Electronic Supplementary Information

# Charge Density Modulation on Asymmetric Fused-Ring Acceptors for High-Efficiency Photovoltaic Solar Cells

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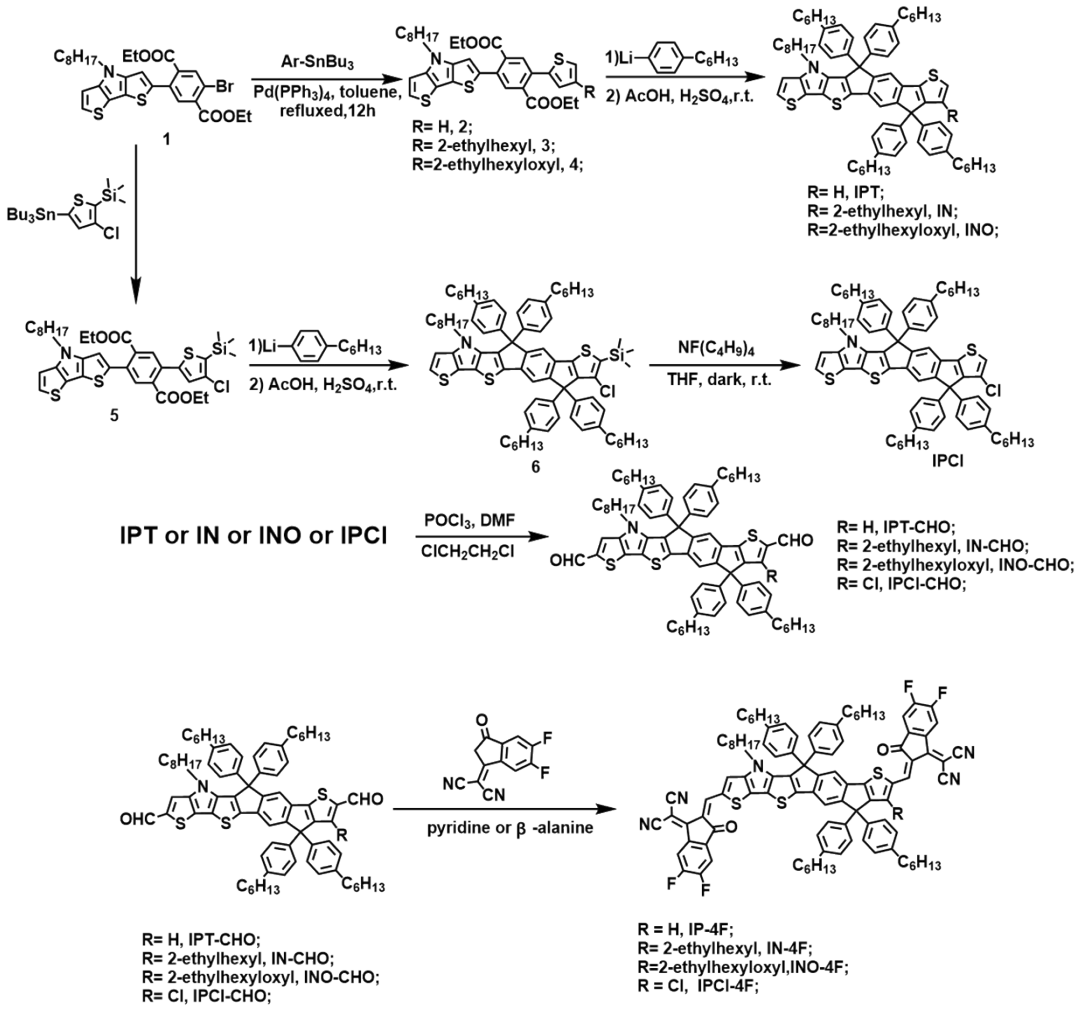
## 1. Materials and Synthesis

All commercially available chemicals and solvents were purchased from Aladdin, Sigma-Aldrich, or J&K Chemical Co., and used without further purification. 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile were purchased from Derthon Optoelectronic Materials Science Technology Co. LTD.. Non-fullerene IT-4F was purchased from SunaTech Inc., while polymer donor PM6 was purchased from Solarmer Materials Inc.. Compound **1** was synthesized according to ours previous work. Anhydrous THF and toluene were freshly distilled over sodium wire prior to use. Detailed synthesis for the intermediate compound for IN-4F, INO-4F, IP-4F and IPCl-4F are described in the following.




**Scheme S1.** Synthesis of IN-4F, INO-4F, IP-4F and IPCl-4F.

**Diethyl 2-(4-octyl-4H-dithieno[3,2-*b*:2',3'-*d*]pyrrol-2-yl)-5-(thiophen-2-yl)terephthalate (compound 2):** Towards a bottom flask was charged with compound **1**(0.57 g, 1 mmol), tributyl(4-thiophen-2-yl)stannane (0.47 g, 1.3 mmol), and toluene (12 mL), and purged with argon for 20 min. $Pd(PPh_3)_4$ (55.8 mg, 43.8 μmol) were added as catalyst subsequently under argon. The resultant mixture was refluxed for 12 h. After cooling to room temperature, the mixture was extracted three times with dichloromethane, dried with $MgSO_4$ and concentrated in vacuum. The crude product was purified by silica column chromatography, and Compound **2** (0.46 g) was obtained as a yellow oil in a yield of 80%. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.80 (s, 1H), 7.40 (d, $J$ = 3.8 Hz, 1H), 7.17 (d, $J$ = 5.3 Hz, 1H), 7.12 (d, $J$ = 2.3 Hz, 1H), 7.09

(m, 2H), 7.02 (d, *J* = 5.3 Hz, 1H), 4.29 - 4.18 (m, 6H), 1.90-1.87 (m, 2H), 1.37 - 1.22 (m, 10H), 1.17 (m, 6H), 0.88 (t, *J* = 6.9 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 168.36, 167.93, 144.95, 144.78, 140.71, 137.29, 134.26, 134.11, 134.09, 133.04, 131.80, 131.76, 127.49, 127.05, 126.56, 123.80, 115.98, 114.86, 111.10, 111.04, 61.87, 61.78, 47.59, 31.92, 30.53, 29.39, 29.27, 27.15, 22.74, 14.23, 14.09, 13.95.

**Diethyl 2-(4-octyl-4H-dithieno[3,2-*b*:2',3'-*d*]pyrrol-2-yl)-5-(4-(2-ethylhexyl) thiophen-2-yl)terephthalate (compound 3):** The synthetic method of compound **3** was similar to the synthesis of compound **2**. Compound **3** (0.55 g) was obtained as a yellow oil in a yield of 81%. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.80 (s, 1H), 7.16 (d, *J* = 5.3 Hz, 1H), 7.09 (s, 1H), 7.01 (d, *J* = 5.3 Hz, 1H), 6.96 (dd, *J* = 12.8, 1.4 Hz, 2H), 4.30 - 4.24 (m, 4H), 4.19 (t, *J* = 7.0 Hz, 2H), 2.58 (dd, *J* = 6.9, 2.9 Hz, 2H), 1.88 (t, *J* = 7.2 Hz, 2H), 1.37 - 1.26 (m, 19H), 1.20 (t, *J* = 7.1 Hz, 3H), 1.16 (d, *J* = 7.1 Hz, 3H), 0.93 (dd, *J* = 8.1, 5.1 Hz, 6H), 0.88 (d, *J* = 7.1 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 163.03, 162.82, 139.57, 139.42, 137.15, 134.83, 132.02, 128.69, 128.67, 128.65, 127.88, 126.18, 126.15, 123.49, 118.38, 116.81, 110.59, 109.51, 105.68, 105.64, 56.43, 56.37, 42.20, 35.12, 29.30, 27.26, 26.54, 25.14, 24.00, 23.89, 23.67, 21.77, 20.32, 17.83, 17.36, 8.93, 8.83, 8.70, 8.59, 5.60.

**Diethyl 2-(4-octyl-4H-dithieno[3,2-*b*:2',3'-*d*]pyrrol-2-yl)-5-(4-((2-ethylhexyl)oxyl)-thiophen-2-yl)terephthalate (compound 4):** The synthetic method of compound **4** was similar to the synthesis of compound **2**. Compound **3** (0.54 g) was obtained as a yellow oil in a yield of 78%. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.78 (s, 1H), 7.17 (d, *J* = 5.4 Hz, 1H), 7.08 (s, 1H), 7.01 (d, *J* = 5.2 Hz, 1H), 6.82 (d, *J* = 1.7 Hz, 1H), 6.31 (d, *J* = 1.8 Hz, 1H), 4.27 (dt, *J* = 14.1, 7.1 Hz, 4H), 4.19 (t, *J* = 7.1 Hz, 2H), 3.86 (d, *J* = 4.4 Hz, 2H), 1.87 (p, *J* = 6.8 Hz, 2H), 1.55 - 1.40 (m, 4H), 1.37 - 1.31 (m, 8H), 1.26-1.21 (m, 10H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.96 - 0.92 (m, 6H), 0.87 (t, *J* = 7.0 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 162.92, 162.52, 152.38, 139.56, 139.39, 133.75, 131.90, 128.97, 128.68, 128.52, 127.74, 126.33, 125.97, 118.40, 114.29, 110.61, 109.48, 105.72, 105.63, 92.92, 67.29, 56.47, 56.44, 42.22, 34.11, 26.52, 25.25,

25.14, 24.00, 23.88, 23.82, 21.76, 18.59, 17.81, 17.35, 8.86, 8.82, 8.69, 8.56, 5.87.

