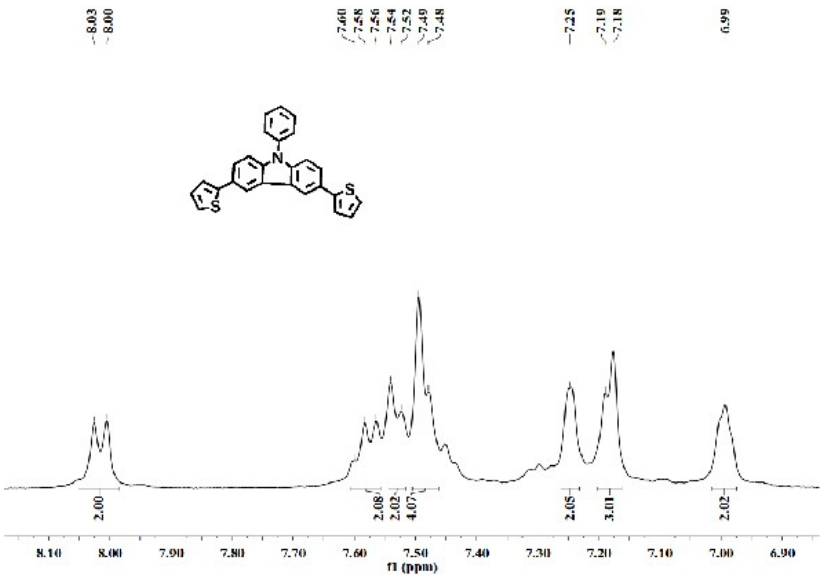


Figure S3 ^{1}H NMR spectrum of **compound 6**

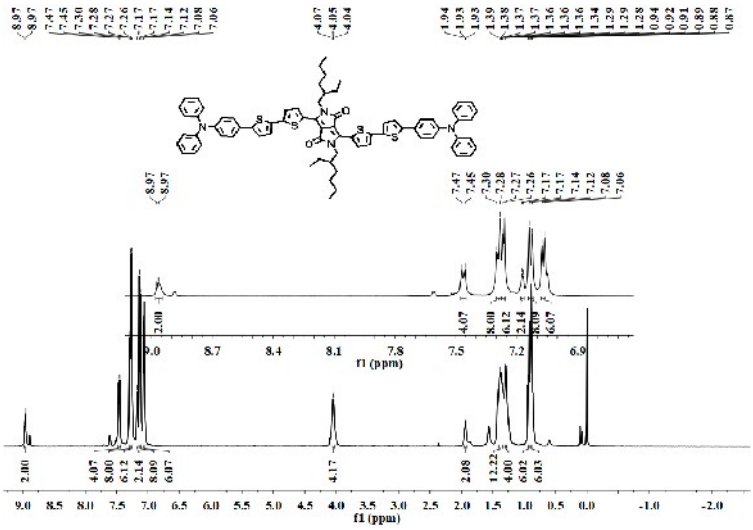


Figure S4 ^{1}H NMR spectrum of **compound $(TPA)_2DPP$**

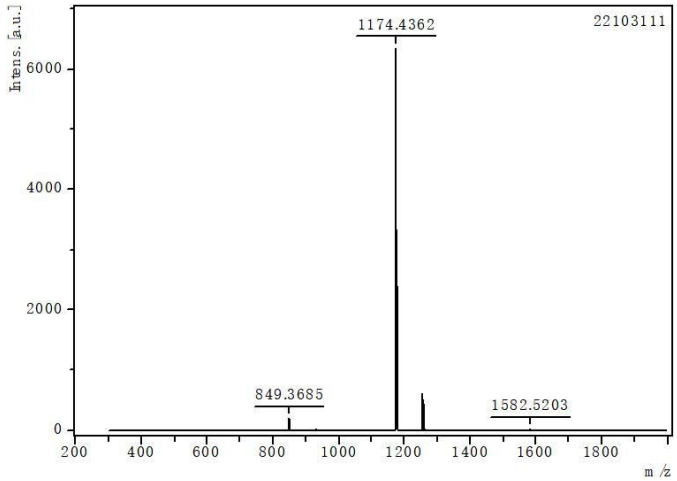


Figure S5 MALDI-TOF HRMS spectrum of **$(TPA)_2DPP$** (calcd for $C_{74}H_{70}N_4O_2S_4$:1174.4376)

