Supplementary Information (SI) for ChemComm.

Dual Acceptor–Clamped Diketopyrrolopyrrole for High Performance Monopolar n-Type transistors

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1. General information

The DPP tin reagent was commercially available and used as received. The other chemicals were purchased from Alfa-Aesar, Sigma-Aldrich, Adamas-beta, and were used without further purification. Solvents were purified and dried according to standard methods prior to use. ^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker DMX-600NMR Spectrometer. High-resolution mass spectra (HRMS) were recorded on a BRUKER BIFLEX III Mass Spectrometer System operating in a APCI mode. UV-vis absorption spectra were recorded on a Shimadzu UV-2600 spectrophotometer (Japan). The thermal stability of DNTDPP was tested with a thermogravimetric analyzer (Q50 from TA Company, USA). During the experiments, the heating rate was 10 °C/min, the nitrogen flow rate was 50 mL/min, and the temperature range was 30–600 °C. The differential scanning calorimetry (DSC) measurements were obtained on a setup of DSC3500 Sirius with a heating rate of 10 °C/min under nitrogen atmosphere. Cyclic voltammetric measurements (CV) were carried out in a conventional three-electrode cell using glassy carbon as working electrodes of 2 mm diameter, a platinum wire as counter electrode, and an Ag/AgCl reference electrode on a computer-controlled CHI660E instruments at room temperature.

2. Synthesis of DNTDPP

Compound 1 was synthesized following the procedure reported previously, except that the amount of N-bromosuccinimide (NBS) was reduced from 8.4 equivalents to 2.5 equivalents.[1] The filtrated crude product was used directly without further purification.

Synthesis of compound 2. The boronic ester (686 mg, 1.4 mmol), compound 1 (358 mg, 1 mmol), K_2CO_3 (179.4 mg, 1.3 mmol) and $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol) were dissolved in 15 mL degassed 1,4-dioxane aqueous solution (1,4-dioxane : H_2O = 4 : 1), followed by nitrogen flashed 3 times. The mixture was heated to 90 °C for 18 h, and then cooled to room temperature. After dissolution in dichloromethane, the resulting solution was extracted with water. Then, the solvent was removed, and the residue was purified by chromatography (eluent: DCM/hexane=1:3) to give compound 2 as yellow solid (yield: 49%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.31 (s, 1H), 7.91 (d, *J* = 10.6 Hz, 1H), 7.24 (s, 1H), 2.68 (d, *J* = 6.8 Hz, 2H), 1.72 (p, *J* = 6.1 Hz, 1H), 1.38 – 1.20 (m, 32H), 0.85 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.36, 159.62, 156.43, 154.64, 152.65, 147.06, 142.55, 134.07, 131.04, 125.91, 118.67, 115.29, 114.87, 106.09, 39.10, 35.03, 33.43, 33.41, 31.97, 30.12, 30.11, 29.76, 29.72, 29.42, 26.73, 26.72, 22.73, 14.16. HR-MS: m/z [MH$^+$] calculated for $C_{34}H_{45}F_2N_4S_3^+$: 643.2752, found: 643.2749.

Synthesis of compound 3. The compound 2 (300 mg, 0.47 mmol), 1,3-dibromo-5,5-dimethylhydantoin(80 mg, 0.28 mmol), and 3-nitrobenzenesulfonic acid (12.6 mg, 0.06 mmol)were dissolved in 4 mL hexafluoroisopropanol. The mixture was subjected to reflux in darkness for 24 hours, and then cooled to room temperature. After dissolution in dichloromethane, the resulting solution was extracted with water. Then, the solvent was removed, and the residue was purified by chromatography (eluent: DCM/hexane=1:4) to give compound 3 as yellow solid (yield: 87%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 7.95 (d, *J* = 10.6 Hz, 1H), 2.61 (d, *J* = 7.1 Hz, 2H), 1.85 – 1.73 (m, 1H), 1.37 – 1.20 (m, 32H), 0.85 (td, *J* = 7.0, 2.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.31, 159.52, 156.48, 154.72, 152.30, 146.82, 141.93, 133.49, 131.23, 118.49, 116.01, 115.26, 113.71, 106.17, 38.66, 34.28, 33.44, 33.41, 31.92, 30.06, 30.04, 29.71, 29.69, 29.67, 29.65, 29.37, 26.60, 22.68, 14.11. HR-MS: m/z [MH$^+$] calculated for $C_{34}H_{44}BrF_2N_4S_3^+$: 721.1874, found: 721.1871.