**Diethyl 2-(4-chloro-5-(trimethylsilyl)thiophen-2-yl)-5-(4-octyl-4*H*-dithieno[3,2-*b*:2',3'-*d*]pyrrol-2-yl)terephthalate (compound 5):** The synthetic method of compound **5** was similar to the synthesis of compound **2**. Compound **5** (0.50 g) was obtained as a yellow oil in a yield of 84%. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.74 (s, 1H), 7.18 (d, 1H), 7.08 (s, 1H), 7.04 (s, 1H), 7.01 (d, 1H), 4.27 (m, 4H), 4.19 (m, 2H), 1.87 (m, 2H), 1.35 - 1.23 (m, 10H), 1.18 (m, 6H), 0.87 (m, 3H), 0.42 (s, 9H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 168.26, 167.57, 145.24, 145.09, 144.85, 137.12, 134.83, 134.28, 133.69, 133.63, 132.13, 132.06, 131.57, 131.52, 129.47, 123.97, 116.20, 114.93, 111.26, 111.08, 61.98, 61.92, 47.67, 31.96, 30.58, 29.44, 29.32, 27.21, 22.78, 14.25, 14.14, 13.91.

**Compound IPT:** A solution of 4-hexyl-1-bromobenzene (1.3 g, 5.2 mmol) in anhydrous THF (30 mL) was placed at -78°C for 10 min, then n-BuLi (1.9 mL, 4.8 mmol, 2.5 M in hexane) was added to the solution slowly. After the mixture was stirred for 2 h at -78°C under nitrogen, compound 3 (410.0 mg, 0.7 mmol) in THF (5 mL) was then added to the solution in a minute. The reaction mixture was warmed to room temperature and stirred for 2 h. The solvent of the mixture was evaporated under vacuum. The light yellow residue was dissolved in octane (80 mL) and acetic acid (40 mL), then 0.1 mL concentrated $H_2SO_4$ was added dropwise. The solution was stirred at room temperature for 1 h before quenched by water. The organic layer was extracted with petroleum ether (2×100 mL) and washed with water for three times. The combined organic phase was dried over anhydrous $MgSO_4$. The solvent in the mixture was evaporated under vacuum, and the residue was purified by silica gel column chromatography (petroleum ether/dichloromethane=9:1 v/v) to obtain a viscous yellow liquid (700 mg, 91%). $^{1}$H NMR (500 MHz, $CD_2Cl_2$) δ 7.50 (s, 1H), 7.44 (s, 1H), 7.38 (d, $J$ = 8.1 Hz, 4H), 7.28 (d, $J$ = 4.9 Hz, 1H), 7.18 (d, $J$ = 8.1 Hz, 4H), 7.17 - 7.10 (m, 10H), 7.01 (d, $J$ = 4.9 Hz, 1H), 6.95 (d, $J$ = 5.2 Hz, 1H), 3.81 - 3.74 (m, 2H), 2.62 - 2.57 (m, 8H), 1.64 - 1.57 (m, 8H), 1.39 - 1.28 (m, 28H), 1.25 - 1.15 (m, 4H), 1.12 - 1.02 (m,

4H), 0.92 - 0.88 (m, 15H). $^{13}$C NMR (125 MHz, $CD_2Cl_2$) δ 156.79, 156.09, 153.92, 145.00, 142.44, 142.41, 142.07, 141.61, 140.69, 140.36, 139.88, 138.93, 136.19, 135.24, 129.06, 128.81, 128.78, 128.17, 127.88, 123.39, 123.29, 118.09, 116.43, 116.40, 116.28, 111.98, 63.10, 62.90, 48.70, 35.91, 32.34, 32.16, 31.91, 31.84, 30.76, 29.76, 29.71, 29.58, 29.56, 27.22, 23.11, 23.05, 14.34, 14.32.

**Compound IN:** The synthetic method of **IN** was similar to the synthesis of **IPT**. Compound **7** (0.67 g) was obtained as a yellow oil in a yield of 78%. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.34 - 7.28 (m, 5H), 7.18 (dd, *J* = 8.4, 2.2 Hz, 4H), 7.06 (dt, *J* = 7.9, 3.2 Hz, 9H), 6.88 (d, *J* = 5.3 Hz, 1H), 6.79 (s, 1H), 3.79 - 3.63 (m, 2H), 2.56 (m, 8H), 2.18 (d, *J* = 6.1 Hz, 2H), 1.60-1.56 (m, 8H), 1.34-1.28 (m, 24H), 1.20 - 1.11 (m, 6H), 1.10 - 0.93 (m, 12H), 0.89-0.86 (m, 18H), 0.81 (t, *J* = 7.3 Hz, 3H), 0.62 (t, *J* = 7.0 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 151.17, 150.71, 149.18, 138.99, 136.33, 136.28, 136.05, 135.31, 134.47, 134.41, 133.54, 132.97, 130.70, 129.74, 123.51, 123.39, 122.94, 122.77, 122.75, 117.18, 116.80, 112.17, 110.80, 110.12, 109.65, 106.21, 57.75, 57.09, 42.97, 32.60, 30.29, 30.27, 27.83, 26.81, 26.62, 26.46, 26.44, 26.09, 26.05, 26.02, 25.07, 24.02, 24.01, 23.89, 23.84, 23.35, 21.56, 19.89, 17.76, 17.38, 17.32, 8.85, 8.81, 5.11.

**Compound INO:** The synthetic method of **INO** was similar to the synthesis of **IPT**. Compound **8** (0.69 g, 79% yield) was obtained as a yellow oil. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.36 (s, 2H), 7.32 (dd, *J* = 8.4, 2.3 Hz, 4H), 7.20 (dd, *J* = 8.3, 1.5 Hz, 5H), 7.09 – 7.06 (m, 5H), 7.02 (d, *J* = 7.7 Hz, 4H), 6.89 (d, *J* = 5.3 Hz, 1H), 3.78 (dd, *J* = 4.7, 1.7 Hz, 2H), 3.76 - 3.69 (m, 2H), 2.56 (m, 8H), 1.61 - 1.56 (m, 8H), 1.34 - 1.17 (m, 41H), 1.05-1.02 (m, 4H), 0.89 - 0.86 (m, 18H), 0.80 (t, *J* = 7.5 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 150.72, 148.49, 148.11, 139.04, 138.71, 136.37, 135.78, 135.36, 135.18, 134.91, 134.69, 134.38, 133.47, 130.81, 129.82, 123.52, 123.23, 123.20, 122.97, 122.51, 122.49, 117.29, 112.32, 110.80, 110.42, 106.22, 92.31, 65.93, 58.00, 57.12, 48.16, 42.98, 34.25, 30.33, 30.28, 26.64, 26.50, 26.45, 26.09, 26.06, 26.02, 25.44, 25.08, 24.05, 24.02, 23.94, 23.91, 23.87, 21.58, 18.60, 17.75, 17.40, 17.34, 8.85,

8.83, 6.00.