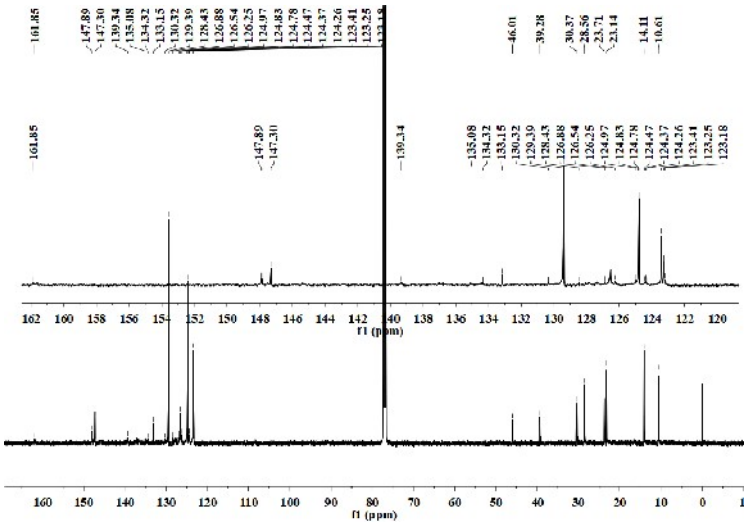


Figure S6 ^{13}C NMR spectrum of **$(TPA)_2DPP$**

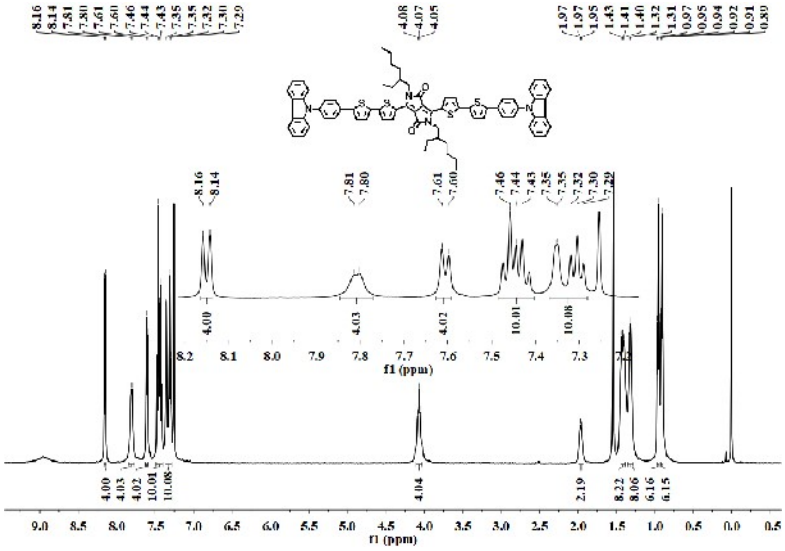


Figure S7 ^{1}H NMR spectrum of **compound $(PCZ)_2DPP$**

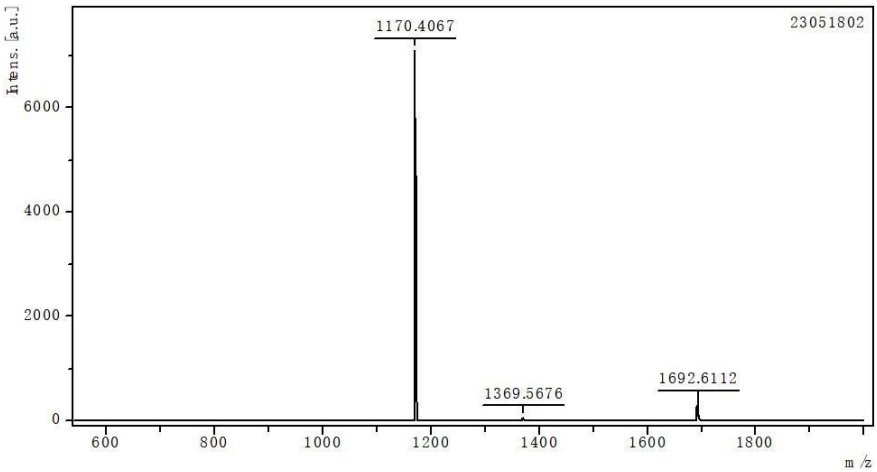


Figure S8 MALDI-TOF HRMS spectrum of **$(PCZ)_2DPP$** (calcd for C74H66N4O2S4:1170.4063)