Synthesis of DNTDPP. The compound 3 (180 mg, 0.25 mmol) and DPP tin reagent (118.8 mg, 0.1 mmol) were dissolved in 10 mL degassed anhydrous toluene, followed by nitrogen flashed 3 times and frozen by liquid nitrogen. Then, $Pd_2(dba)_3$ (9.2 mg, 0.01 mmol) and P-(*o*-tol)$_3$ (6 mg, 0.02 mmol) were added and the system was flashed with nitrogen again. The mixture was heated to 90 °C for 18 h, and then cooled to room temperature. After eluted through a short silicon/KF (4/1, w/w) column, the solvent was removed, and the residue was purified by chromatography (eluent: DCM/hexane=1:1) to give DNTDPP as blue-black solid (yield: 52%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 9.12 (d, *J* = 4.1 Hz, 2H), 8.43 (s, 2H), 7.96 (d, *J* = 10.5 Hz, 2H), 7.47 (d, *J* = 4.1 Hz, 2H), 4.11 (d, *J* = 7.8 Hz, 4H), 2.94 (d, *J* = 7.3 Hz, 4H), 2.05 (s, 2H), 1.96 – 1.86 (m, 2H), 1.31 – 1.16 (m, 128H), 0.84 – 0.81 (m, 24H). ^{13}C NMR (151 MHz, $C_2Cl_4D_2$) δ 161.74, 159.71, 157.04, 155.27, 154.93, 152.73, 147.21, 141.43, 140.95, 139.75, 136.29, 134.90, 131.17, 130.01, 127.66, 120.50, 118.65, 115.83, 114.33, 108.97, 106.45, 46.90, 39.23, 38.30, 34.92, 34.02, 31.98, 31.97, 31.95, 31.80, 31.76, 30.24, 30.21, 29.80, 29.76, 29.73, 29.72, 29.68, 29.60, 29.41, 29.38, 29.36, 26.85, 26.63, 26.61, 22.70, 14.10. MALDI-TOF: m/z [MH$^+$] calculated for $C_{122}H_{173}F_4N_{10}O_2S_8^+$: 2143.1473, found: 2143.1442.

3. TGA and DSC

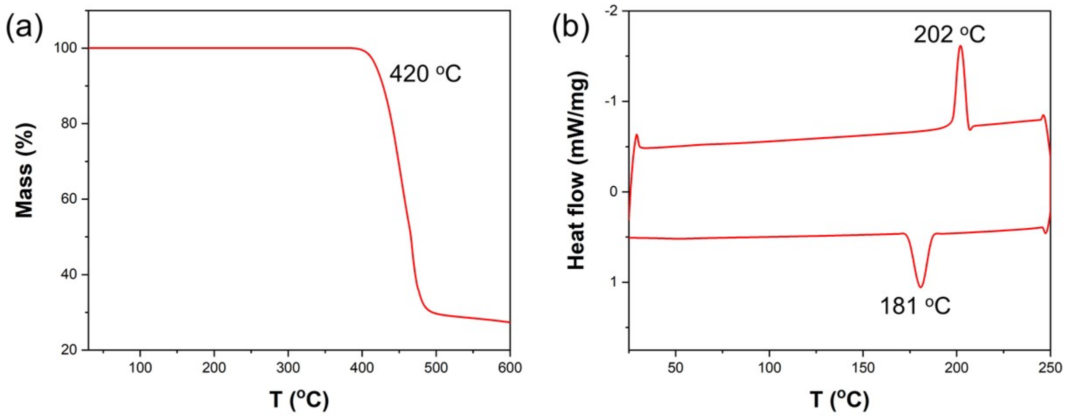

Figure S1. TGA (a) and DSC (b) analysis for DNTDPP.

