

## Thionating Iso-diketopyrrolopyrrole-based Polymers: From P-type to Ambipolar Field Effect Transistors with Enhanced Charge Mobility

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### Experiment Section

**Materials.** All reagents were purchased from commercial sources and used without further purification unless otherwise noted. **IsoDPP** was prepared according to literature methods.<sup>1</sup> **DTS** was obtained from Zhongsheng Huateng company. Lawesson's reagent was obtained from Sigma-Aldrich.

### Methods and Instrumentation

Infrared spectra were collected on Nicolet-6700 FTIR spectrometer by casting films on KBr plates from solution. NMR spectra were obtained using a Mercury 300 spectrometer. The thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed under nitrogen atmosphere (20 ml/min) using a

Netzsch TGA (209F1) and Netzsch DSC (204F1) (heating rate: 10 °C/min). UV/vis absorption spectra were recorded using a dual-beam grating Hitachi U-4100 absorption spectrometer. The solution UV/Vis absorption spectra of all compounds were recorded in chloroform at a concentration of 0.1 mg/ml. The thin film UV/Vis absorption spectra were measured by using spin-coated thin film (8 mg/ml monomers or 5 mg/ml polymers in chloroform on quartz glass substrate, 1500 rpm for 2 min). Cyclic voltammograms were recorded using a potentiostat PG 390 from Heka Company. The thin films of the monomers or polymers were cast on an ITO electrode and cycled in acetonitrile (inside of Ar-filled glove box) containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as electrolyte salt. Reference and counter electrodes were platinum. The voltage data were calculated for the ferrocene/ferrocenium redox couple. The scan rate was 100 mV s<sup>-1</sup>, the temperature was 20 °C. Molecular weights of the polymers were determined upon gel permeation chromatography (GPC, HLC-8320GPC). The calibration standard is polystyrene. All GPC measurements were carried out in CHCl<sub>3</sub> at 45 °C. Thin film X-ray diffraction (XRD) experiments operating at 3 KWatt were performed on a Powder X-ray Diffractometry (INCA Energy, Oxford Instruments). The films were prepared by drop-coating of polymer solution (5 mg / ml in chloroform).

### **OFET Device Fabrication and Testing**

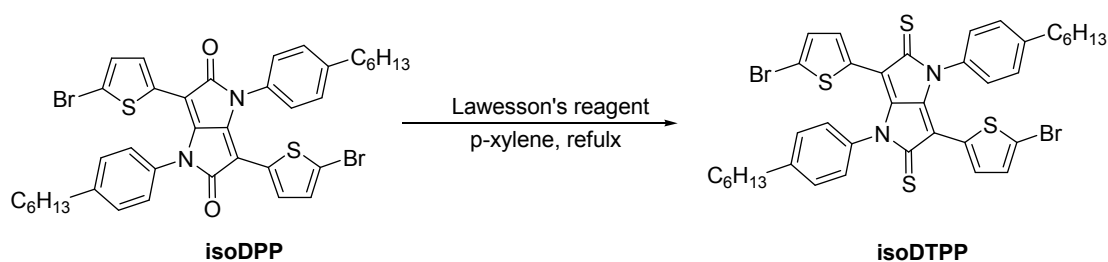
Bottom gate, bottom contact (BGBC) field effect transistors configuration was used to fabricate devices. Highly doped Si (n<sup>++</sup>) wafer with 300 nm thermal oxide (Silicon Quest International) was used as the substrate, where the doped silicon layer was used