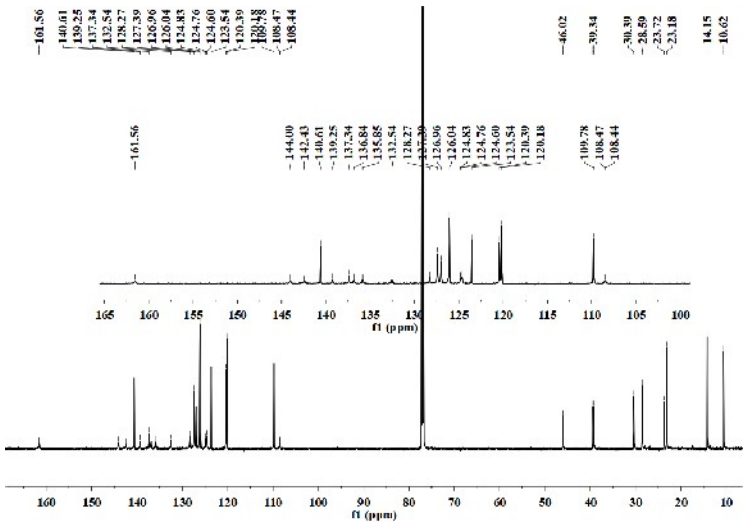


Figure S9 ^{13}C NMR spectrum of **$(PCZ)_2DPP$**

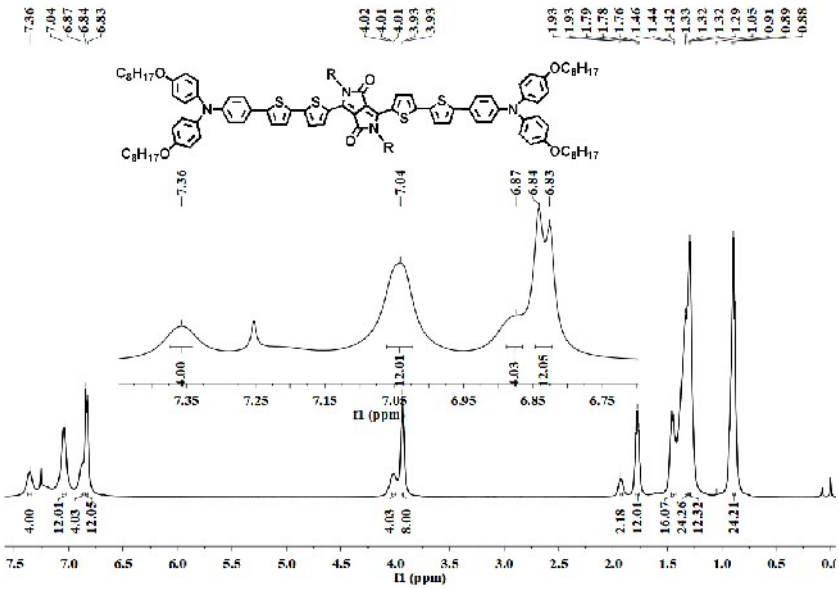


Figure S10 ^{1}H NMR spectrum of **compound $(RTPA)_2DPP$**

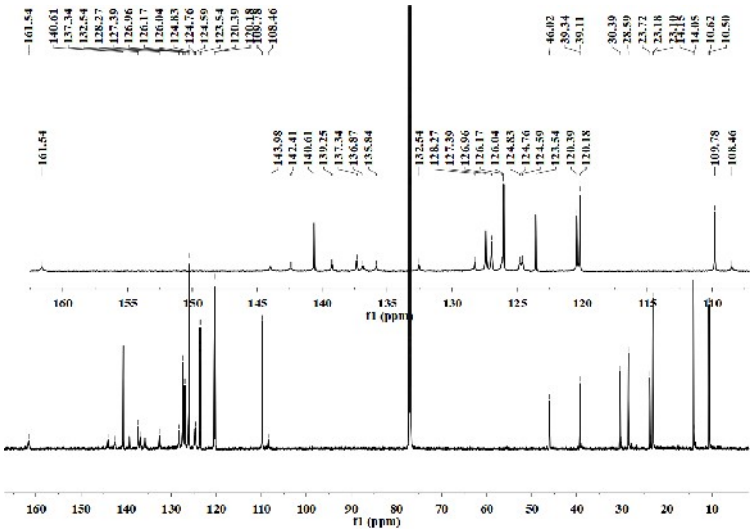


Figure S11 MALDI-TOF HRMS spectrum of **$(RTPA)_2DPP$** (calcd for $C_{100}H_{134}N_4O_2S_4$:1686.9181)