4. CV measurement

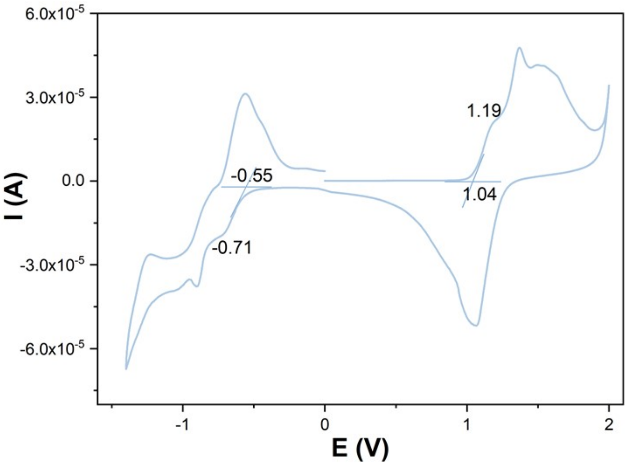

Figure S2. Cyclic voltammetry of DNTDPP in film

5. LUMO/HOMO orbitals of DNTDPP without FNTz

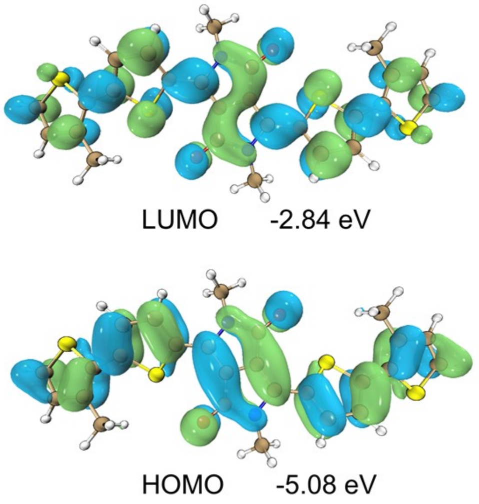

Figure S3. LUMO/HOMO orbitals of DNTDPP withou FNTz

6. OTFTs devices fabrication

Top-gate/bottom-contact (TGBC) organic thin-film transistors were assembled on BF33 substrates. Al source–drain electrodes were first patterned onto the BF33 by thermal evaporation under high vacuum about 55nm. The semiconductor layer was then formed by spin-coating a chloroform solution of the DNTDPP at 4 mg/mL, followed by thermal treatment on a hot plate under nitrogen for 10 minutes; the optimal annealing temperature was determined to be 100 °C. Subsequently, a CYTOP dielectric layer of approximately 600 nm was deposited by spin-coating at 2000 rpm for 60 s and cured at 85 °C for 1 hour in a nitrogen atmosphere. Finally, an Al gate electrode (~80 nm) was thermally evaporated through a shadow mask to complete the transistor structure.

The transfer and output curves of OTFTs were measured in glovebox using a Keithley 4200 SCS semiconductor parameter analyzer. The mobilities were determined in the saturation regime by the following equation:

$$I_{DS} = \frac{W}{2L}\mu C_i (V_{GS} - V_{th})^2$$

Where I_{DS} is the drain electrode collected current; L and W are the channel length and width, respectively; μ is the charge mobility of the device; C_i is the capacitance per unit area of the gate dielectric layer, estimated by $C_i = \varepsilon_0\varepsilon_r/d$ to be 2.95 nF cm^{-2}; V_{GS} and V_{th} are the gate and the threshold voltages, respectively. The V_{th} of the device was obtained by extrapolating the $(I_{DS,sat})^{1/2}$ vs. V_{GS} plot to $I_{DS} = 0$.