as back gate (G) and the oxide as the dielectric materials ( $C_i$ , capacitance of  $10 \text{ nF} \cdot \text{cm}^{-2}$ ). After cleaning the substrate with Piranha ( $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2 = 3/1, \text{v/v}$ ), DI water and acetone, oxygen plasma etching (10 min, PDC-001), the substrate was immersed in OTS solution (5 % in toluene) at room temperature overnight in an Ar-filled glove box. Subsequently source (S) and drain (D) electrodes (gold, thickness: 50 nm) were deposited on the wafer through a shadow mask by electron-beam evaporation. The distance between source and drain electrode is  $30 \mu\text{m}$  and the channel width is  $1000 \mu\text{m}$ . 5 mg/ml polymer solution (in toluene) was dropped on the surface of the substrate through a syringe (with PTFE filter,  $0.45 \mu\text{m}$ ). The glass Petri dish was then covered for evaporating the solvent slowly at room temperature for 24 h. The device is then measured as "as prepared" device. The "as prepared" transistor device was then annealed at  $140 \text{ }^\circ\text{C}$  for 5 min on a hot plate in Ar-filled glove box. Then these devices were measured again as "annealed" device. The same device was exposed in an ambient environment for different time period and measured again. The field effect mobility was calculated using  $I_{SD} = (W/2L) \cdot \mu C_i (V_G - V_T)^2$  based on the saturation region of the output characteristic of the devices where  $L$  and  $W$  are the channel length and width;  $C_i$  is the capacitance of gate oxide,  $V_{SD}$  is voltage between source and drain electrodes;  $I_{SD}$  is the current between source and drain electrodes;  $V_G$  is the gate voltage.

## **Monomer synthesis**

**IsoDPP** were prepared according the literature.<sup>1</sup> The obtained product was purified by crystallization from dichloromethane/MeOH (2/1) two times to obtain a orange solid product.

### **IsoDTTP**



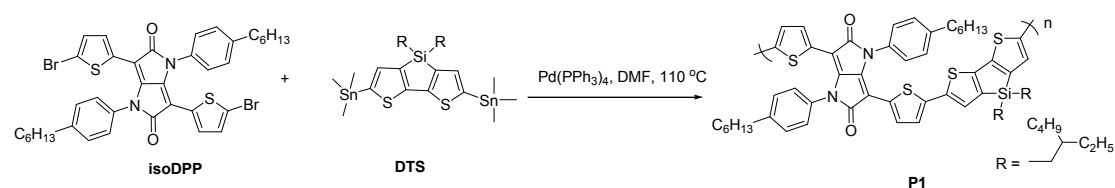
**IsoDPP** (776 mg, 1 mmol) and Lawesson's reagent (808 mg, 2 mmol) were dissolved in anhydrous *p*-xylene (100 ml). The reaction mixture was heated to reflux and stirred for 8 h under nitrogen protection in dark place. After cooling to room temperature, the reaction mixture was diluted with DCM (100 ml), washed with water 3 times. The organic layer was separated, dried over magnesium sulfate and evaporated. Subsequently, The crude product was purified by column chromatography with silica gel and hexane:dichloromethane = 2:1 as eluent to yield **isoDTTP** (630 mg, 78 %). The obtained product was purified by crystallization from dichloromethane/MeOH (3/1) two times in dark environment to obtain a brown solid product (352 mg, yield: 43 %).

<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ<sub>ppm</sub>: 7.19–7.22 (d, 4H, *J* = 8.7 Hz), 7.15–7.18 (d, 4H, *J* = 8.7 Hz), 6.53–6.54 (d, 2H, *J* = 3.9 Hz), 5.97–5.98 (d, 2H, *J* = 3.9 Hz), 2.50–2.73 (m, 4H), 1.6 (s, 4H), 1.36 (s, 22H), 0.92 (t, 6H). <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 196.66, 151.96, 148.83, 144.28, 133.29, 131.84, 133.30, 130.55, 129.07, 127.91, 117.32, 106.93, 35.81, 31.68, 30.79, 28.81, 22.65, 14.06. IR ν [cm<sup>-1</sup>]: 2961, 2925, 2854, 1620, 1514, 1461, 1435, 1406, 1378, 1328, 1287, 1259, 1241, 1204, 1193, 1175, 1111. Anal. Calc. for

$C_{38}H_{38}N_2S_4Br_2$ : C, 56.29 %; H, 4.71 %; N, 3.45 %; S, 15.80 % (calc. C, 56.29 %; H, 4.72 %; N, 3.46 %; S, 15.82 %). UV/Vis (thin film): 510 nm; UV/Vis ( $CHCl_3$ ): 509 nm.  $\epsilon$  (509) /L mol<sup>-1</sup>cm<sup>-1</sup>:  $4.2 \times 10^4$ .