**Compound IPCl:** A solution of 4-hexyl-1-bromobenzene (1.2 g, 4.7 mmol) in anhydrous THF (40 mL) was placed at -78°C for 10 min, then *n*-BuLi (1.8 mL, 4.4 mmol, 2.5 M in hexane) was added to the solution slowly. After the mixture was stirred for 2 h at -78°C under nitrogen, compound **5** (440.0 mg, 628.2 μmol) in THF (5 mL) was then added to the solution in a minute. The reaction mixture was warmed to room temperature and stirred for 2 h. The solvent of the mixture was evaporated under vacuum. The light yellow residue was dissolved in octane (80 mL) and acetic acid (40 mL), then 0.1 mL concentrated $H_2SO_4$ was added dropwise. The solution was stirred at room temperature for 1 h before quenched by water. The organic layer was extracted with petroleum ether (2×60 mL) and washed with water for two times. The combined organic phase was dried over anhydrous $MgSO_4$. The solvent in the mixture was evaporated under vacuum, and the residue was dissolved in anhydrous THF (50 mL). Then several drops of $Bu_4NF$ was slowly added to the solution at room temperature. The mixture was stirred about 5 min before quenched by water. The organic layer was extracted with petroleum ether (2×60 mL) and washed with water for two times. The combined organic phase was dried over anhydrous $MgSO_4$. The solvent in the mixture was evaporated under vacuum, and the residue was purified by silica gel column chromatography (petroleum ether/dichloromethane=9:1 v/v) to obtain a viscous yellow liquid (650 mg, 90%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.35 - 7.30 (m, 5H), 7.20 (d, 4H), 7.10 (m, 9H), 7.04 (s, 1H), 6.91 (d, 1H), 3.74 - 3.68 (m, 2H), 2.59 - 2.53 (m, 8H), 1.62 - 1.54 (m, 8H), 1.30 (m, 28H), 1.16 (m, 4H), 1.08 - 0.97 (m, 4H), 0.87 (m, 15H). $^{13}$C NMR (125 MHz, $CD_2Cl_2$) δ 156.92, 155.64, 150.11, 145.18, 143.12, 142.53, 142.44, 141.03, 140.15, 139.83, 139.41, 138.81, 137.39, 134.32, 129.09, 128.88, 128.58, 123.55, 122.94, 122.03, 118.48, 116.45, 116.14, 115.64, 112.00, 64.06, 62.94, 48.74, 35.99, 35.94, 32.37, 32.19, 31.88, 31.86, 30.78, 29.79, 29.74, 29.65, 29.61, 27.26, 23.14, 23.08, 14.38, 14.35.

**Compound IPT-CHO:** A mixed solution of **IPT** (600.0 mg, 538.2 μmol) in

anhydrous DMF (4 mL) and anhydrous 1,2-dichloroethane (12 mL) was placed at 0°C for 10 min, then phosphorus oxychloride ($POCl_3$, 0.5 mL) was slowly added to the solution under nitrogen. After being stirred at 0°C for several minutes, the mixture was warmed to 70°C for 3 h. The reaction mixture was poured into a solution of $Na_2CO_3$ (21.2 g, 0.2 mol) in water (200 mL). The mixture was vigorously stirred at room temperature for 6 h. The organics were extracted with a mixed solvent of ethyl acetate and petroleum ether (1:9, v/v). The combined organic layer was washed with water and dried with anhydrous $Mg_2SO_4$. The solvent was evaporated under vacuum, and the residue was purified by silica gel column chromatography (petroleum ether/dichloromethane=1:1 v/v) to obtain an orange solid (570 mg, 90%). $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 9.85 (s, 1H), 9.81 (s, 1H), 7.67 (s, 2H), 7.59 (s, 1H), 7.54 (s, 1H), 7.37 (d, J = 8.0 Hz, 4H), 7.19 - 7.10 (m, 12H), 3.82 (t, J = 8.1 Hz, 2H), 2.59 (m, 8H), 1.63 - 1.56 (m, 8H), 1.41 - 1.27 (m, 28H), 1.24 - 1.03 (m, 8H), 0.92 - 0.87 (m, 15H). $^{13}$C NMR (125 MHz, $CD_2Cl_2$) δ 183.05, 183.02, 157.77, 156.68, 155.39, 151.00, 146.27, 145.30, 144.59, 143.91, 142.91, 142.60, 141.29, 140.95, 140.75, 137.99, 137.90, 134.72, 132.35, 129.02, 128.97, 128.06, 124.30, 120.46, 119.10, 118.17, 117.15, 63.37, 63.08, 48.83, 35.88, 32.30, 32.13, 31.85, 31.78, 30.81, 29.73, 29.67, 29.55, 29.51, 27.19, 23.09, 23.03, 14.32, 14.30. MALDI-TOF MS (m/z): $[M+H]^+$ calcd. for $C_{78}H_{91}NO_2S_3$, 1169.6212; found, 1169.6205.

**Compound IN-CHO:** The synthetic method of **IN-CHO** was similar as for **IPT-CHO**. Compound **11** (0.55 g) was obtained as an orange oil in a yield of 85%. $^1$H NMR (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 9.86 (s, 1H), 7.54 (d, *J* = 5.2 Hz, 2H), 7.43 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 4H), 7.22 (dd, *J* = 8.2, 5.5 Hz, 4H), 7.13 (td, *J* = 6.5, 3.3 Hz, 8H), 3.84 - 3.76 (m, 2H), 2.61 (m, 10H), 1.62 (m, 8H), 1.34 (m, 30H), 1.21 (m, 4H), 1.11 - 1.02 (m, 6H), 0.96 - 0.87 (m, 20H), 0.80 (t, *J* = 7.3 Hz, 3H), 0.62 (t, *J* = 7.4 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 177.39, 177.17, 153.40, 151.73, 150.47, 146.26, 142.88, 140.16, 138.80, 138.43, 136.99, 136.85, 135.67, 134.90, 134.80, 133.42, 133.37, 132.60, 132.51, 132.47, 128.85, 123.39, 123.35, 123.28, 123.19, 119.25, 113.26,

111.94, 110.34, 58.22, 57.28, 43.12, 33.92, 30.31, 30.28, 26.85, 26.63, 26.48, 26.45, 26.36, 26.16, 26.09, 26.01, 25.17, 24.46, 24.04, 24.02, 23.91, 23.89, 23.87, 23.39, 21.57, 19.72, 17.66, 17.40, 17.35, 8.85, 5.27. MALDI-TOF MS (*m*/*z*): $[M+H]^+$ calcd. for $C_{86}H_{107}NO_2S_3$, 1281.7464; found, 1281.7461.

**Compound INO-CHO**: The synthetic method of **INO-CHO** was similar as for **IPT-CHO**. Compound **INO-CHO** (0.55 g) was obtained as an orange oil in a yield of 85%. $^1$H NMR (500 MHz, $CDCl_3$) δ 10.01 (s, 1H), 9.83 (s, 1H), 7.50 (s, 1H), 7.48 (s, 1H), 7.36 (s, 1H), 7.28 (dd, *J* = 8.1, 1.5 Hz, 4H), 7.17 (d, *J* = 8.1 Hz, 4H), 7.10 (d, *J* = 6.8 Hz, 4H), 7.06 (d, *J* = 6.7 Hz, 4H), 3.92 (d, *J* = 5.4 Hz, 2H), 3.78 - 3.72 (m, 2H), 2.63 - 2.49 (m, 8H), 1.57 (dd, *J* = 11.6, 5.0 Hz, 8H), 1.32 - 1.19 (m, 44H), 0.88 - 0.86 (m, 19H), 0.75 (t, *J* = 7.5 Hz, 3H). $^{13}$C NMR (125 MHz, $CDCl_3$) δ 182.95, 181.35, 158.86, 157.24, 156.72, 150.81, 146.35, 145.49, 144.32, 143.89, 142.55, 142.17, 140.58, 140.35, 139.20, 138.14, 137.90, 134.61, 128.85, 128.80, 128.66, 128.61, 128.44, 128.42, 127.22, 124.74, 118.87, 117.54, 116.55, 78.40, 64.04, 62.81, 48.63, 40.39, 35.82, 35.79, 32.13, 31.99, 31.96, 31.78, 31.61, 31.59, 31.51, 30.69, 30.47, 30.35, 29.97, 29.55, 29.52, 29.42, 29.38, 29.24, 27.08, 23.51, 23.21, 22.91, 22.86, 14.37, 14.35, 14.33, 11.29. MALDI-TOF MS (*m*/*z*): $[M+H]^+$ calcd. for $C_{86}H_{107}NO_3S_3$, 1297.7413; found, 1297.7411.

**Compound IPCl-CHO:** The synthetic method of **IPCl-CHO** was similar as for **IPT-CHO**. Compound **IPCl-CHO** (0.55 g) was obtained as an orange oil in a yield of 87%. $^1$H NMR (500 MHz, $CD_2Cl_2$) δ 9.95 (s, 1H), 9.85 (s, 1H), 7.63 (s, 1H), 7.58 (s, 1H), 7.49 (s, 1H), 7.34 (d, 4H), 7.22 (d, 4H), 7.14 (m, 8H), 3.83 - 3.77 (m, 2H), 2.59 (m, 8H), 1.60 (m, 8H), 1.39 - 1.26 (m, 28H), 1.19 (m, 4H), 1.13 - 1.00 (m, 4H), 0.89 (m, 15H). $^{13}$C NMR (125 MHz, $CD_2Cl_2$) δ 183.04, 181.77, 157.85, 157.28, 151.74, 151.14, 145.02, 144.69, 143.79, 142.97, 142.92, 141.25, 140.93, 138.98, 138.27, 137.83, 137.39, 133.83, 131.37, 129.05, 128.96, 128.78, 128.74, 124.21, 120.44, 119.37, 117.87, 116.41, 64.35, 63.07, 48.83, 35.92, 35.88, 32.30, 32.13, 31.80, 31.78, 30.80, 29.72, 29.67, 29.56, 27.19, 23.09, 23.03, 14.31, 14.29. MALDI-TOF MS (*m*/*z*): $[M+H]^+$

calcd. for $C_{78}H_{90}ClNO_2S_3$, 1203.5822; found, 1203.5817.