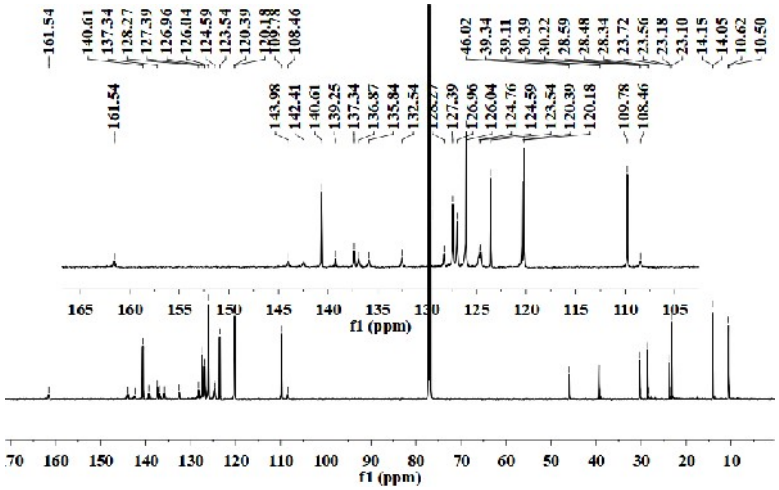


Figure S12 ^{13}C NMR spectrum of **(RTPA)$_2$DPP**

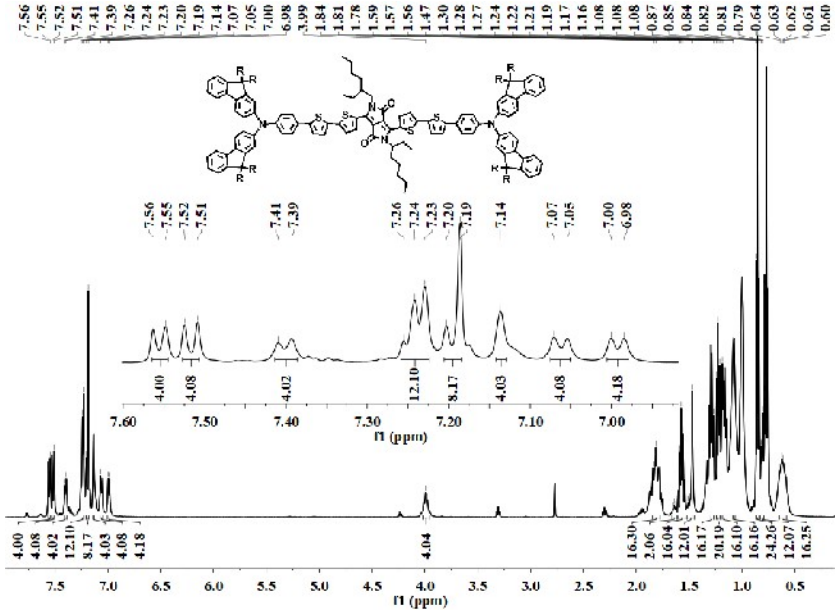


Figure S13 ^{1}H NMR spectrum of **compound (FTPA)$_2$DPP**

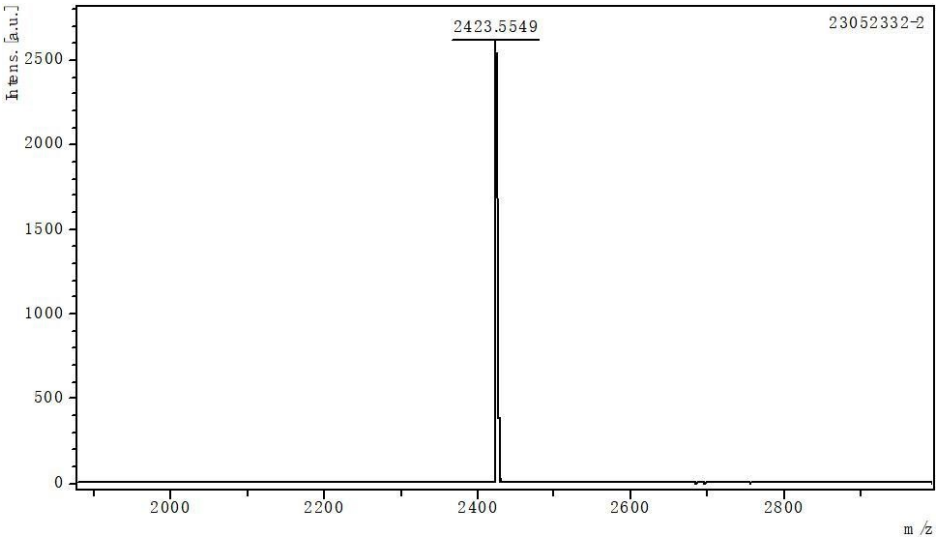


Figure S14 MALDI-TOF HRMS spectrum of **(FTPA)$_2$DPP** (calcd for $C_{166}H_{214}N_4O_2S_4$:2423.5650)