## Polymerization

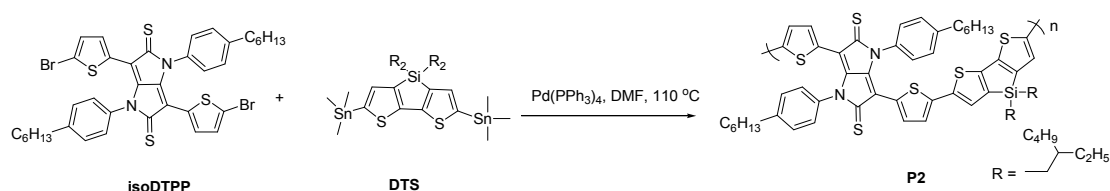
### P1



In a Schlenk flask, **isoDPP** (77.6 mg, 0.1mmol), **DTS** (74.6 mg, 0.1 mmol) were dissolved in toluene/DMF = 4/1 (in total of 5 ml). The mixture was degassed for 5 min using ultrasonication under  $N_2$  protection.  $Pd(PPh_3)_4$  (3 mg, 0.0025mmol) was quickly added into the mixture under  $N_2$  protection. Subsequently, the mixture was degassed for 5 min at room temperature using ultrasonication. The reaction temperature was increased to 110 °C and kept for 48 h in dark place. After cooling, the blue solution was diluted with DCM (50 ml) and extracted with brine (2×50 ml) and water (50 ml). The organic phase was dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated. The polymer was dissolved again in minimum DCM and precipitated with methanol to give a dark solid (82.0 mg, yield: 79.1 %). The product was purified by Soxhlet extraction with methanol, n-hexane, and THF to remove the oligomers and impurities. Finally, it was washed with chloroform to collect the product P1 (55.1 mg, yield: 53.2 %). Molecular weight (GPC, THF):  $M_w = 45.2$  KDa, PDI = 2.1. <sup>1</sup>H-NMR (300 MHz,  $CDCl_3$ )  $\delta$  ppm: 7.25-7.36 (br, 6H), 6.70-6.82 (br, 2H), 6.12-6.35 (br, 2H), 2.65-2.76 (br, 4H), 1.69 (s, 4H), 1.35 (s, 2H), 1.15-1.20 (br, 16H), 0.70-0.98 (br, 18H).

IR  $\nu$  [ $\text{cm}^{-1}$ ]: 3052, 2954, 2927, 2855, 1634, 1512, 1440, 1408, 1378, 1355, 1305, 1256, 1178, 1144, 1114, 1095, 1048, 1026. UV/Vis (thin film): 610 nm; UV/Vis ( $\text{CHCl}_3$ ): 595 nm.  $\epsilon(595) = 6.1 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

## P2



The synthesis was carried out as described for **P1** except that **isoDTPP** instead of **isoDPP** was used as monomer. A dark green solid was obtained (53.2mg, yield: 58.3%). Molecular weight (GPC, THF):  $M_w = 41.3 \text{ kDa}$ , PDI = 1.9.  $^1\text{H-NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm: 7.18-7.24 (br, 6H), 6.67-6.81 (br, 2H), 6.10-6.31 (br, 2H), 2.62-2.81 (br, 4H), 1.67 (s, 4H), 1.35 (s, 2H), 1.15-1.20 (br, 16H), 0.70-0.98 (br, 18H). IR  $\nu$  [ $\text{cm}^{-1}$ ]: 3067, 2957, 2927, 2856, 1725, 1634, 1512, 1441, 1408, 1378, 1355, 1307, 1257, 1178, 1114, 1095, 1049, 1027. UV/Vis (thin film): 633 nm; UV/Vis ( $\text{CHCl}_3$ ): 615 nm.  $\epsilon(615) = 4.2 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ .

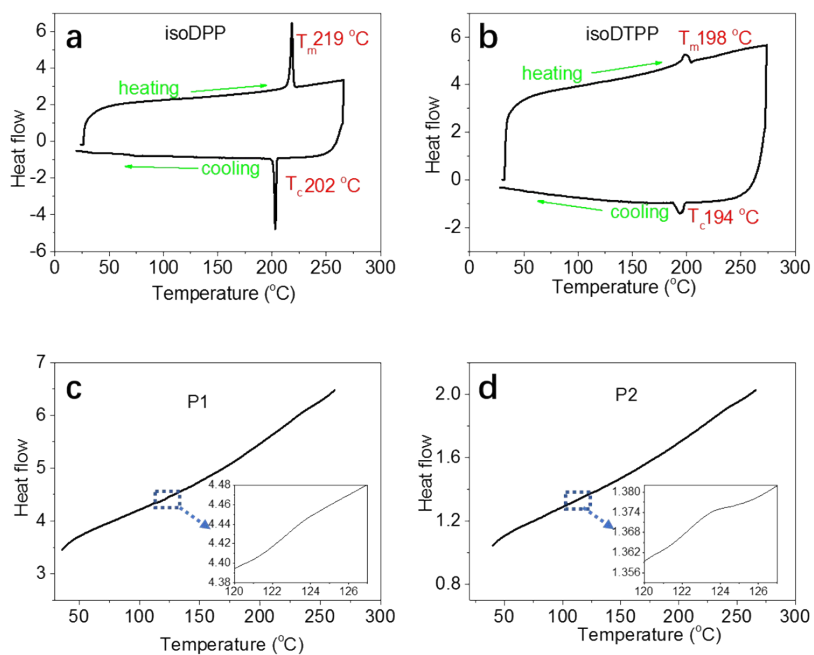


Figure S1. DSC curves of monomers (a, **isoDPP**; b, **isoDTPP**, second heating-cooling cycle) and polymers (c, **P1**; d, **P2**, second heating DSC spectra). The insert is the enlargement of c from 120 °C to 127 °C with intensity from 4.38 to 4.48, and d from 120 °C to 127 °C with intensity from 1.356 to 1.380, respectively.