7. Temperature-dependent mobilities

Table S1. The annealing temperature-dependent electron mobilities of DNTDPP

annealing temperature (°C)	90	100	120	160
$\mu_{e, ave.}$ (cm^2 V^{-1} s^{-1})	0.91±0.10	1.03±0.07	0.53±0.08	0.036±0.010
$\mu_{e, max.}$ (cm^2 V^{-1} s^{-1})	1.05	1.18	0.67	0.053

8. Time-dependent mobility change in air

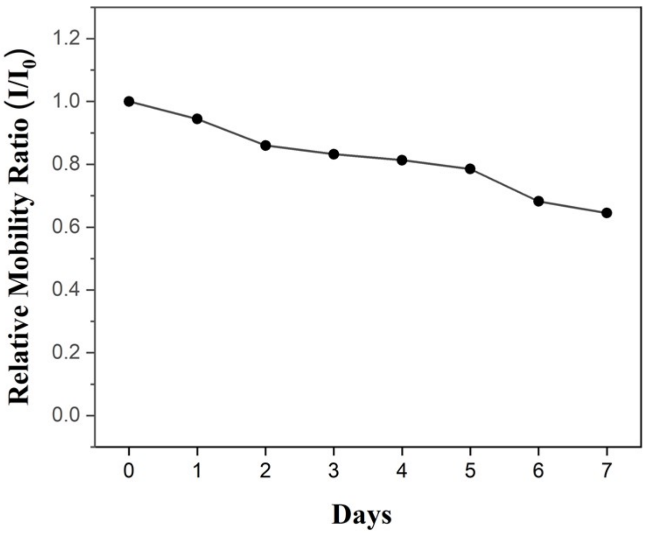

Figure S4. Time-dependent mobility change in air

9. GIWAXS line plot

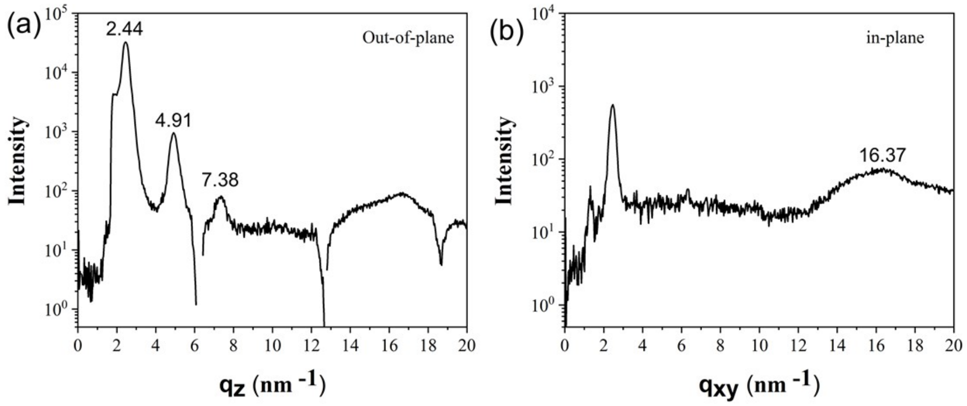

Figure S5. The Out-of-plane (a) and in-plane (in) line plot of 2D GIWAXS of DNTDPP annealed at 100 ^{o}C.

10. ^{1}H NMR and ^{13}C NMR

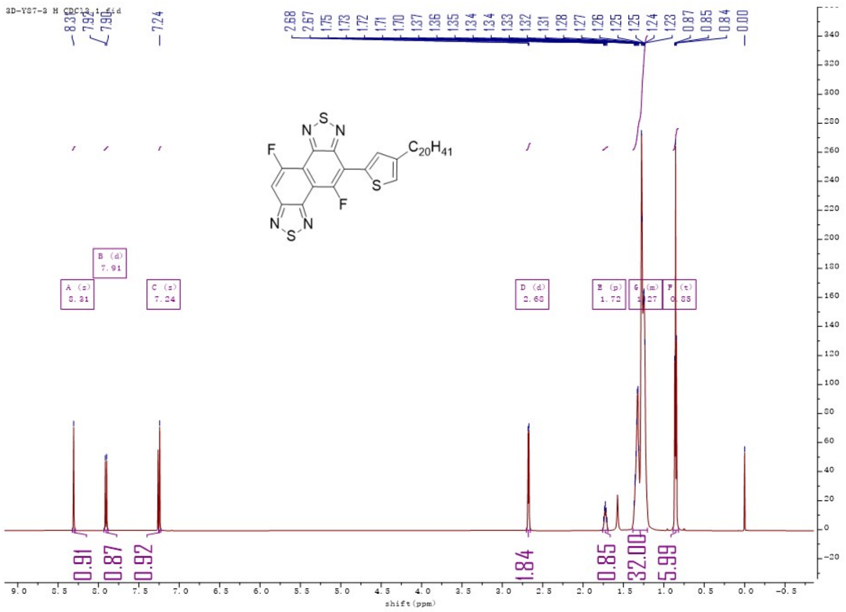

Figure S6. ^{1}H NMR spectra of compound 2 (600 MHz, $CDCl_3$).