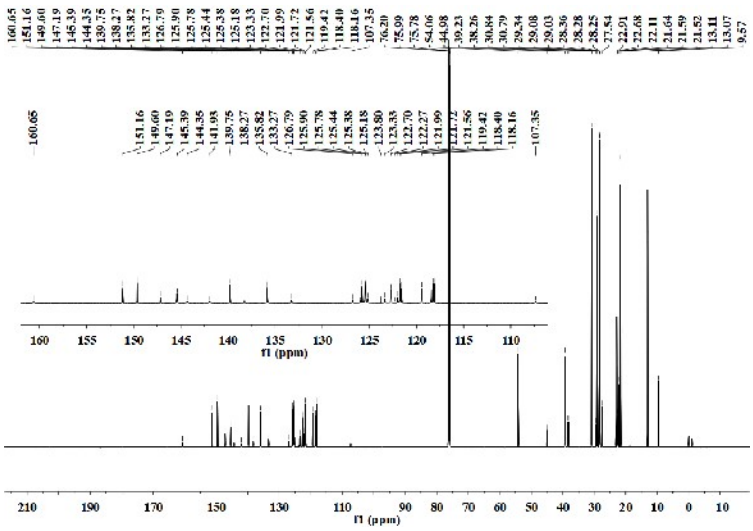


Figure S15 ^{13}C NMR spectrum of **(FTPA)$_2$DPP**

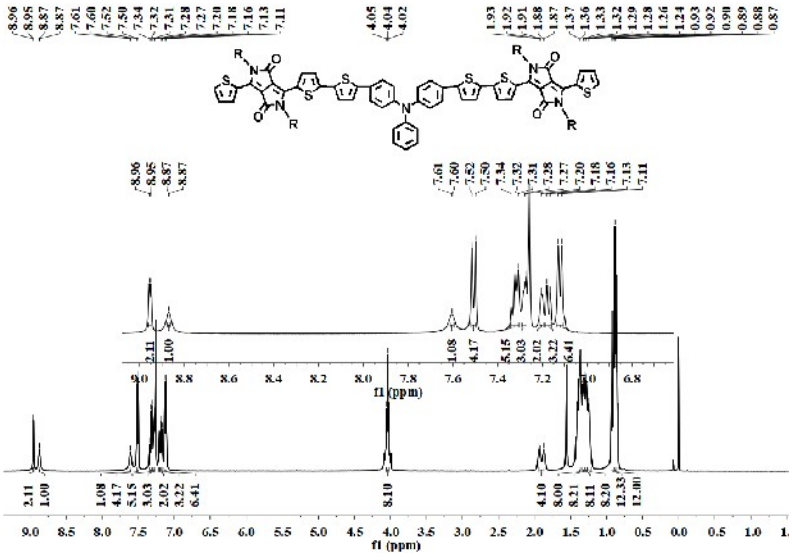


Figure S16 ^{1}H NMR spectrum of **compound (DPP)$_2$TPA**

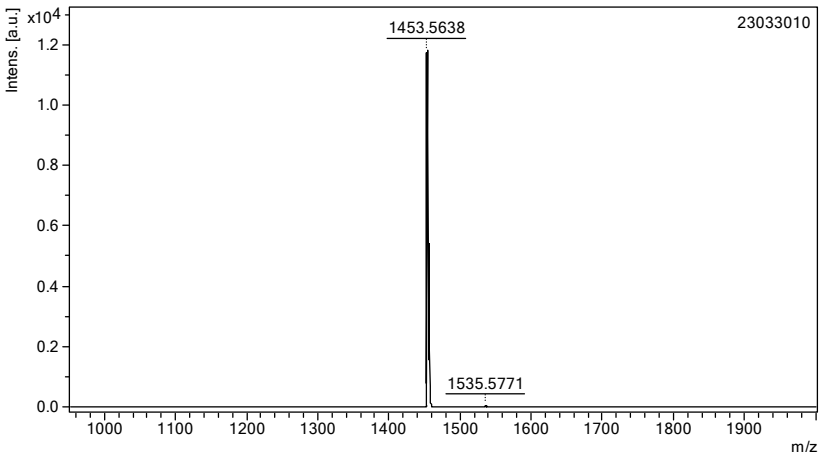


Figure S17 MALDI-TOF HRMS spectrum of **(DPP)$_2$TPA** (calcd for $C_{86}H_{95}N_5O_4S_6$:1453.5703)