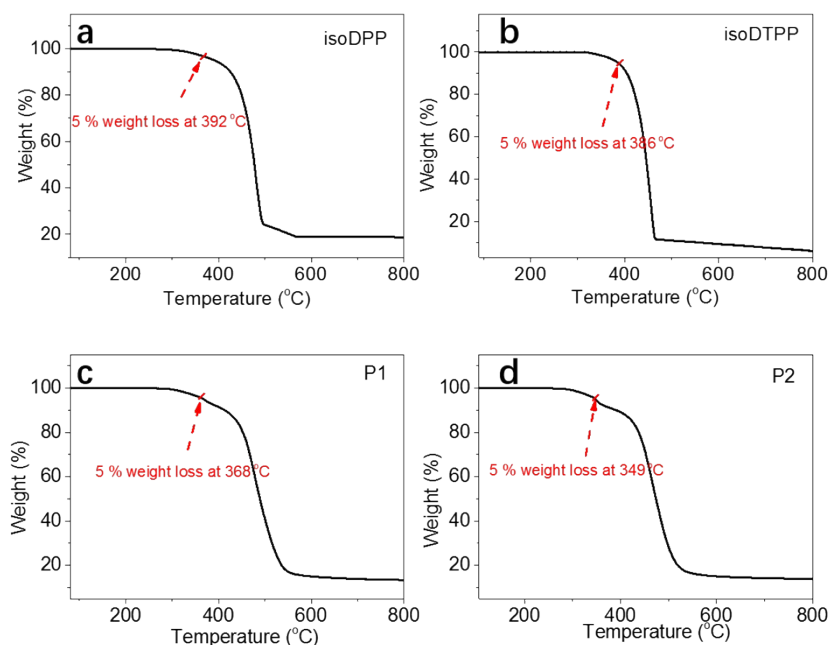


Figure S2. TGA curves of monomers (a, **isoDPP**; b, **isoDTPP**) and polymers (c, **P1**; d, **P2**). All compounds exhibited good thermal stability and no weight loss occurred before 300 °C.



Figure S3. Optical images of the monomer and polymer materials (from left to right is: **isoDPP**, **isoDTPP**, **P1** and **P2**) in solution (first row) and as powder (second row).

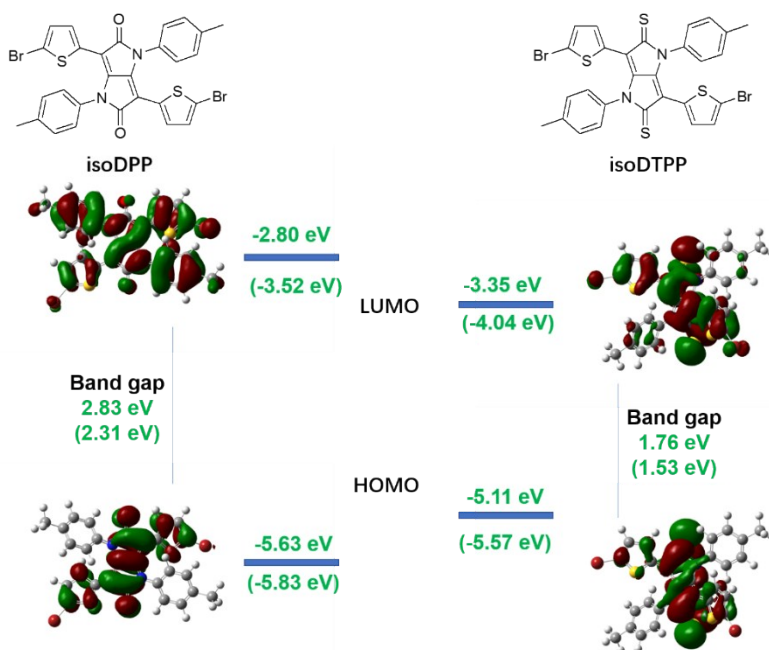


Figure S4. Molecular orbital surfaces of the HOMO, LUMO and band gap of two monomers, as obtained at the B3LYP/6-31G\* level. The HOMO, LUMO, and band gap values calculated by CVdata are also illustrated in the parenthesis.