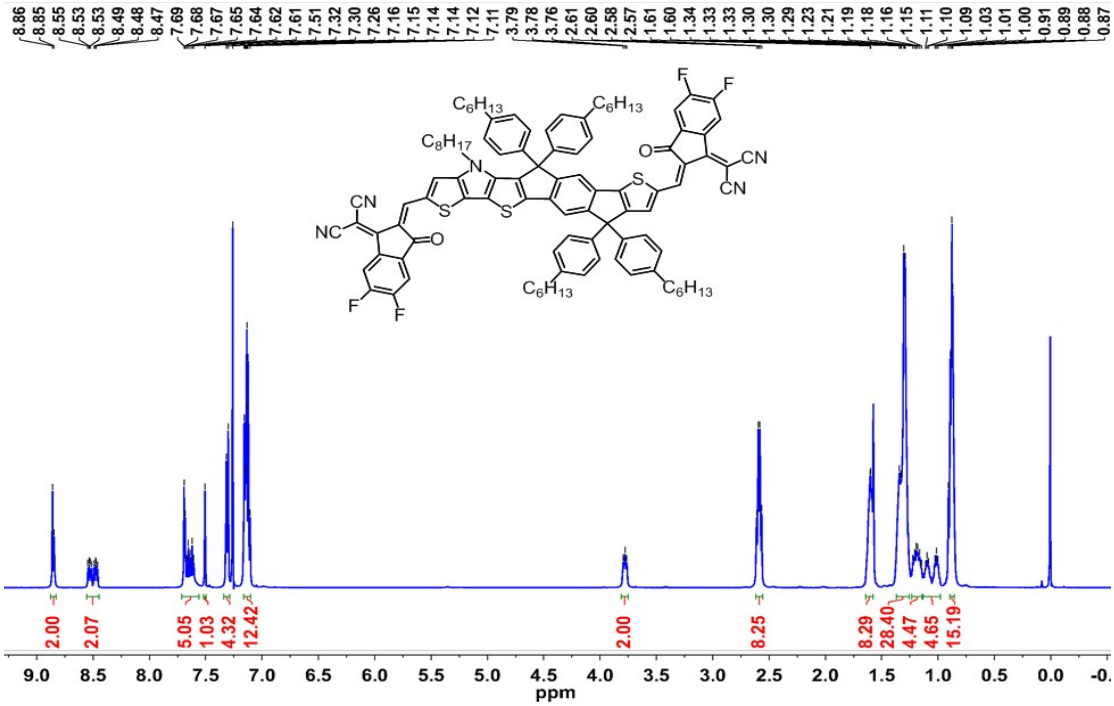



**Figure S1.** $^1$H NMR of **IPT-4F**.

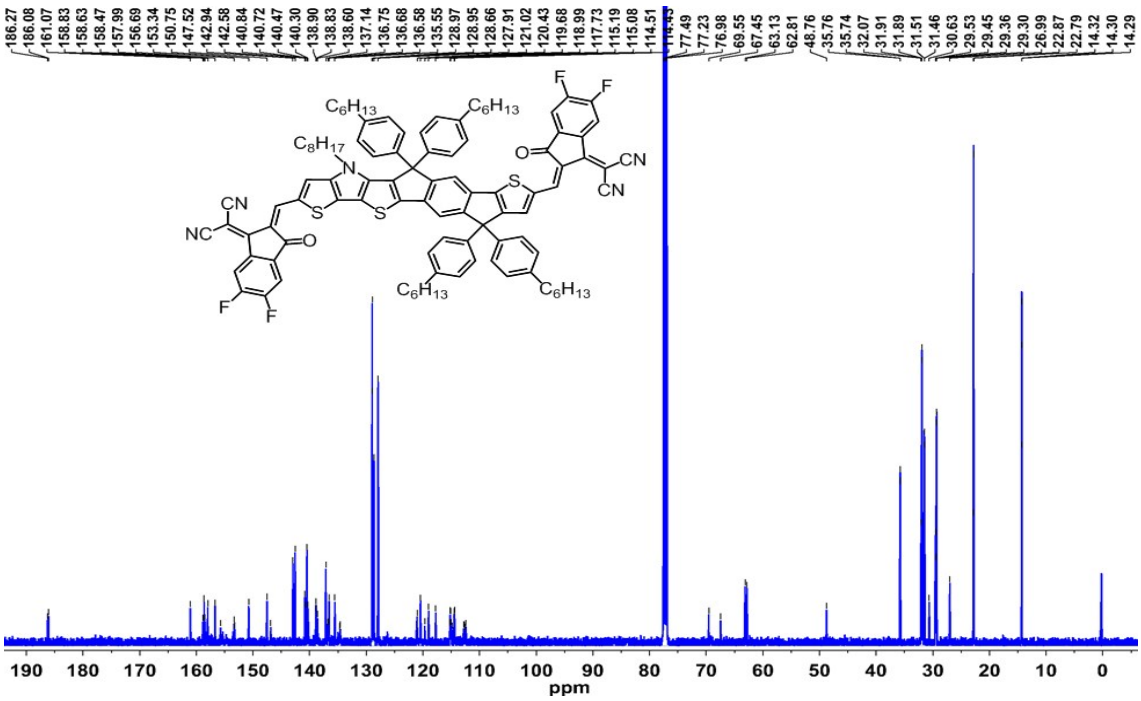



**Figure S2.** $^{13}$C NMR of **IPT-4F**.

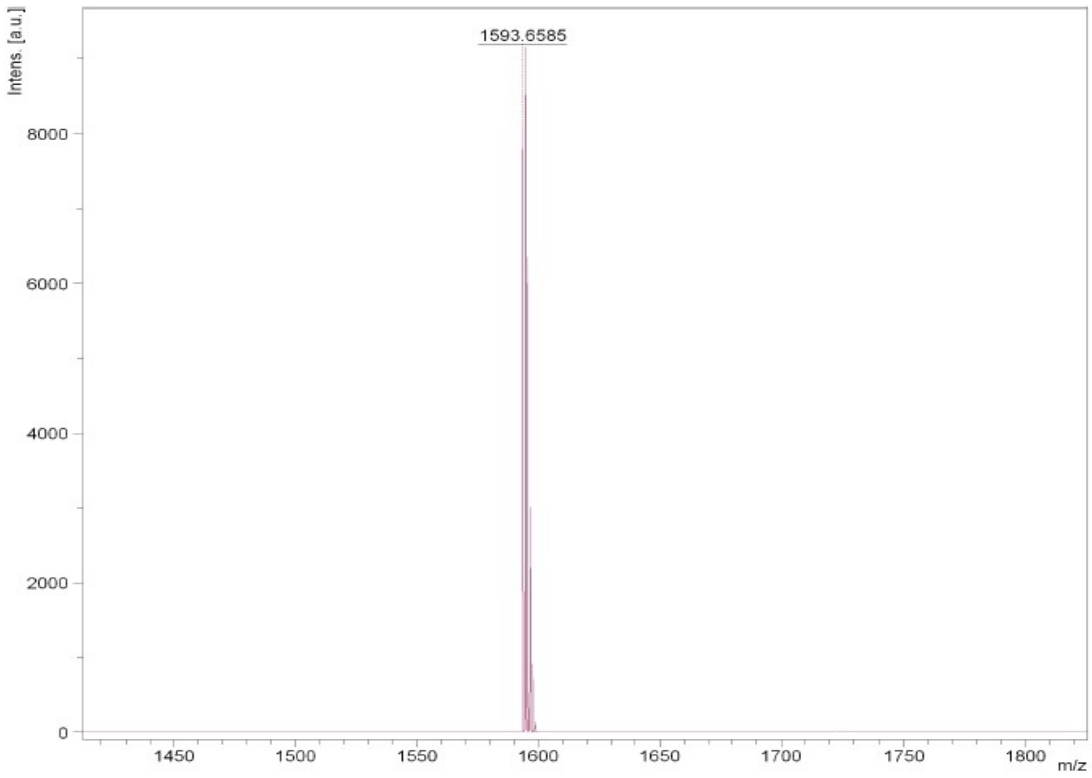



**Figure S3.** Mass spectra of **IPT-4F**.

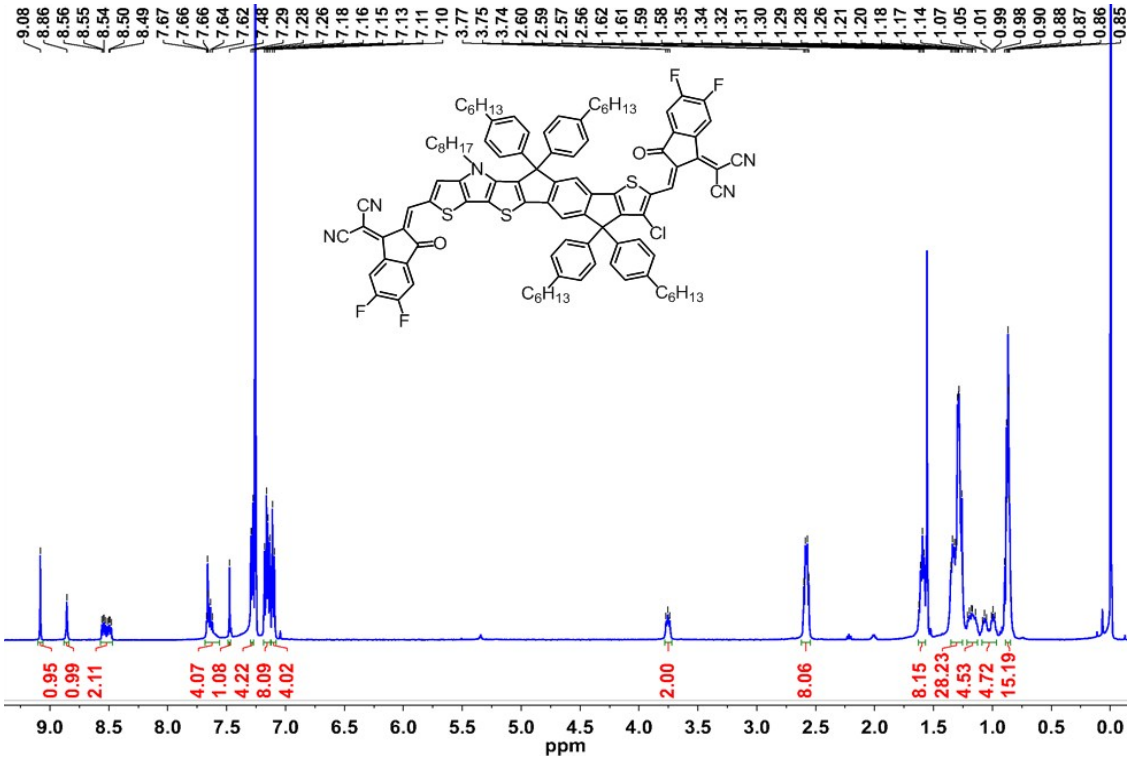



**Figure S4.** $^{1}$H NMR of **IPCl-4F**.

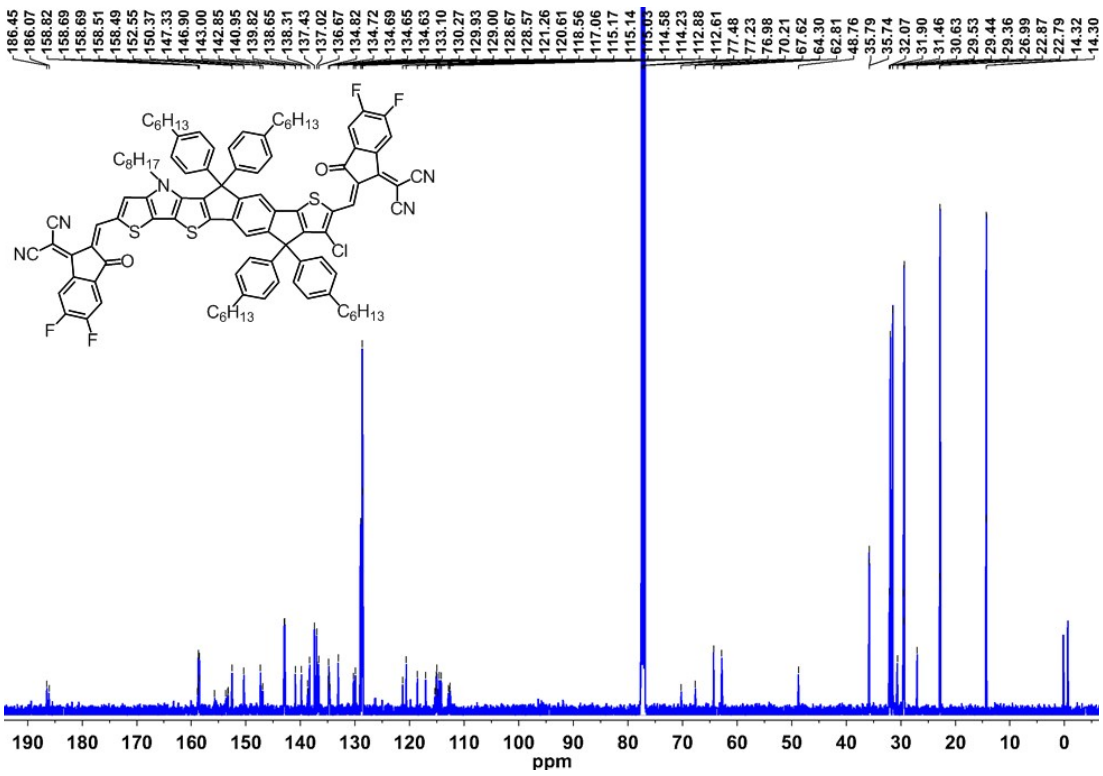



**Figure S5.** $^{13}$C NMR of **IPCl-4F**.

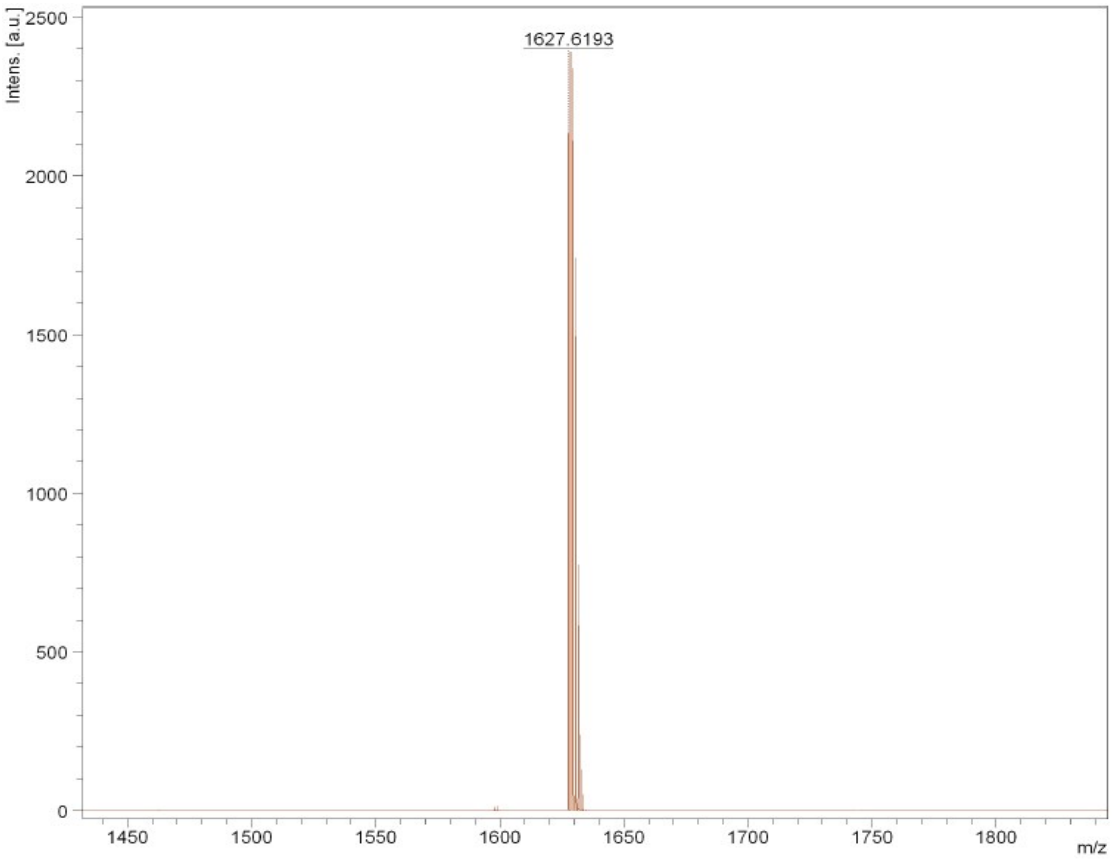



**Figure S6.** Mass spectra of **IPCl-4F**.

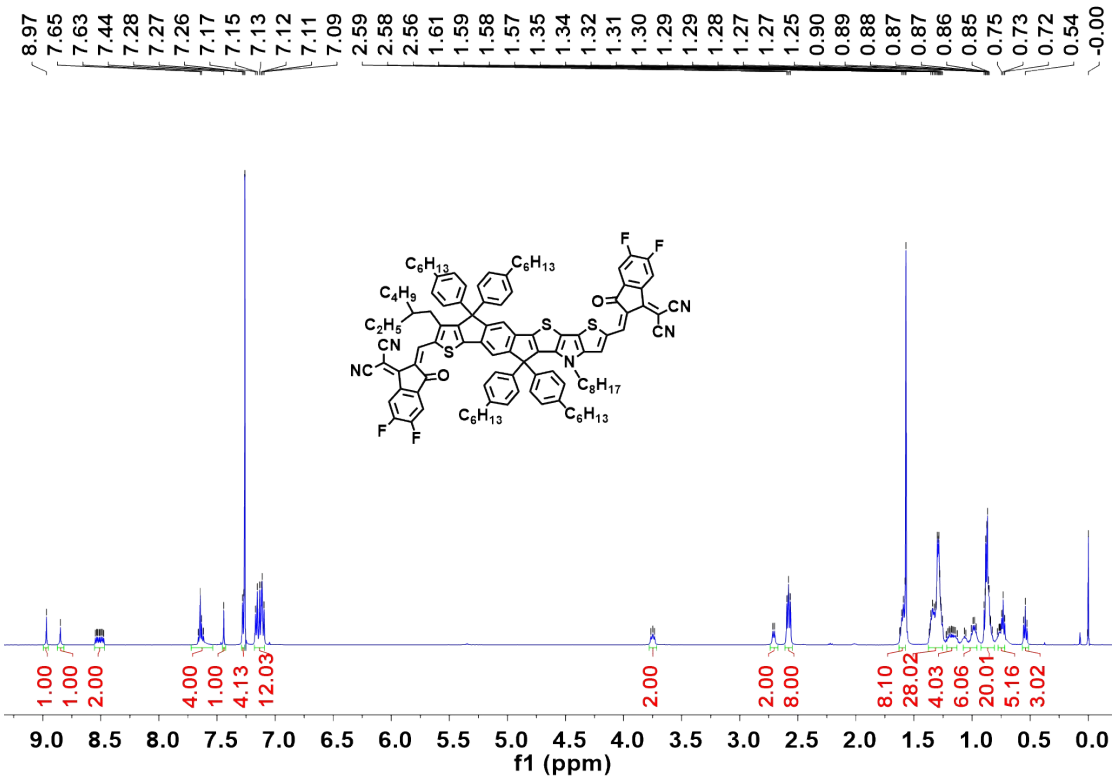