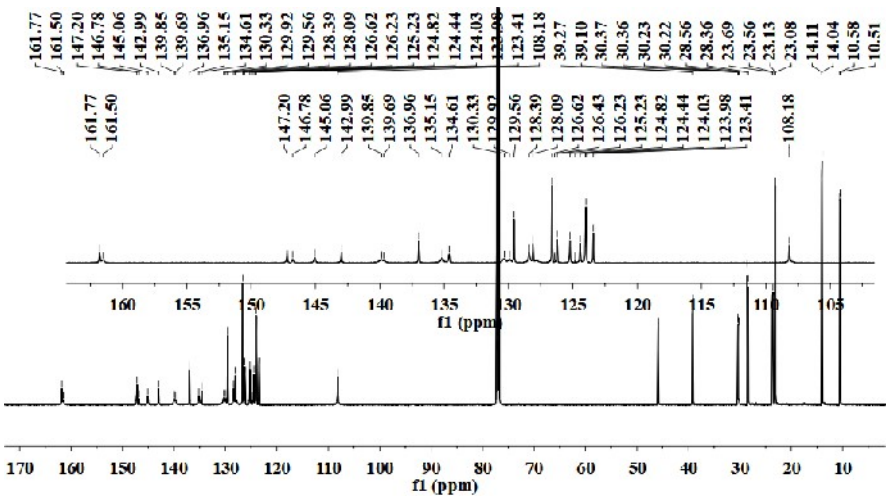


Figure S18 ^{13}C NMR spectrum of **$(DPP)_2TPA$**

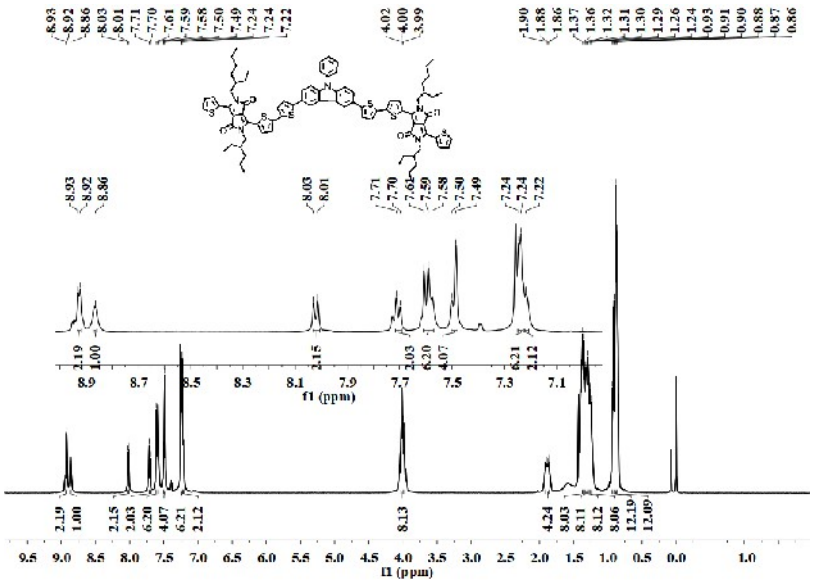


Figure S19 ^{1}H NMR spectrum of **compound $(DPP)_2PCZ$**

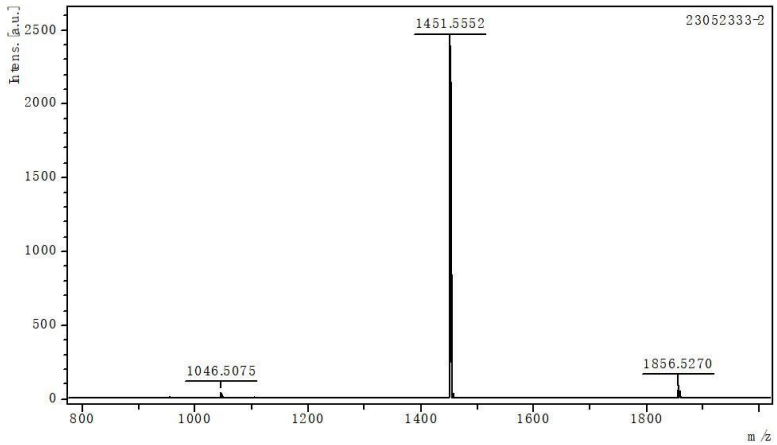


Figure S20 MALDI-TOF HRMS spectrum of **$(DPP)_2PCZ$** (calcd for $C_{86}H_{93}N_5O_4S_6$:1451.5546)