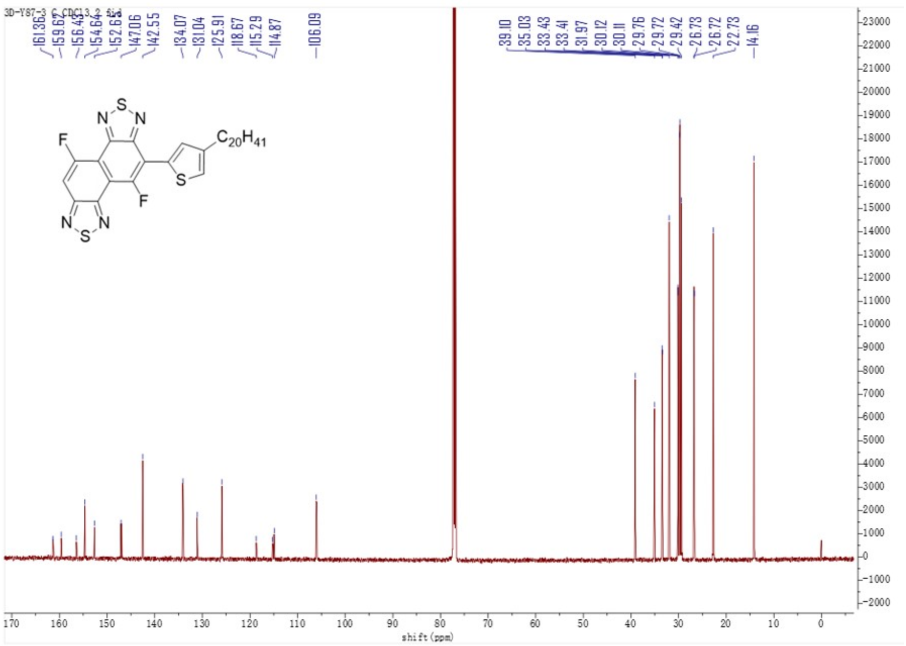

Figure S7. ^{13}C NMR spectra of compound 2 (151 MHz, CDCl$_3$).

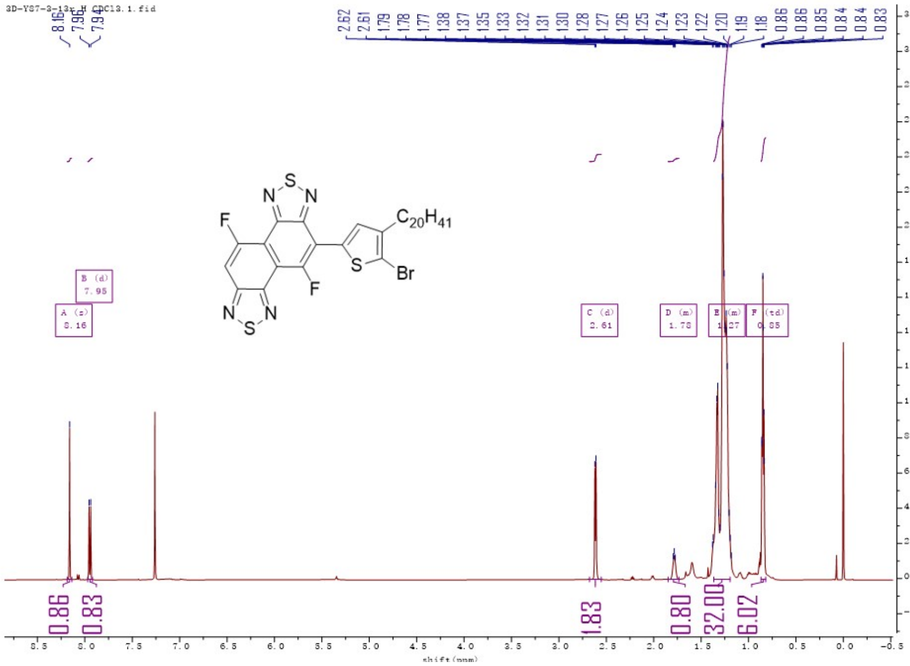

Figure S8. ^{1}H NMR spectra of compound 3 (600 MHz, CDCl$_3$).