**Figure S7.** $^{1}$H NMR of **IN-4F**.

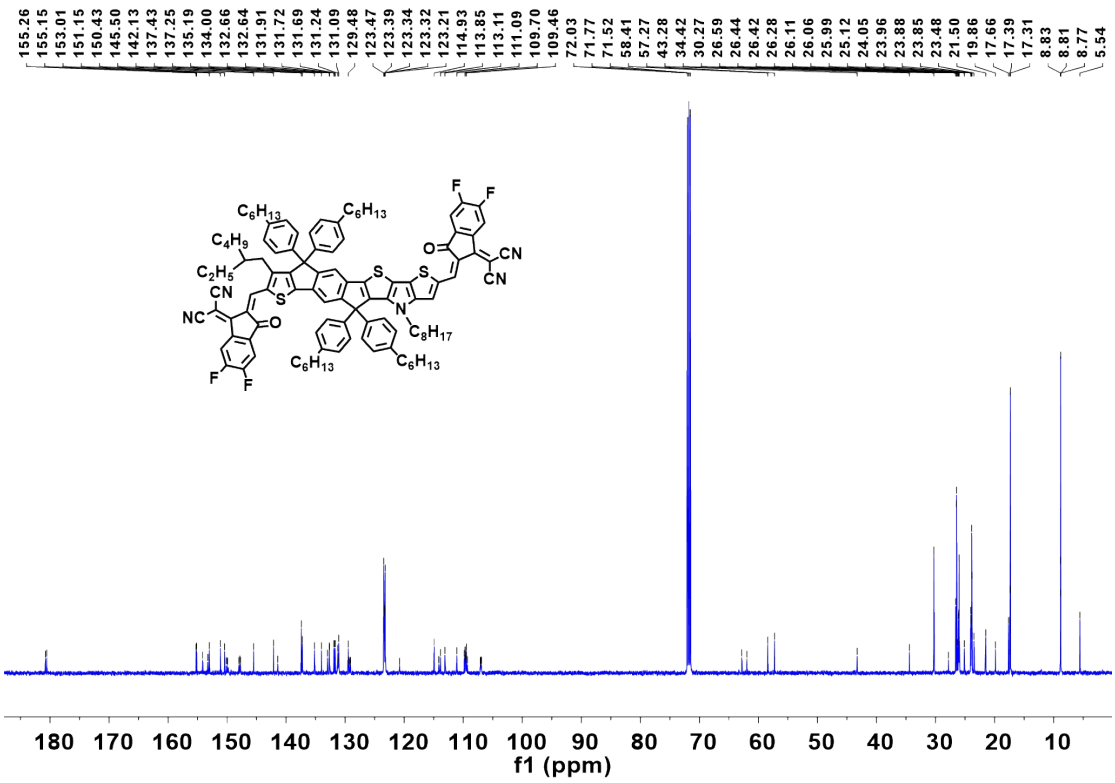



**Figure S8.** $^{13}$C NMR of **IN-4F**.

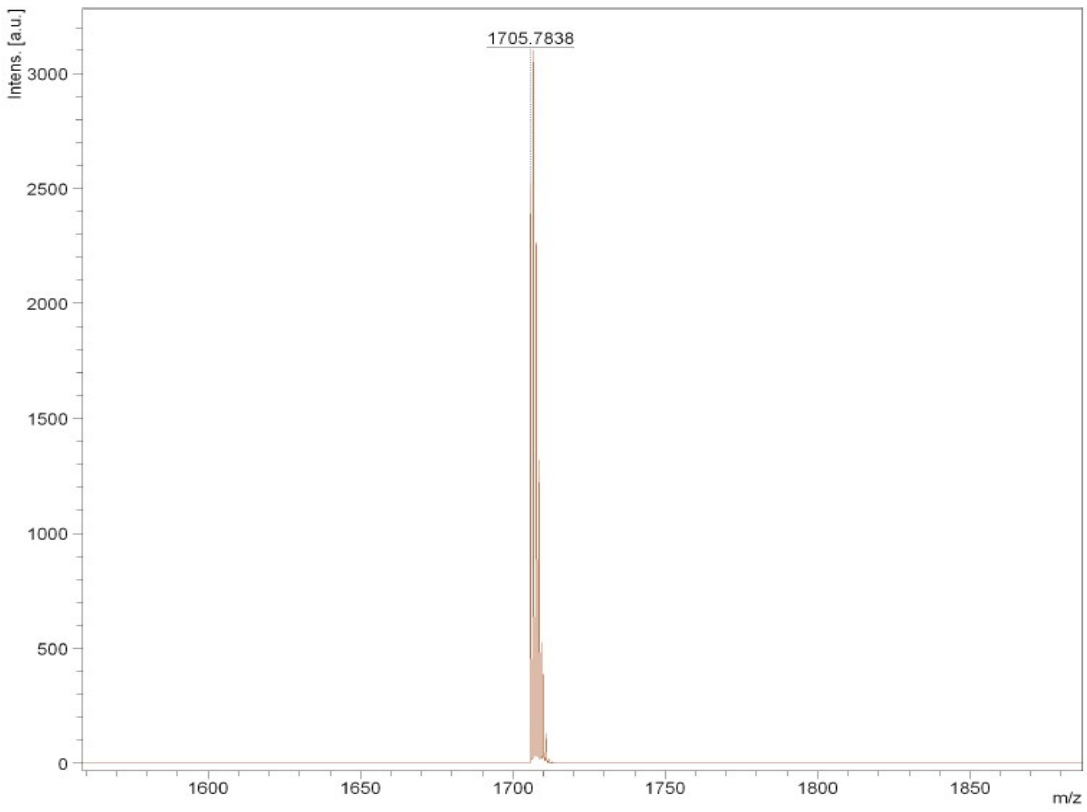



**Figure S9.** Mass spectra of **IN-4F**.

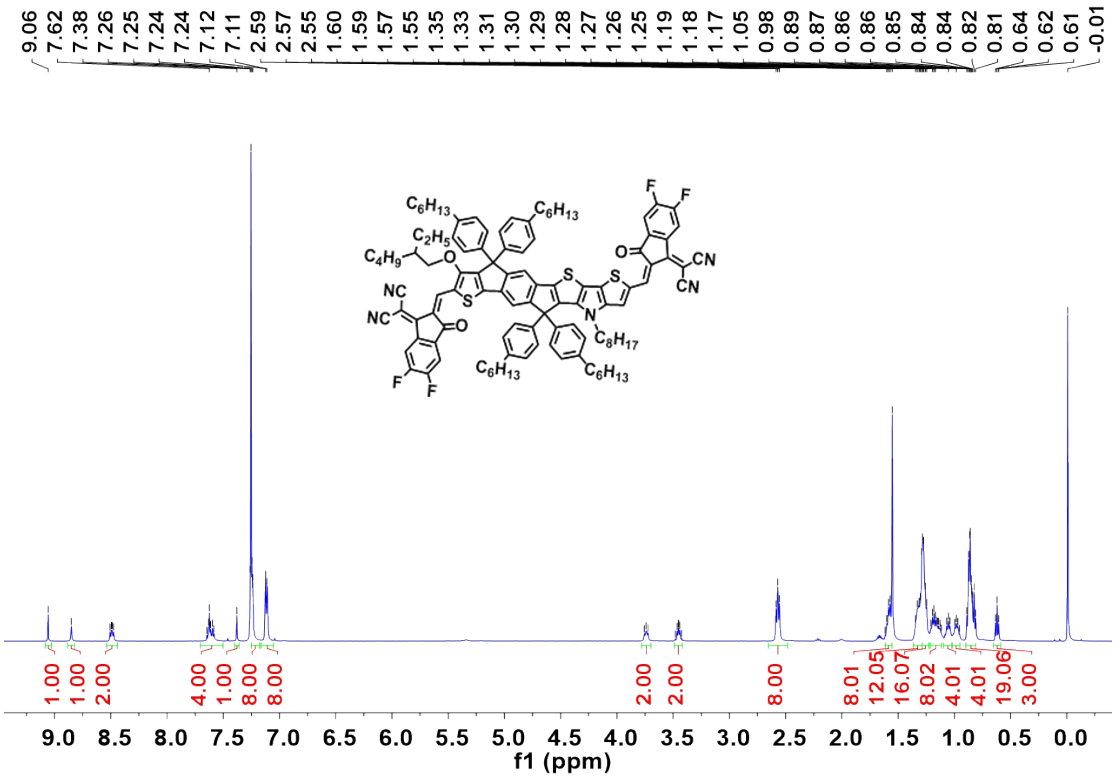



**Figure S10.** $^{1}$H NMR of **INO-4F**.

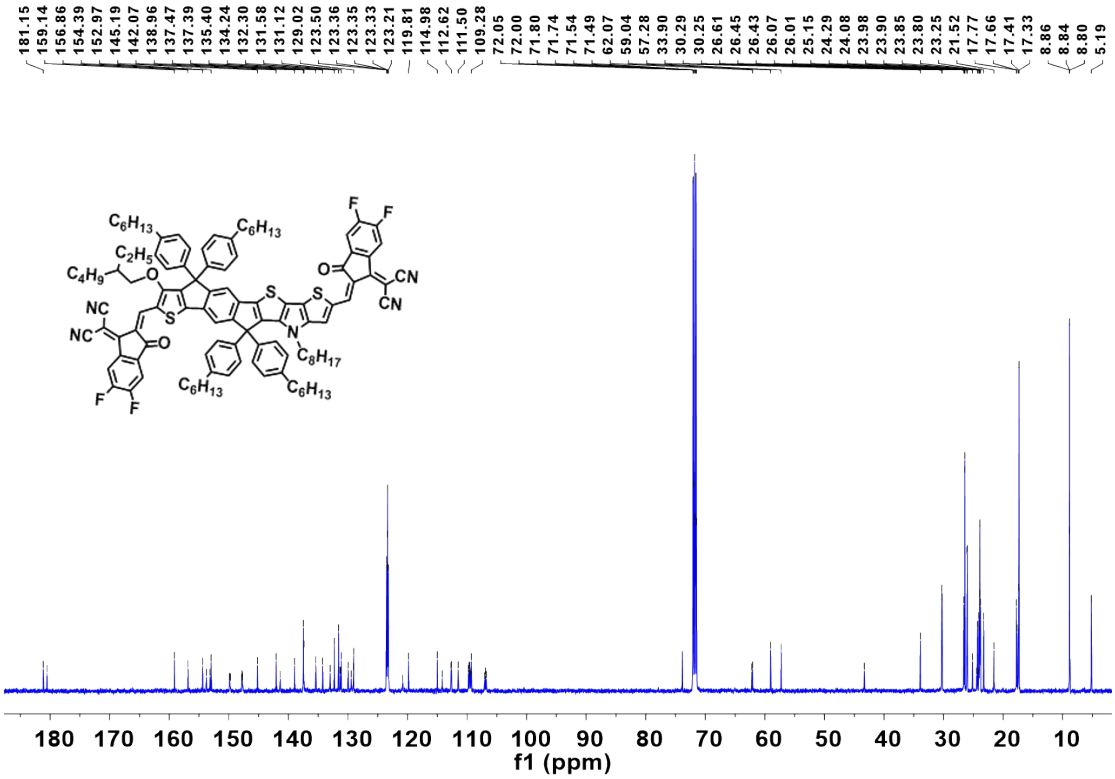



**Figure S11.** $^{13}$C NMR of **INO-4F**.

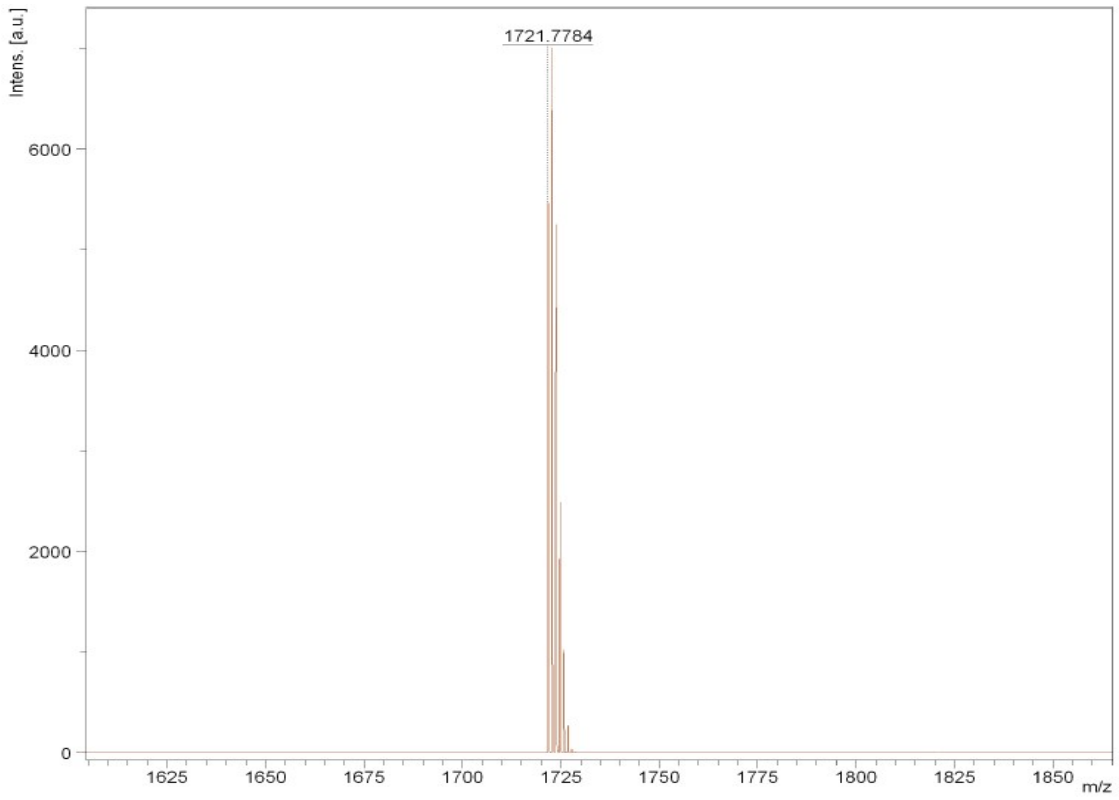