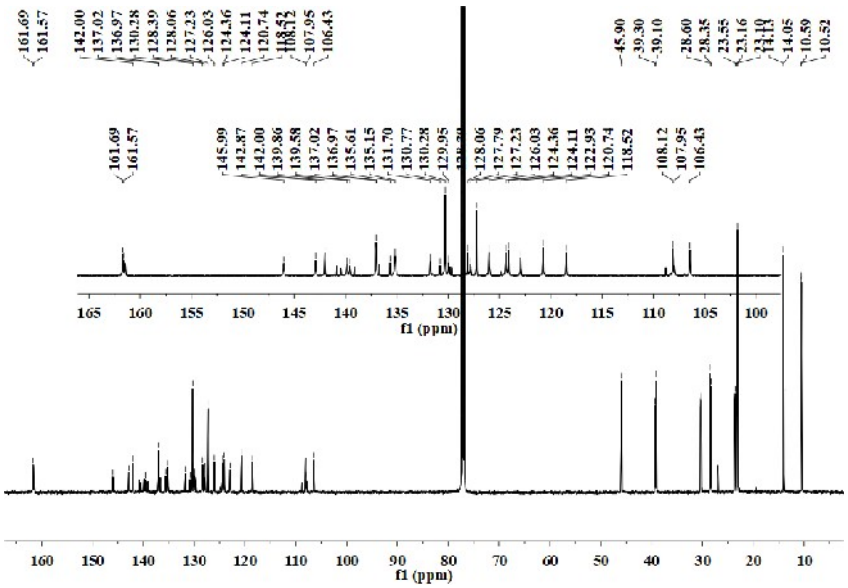


Figure S21 ^{13}C NMR spectrum of **$(DPP)_2PCZ$**

4. CV curve of Fc/Fc^+

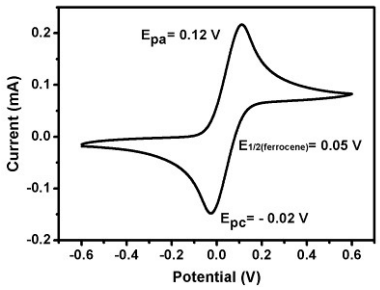


Figure S22 The CV curve of **Fc/Fc^+** in 0.1 M Bu_4NBF_4/CH_2Cl_2 solution at a scan rate of 100 mV s^{-1} under nitrogen.

5. Photovoltaic properties of reference molecules

Table S1 Photovoltaic data of organic active layer devices based on reference molecules[12,13]

Organic active layer of devices	Ratio(w:w)	μ_h ($cm^2\ V^{-1}\ s^{-1}$)	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
TPA-DPP-TPA:$PC_{71}BM$	1:1	--	0.74	1.32	0.25	0.25
	1:2	--	0.76	4.44	0.33	1.11
	1:3	--	0.76	5.31	0.33	1.34
	1:4	--	0.75	5.59	0.32	1.35
M1:$PC_{61}BM$	1:2	5.12×10^{-6}	0.49	6.60	0.46	1.48

6. Reference

1. F. Liu, H. Fan, Z. Zhang and X. Zhu, *ACS Appl. Mater. Interfaces*, 2016, **8**, 3661-3668.
2. K. S. Sun, X. Q. Tang, Y. L. Ran, R. G. He, W. Shen and M. Li, *Chem. Phys.*, 2018, **20**, 1664.
3. L. Tanguy, P. Malhotra, S. P. Singh, G. Brisard, G. D. Sharma and P. D. Harvey, *ACS Appl. Mater. Interfaces*, 2019, **11**, 28078-28087.