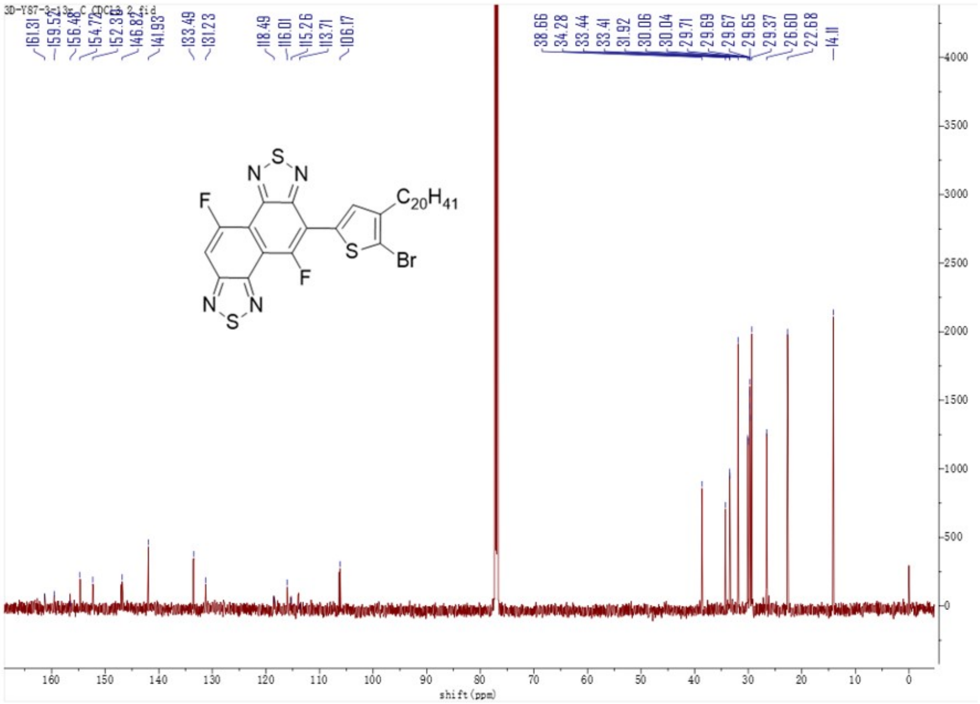

Figure S9. ^{13}C NMR spectra of compound 3 (151 MHz, $CDCl_3$).