**Figure S12.** Mass spectra of **INO-4F**.

## 2. Measurement and Characterization

Chemical structure was determined by $^{1}H$ and $^{13}C$ NMR spectra using Bruker AVANCE 500 MHz spectrometer, and mass spectra on GCT-MS EI and Bruker Daltonics Biflex III MALDI-TOF Analyzer in the MALDI mode. Ultraviolet-visible absorption spectra were recorded on a UV-Vis instrument Evolution 220 (Thermo Fisher). The electrochemical cyclic voltammetry (CV) was conducted on an electrochemical workstation (CHI760E Chenhua Shanghai) with Pt plate as working electrode, Pt slice as counter electrode, and Ag/AgCl electrode as reference electrode in tetrabutylammonium hexafluorophosphate ($Bu_4NPF_6$, 0.1 M) acetonitrile solutions at a scan rate of 50 mV $s^{-1}$. Ferrocene/ferrocenium ($Fc/Fc^{+}$) was used as the internal

standard (the energy level of $Fc/Fc^+$ is -4.8 eV under vacuum), and the formal potential of $Fc/Fc^+$ was measured as 0.35 V vs. Ag/AgCl electrode. Thermogravimetric analysis (TGA) was conducted under nitrogen atmosphere at a heating rate of 20 °C $min^{-1}$ from 50 °C to 800 ℃. The instrument type was TGA/SDTA851E (Mettler Toledo).