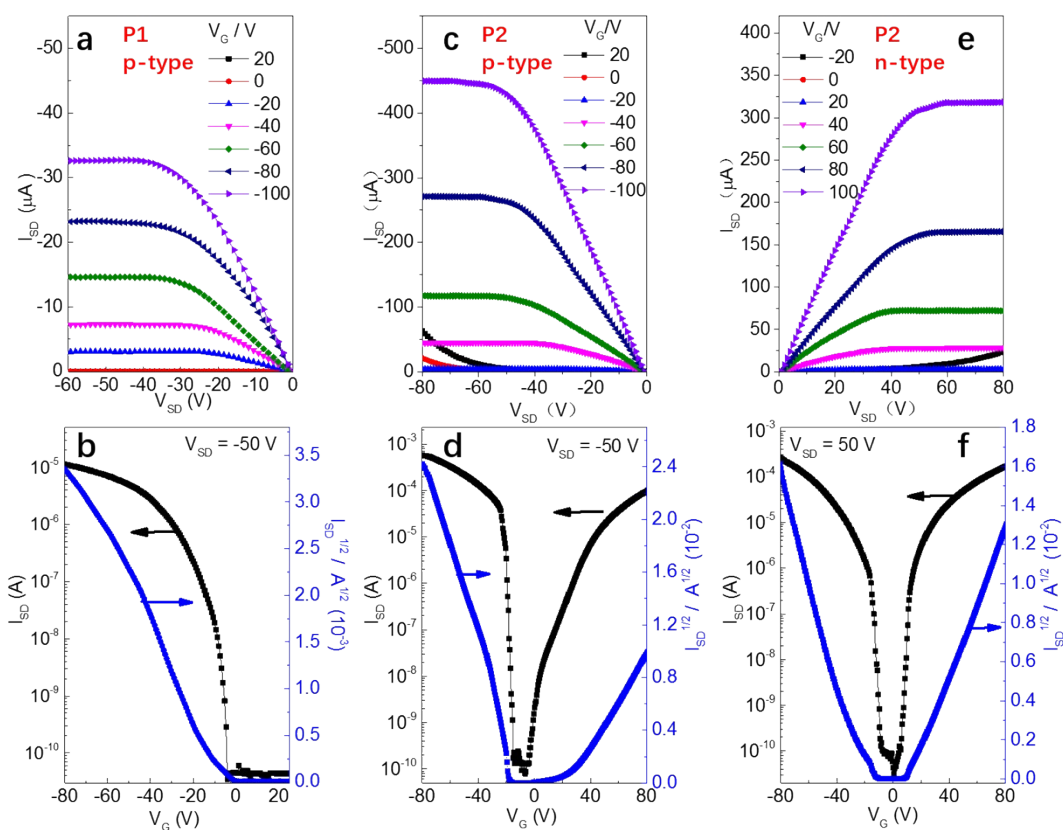


Figure S5 (a,b) The output and transfer characteristics of as prepared FET devices of **P1** (p-type); (c to f) The output and transfer characteristics of as prepared FET devices of **P2** (c,d: p-type; e,f: n-type).

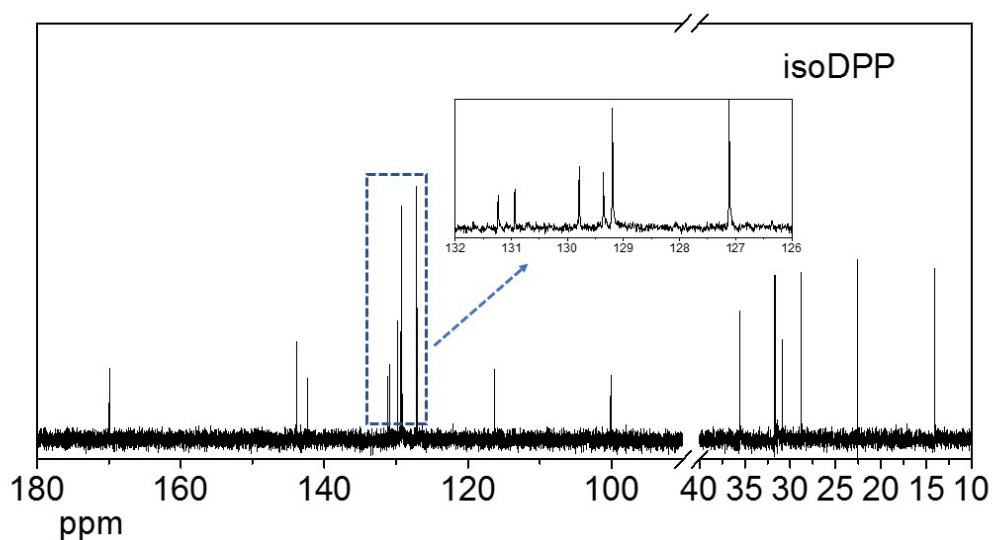


Figure S6.  $^{13}\text{C}$  NMR spectrum of monomer **isoDPP** in  $\text{CDCl}_3$ . The insert is the enlargement of the spectrum from 132 ppm to 126 ppm.