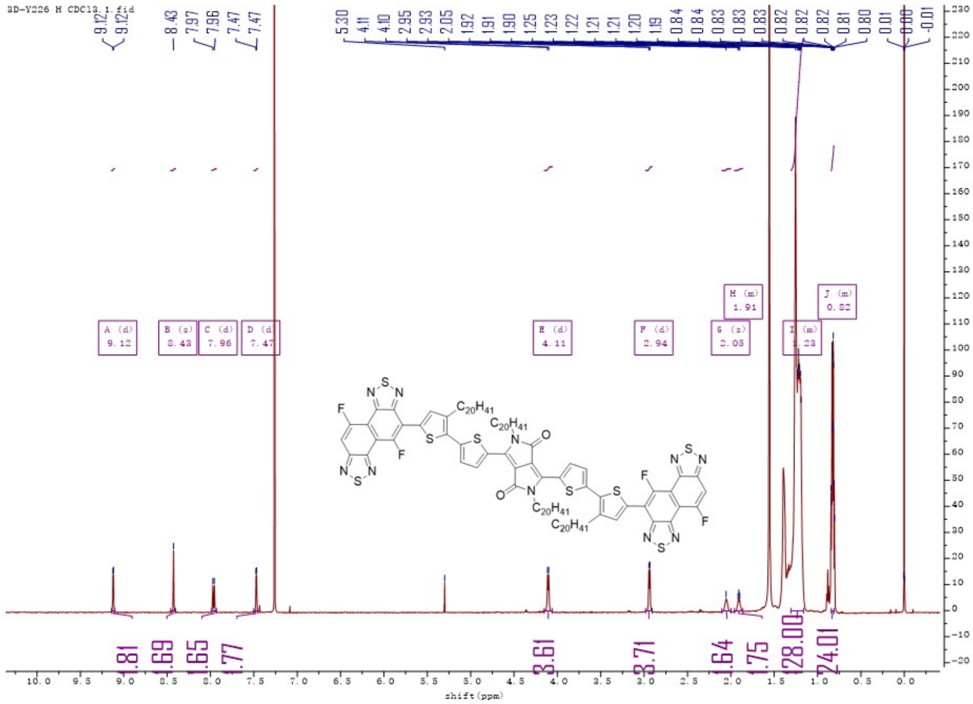

Figure S10. ^{1}H NMR spectra of DNTDPP (600 MHz, $CDCl_3$).

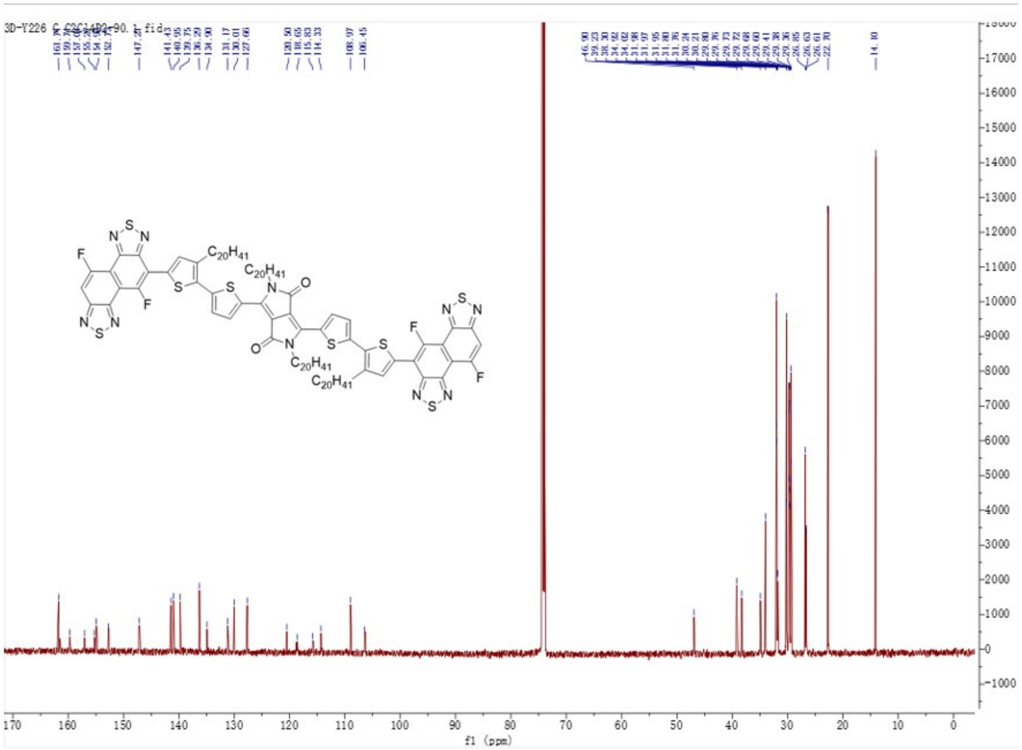

Figure S11. ^{13}C NMR spectra of DNTDPP (151 MHz, $C_2D_2Cl_4$).

11. reference

1. S. Chatterjee, Y. Ie, T. Seo, T. Moriyama, G.-J. A. Wetzelaer, P. W. Blom and Y. Aso, *NPG Asia Mater.*, 2018, **10**, 1016-1028.