## 3.TGA Curve and Absorption Spectra of IPT-Based Acceptors

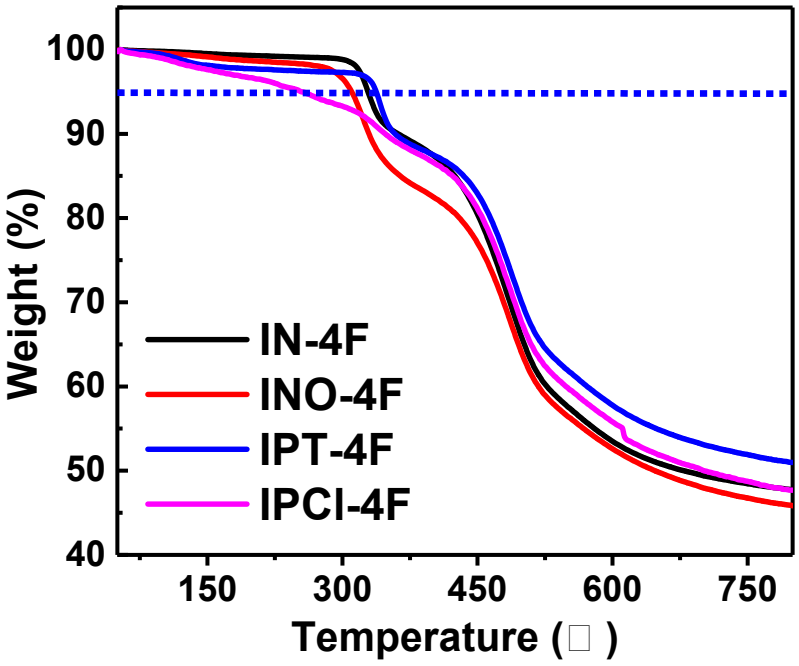



**Figure S13.** TGA curves of **IN-4F**, **INO-4F**, **IPT-4F** and **IPCl-4F**.

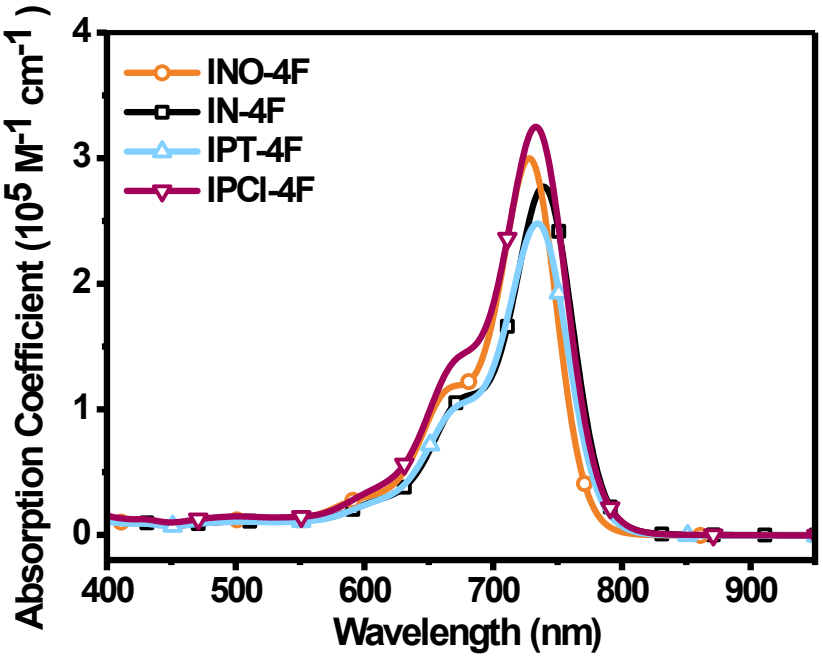



**Figure S14**. Absorption spectra of the IPT-based acceptors in solution.

## 4. Device Data

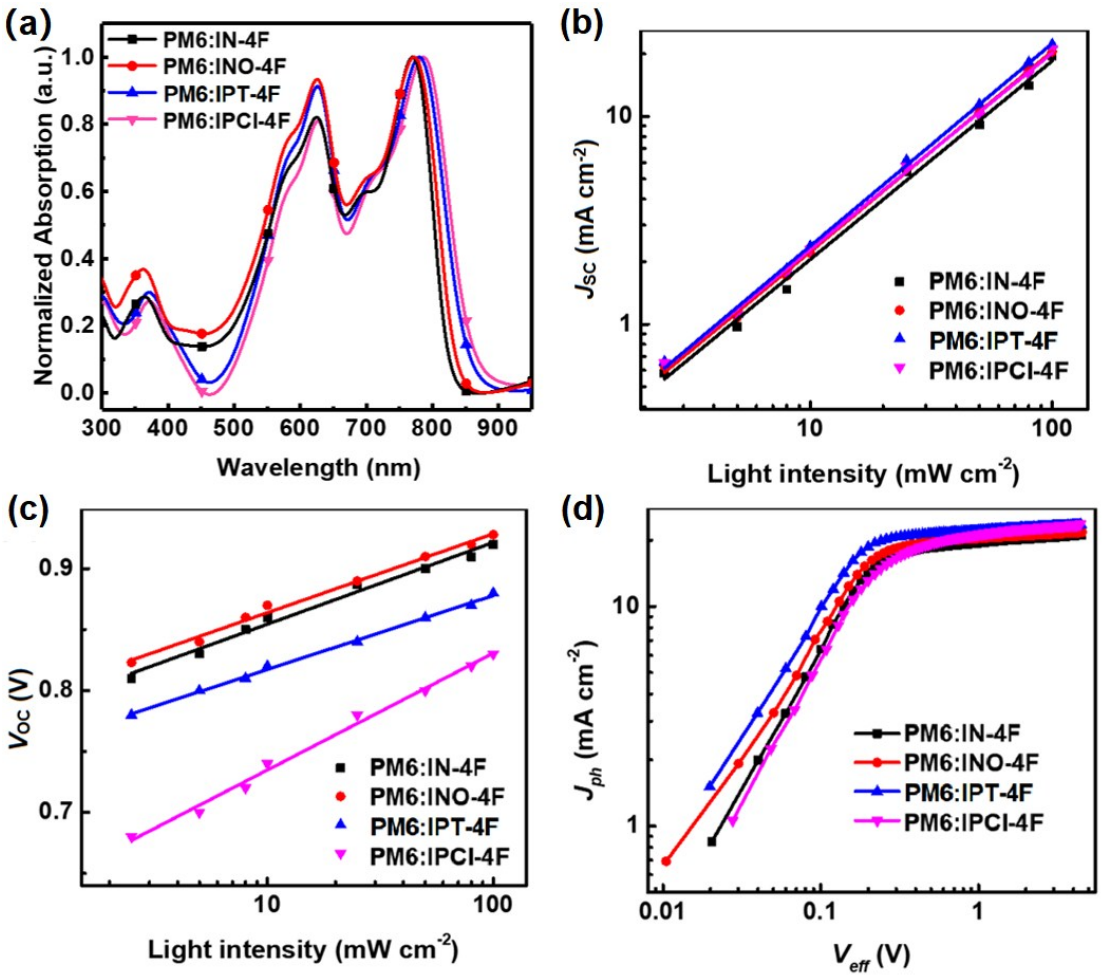



**Figure S15**. (a) Absorption spectra of the optimized blended films. (c) $J_{SC}$ versus light intensity, (c) $V_{OC}$ versus light intensity of the optimized devices, and (d) $J_{ph}$ versus $V_{eff}$.