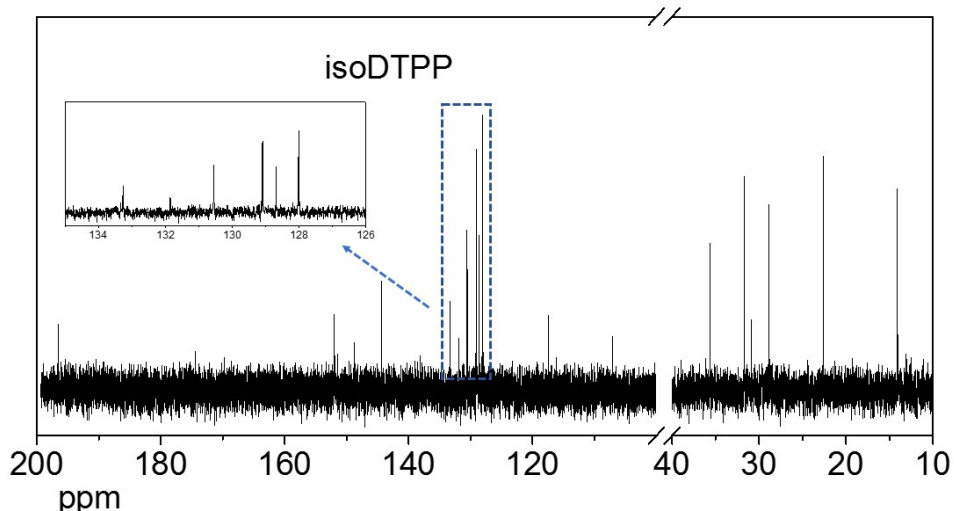


Figure S7.  $^{13}\text{C}$  NMR spectrum of monomer **isoDTPP** in  $\text{CDCl}_3$ . The insert is the enlargement of the spectrum from 135 ppm to 126 ppm.

**Table S1:** The hole mobilities ( $\mu_h$ ), electron mobilities ( $\mu_e$ ), threshold voltage ( $V_{\text{Th}}$ ) and on/off ratios ( $I_{\text{on}}/I_{\text{off}}$ ) of FET device.

polymer	condition	$\mu_h$ ( $\text{cm}^2 \text{V}^{-1}\text{s}^{-1}$ )	$V_{\text{Th}}$ (V)	$I_{\text{on}}/I_{\text{off}}$ ( $\log_{10}$ )	$\mu_e$ ( $\text{cm}^2 \text{V}^{-1}\text{s}^{-1}$ )	$V_{\text{e, Th}}$ (V)	$I_{\text{on}}/I_{\text{off}}$ ( $\log_{10}$ )
<b>P1</b>	RT	0.042 (0.047)	-13	5-6	--	--	--
<b>P1</b>	140 °C	0.081 (0.085)	-11	5-6	--	--	--
<b>P2</b>	RT	0.281 (0.290)	-15	6-7	0.112 (0.119)	10	6-7
<b>P2</b>	140 °C	0.482(0.491)	-14	6-7	0.247 (0.257)	11	6-7

All data were obtained at two conditions: as prepared (RT) and annealed (140°C). The mobility was provided in average (highest) form and the performance is based on more than 10 different FETs. Mobility extracted by fitting the linear part of the plot of  $I_{\text{DS}}^{1/2}$  versus  $V_{\text{G}}$  using the equation  $I_{\text{DS}} = C_i \mu (V_{\text{G}} - V_{\text{Th}})^2 W/2L$ . --no FET behavior was observed.

#### Reference:

1. H. Zhang, I. Welterlich, J.-M. Neudorfl, B. Tieke, C. Yang, X. Chen and W. Yang, *Polym. Chem.*, 2013, **4**, 4682-4689.