4. H. Wang, G. Chen, X. Xu, H. Chen and S. Ji, *Dyes and Pigments*, 2011, **88**, 358-365.
5. L. Wang, X. Yang, X. Wang and L. Sun, *Dyes and Pigments*, 2015, **113**, 581-587.
6. W. Lai, Q. He, D. Chen and W. Huang, *Chem. Lett.*, 2008, **37**, 986-987.
7. S. K. Jeon, B. Thirupathaiah, C. Kim, K. T. Lim, J. Y. Lee and S. Seo, *Dyes and Pigments*, 2015, **114**, 146-150.
8. J. Wang, X. Xu, J. Peng and C. Yao, *Org. Electron.*, 2017, 43, 1-8.
9. T. Kono, N. Masaki, M. Nishikawa, R. Tamura, H. Matsuzaki, M. Kimura and S. Mori, *ACS Appl. Mater.* Interfaces, 2016, **8**, 16677-16683.
10. T. Zhang, D. Liu, Q. Wang, R. Wang, H. Ren and J. Li, *J. Mater. Chem.*, 2011, **21**, 12969-12976.
11. W. Jiang, L. Duan, J. Qiao, G. F. Dong, D. Q. Zhang, L. D. Wang and Y. Qiu. *J. Mater. Chem.*, 2011, **21**, 4918-4926.
12. S. S. Bagde, H. Park, S. Yang, S. Jin and S. Lee, *Chem. Phys. Lett.*, 2015, **630**, 37-43.
13. C. Ji, L. Yin, K. Li, L. Wang, X. Jiang, Y. Sun and Y. Li, *RSC Adv.,* 2015, **5**, 31606-31614.