Supporting Information

Partially removing long branched alkyl side chains of regioregular conjugated backbone based diketopyrolopyrrole polymer for improving field-effect mobility

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1. Experimental Section

1.1 Materials and characterization

All chemicals and reagents were purchased from commercial sources and used without further purification unless otherwise noted. 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene was purchased from Derthon optoelectronic materials science technology Co LTD. **M1**^[1] and **M2**^[2] were synthesized and verified using the literature procedure, respectively. All the reactions were conducted under nitrogen atmosphere.

The molecular modeling calculation was performed with the Gaussian 09 program using the density functional theory with B3LYP/6-31G(d) basis set. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE III 500 MHz machine. Thermogravimetric analyses (TGA) were conducted at heating rate of 100C min⁻¹ under nitrogen gas flow and were taken on a Simultaneous Thermal Analyser (TSA) instrument (STA449C/449F5). Fourier transform infrared (FT-IR) spectroscopy implemented through Nicolet is550 of Thermo Fisher. High temperature gel permeation chromatography (HT-GPC) was carried out on a ShimadzuSIL-20A liquid chromatography instrument using 1,2,4-trichlorobenzene (TCB) as eluent at 150 °C with polystyrenes as standards. UV-vis spectra were performed on a PerkinElmer Lambda 20 UV-vis spectrophotometer. Element Analyzer (EA) was measured Vario EL cube. Cyclic voltammentry (CV) measurements were record with a three-electrode cell under a nitrogen atmosphere in a deoxygenated anhydrous acetonitrile solution of tetra-n-butylammonium hexafluorophosphate (0.1 M). A platinum disk electrode, platinum wire, and Ag/AgCl electrode were used as a working electrode, a counter electrode, and a reference electrode separately, and the polymer films were coated on the surface of platinum disk electrode for evaluation. The CV curves were calibrated using ferrocene/ferrocenium (Fc/Fc^+) redox couple as an external standard, which was performed at the same conditions as other samples. X-ray Diffractometer (XRD) were operated on X' pert3 and Empyrean from Netherlands Panalytical. Atomic Force Microscope (AFM) was characterized using 5500 of America Agilent.

1.2 Synthesis of polymers

1.2.1 Synthesis of reference polymer and t-Boc containing polymers

The reference polymer **P(100-0)**. A mixture of **M2** (0.2038 g, 0.20 mmol), 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (0.0932 g, 0.20 mmol), Pd₂(dba)₃ (3.7 mg, 0.004 mmol), P(*o*-tolyl)₃ (4.9 mg, 0.016 mmol) and anhydrous chlorobenzene (6 mL) was added to in the Schlenk tube. It was performed with evacuation and admission of dry nitrogen (three cycle). The mixture was stirred and heated at 80 °C for 12 hours (the reaction was stopped when the mixed solution in tube started to turn into a gel) under nitrogen. After polymerization, the mixture was cooled down to room temperature and added methanol to gain the precipitate of polymer. The precipitate from methanol was collected and extracted via Soxhlet extractions with methanol, petroleum ether, chloroform and chlorobenzene. The chlorobenzene solution was reprecipitated with methanol. The solid was collected and then dried to obtain the title polymer. (Dark blue solid with a metallic luster, 190 mg, 95%). Elemental Anal. Calcd.: C, 72.24; H, 8.89; N, 2.81; S, 12.85, Found: C, 72.01; H, 8.99; N, 2.84; S, 12.68.

The polymer P(4-1)-Boc. P(4-1)-Boc was synthesized following the procedure used for the synthesis of P(100-0). M1 (0.0263 g, 0.04 mmol), M2 (0.1631 g, 0.16 mmol), 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (0.0932 g, 0.20 mmol), $Pd_2(dba)_3$ (3.7 mg, 0.004 mmol), P(o-tolyl)₃ (4.9 mg, 0.016 mmol) were used. (Dark blue solid with a metallic luster, 178 mg, 96%). Elemental Anal. Calcd.: C, 69.11; H, 7.87; N, 3.13; S, 13.31, Found: C, 69.56; H, 7.30; N, 3.11; S, 13.31.

The polymer **P(10-1)-Boc**. **P (10-1)-Boc** was gained following the procedure used for the synthesis of **P(100-0)**. **M1** (0.0132 g, 0.02 mmol), **M2** (0.2038 g, 0.20 mmol), 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (0.1025 g, 0.22 mmol), $Pd_2(dba)_3$ (4.1 mg, 0.0044 mmol), P(o-tolyl)₃ (5.4 mg, 0.0176 mmol) were used. (Dark blue solid with a metallic luster, 189 mg, 89%). Elemental Anal. Calcd.: C, 70.82; H, 8.43; N, 2.95; S, 13.51, Found: C, 71.17; H, 8.60; N, 2.89; S, 13.02.

The polymer **P(40-1)-Boc**. **P(40-1)-Boc** was synthesized following the procedure used for the synthesis of **P(100-0)**. **M1** (0.0033 g, 0.005 mmol), **M2** (0.2038 g, 0.20 mmol), 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene (0.0955 g, 0.205 mmol), $Pd_2(dba)_3$ (3.8 mg, 0.0041 mmol), P(o-tolyl)₃ (5.0 mg, 0.0164 mmol) were used. (Dark blue solid with a metallic luster, 182 mg, 90%). Elemental Anal. Calcd.: C, 71.86; H, 8.77; N, 2.85; S, 13.03, Found: C, 71.82; H, 8.75; N, 2.86; S, 12.91.

For the reason that these polymers have limited solubility in common solvents at room temperature, they were not carried out the NMR measurements.

1.2.2 *t*-Boc-removed polymers [P(4/1-H, P(10/1)-H and P(40/1)-H)].

They were obtained via simple thermal cleavage of respective *t*-Boc containing polymers. For IR analysis, the *t*-Boc containing polymer samples were pre-annealed at 230 °C for 1 h in vacuum. For UV-vis, XRD, AFM and OFETs measurements, the *t*-Boc containing polymer thin films were annealed at 230 °C for 10 minutes in vacuum.

In addition, P(40/1)-Boc bulk sample was pre-annealed at 230 °C for 1 h in vacuum for gaining P(40/1)-H for measuring its UV-vis spectra, CV curve and EA. In UV-vis spectra testing, its chlorobenzene solution was then deposited on quartz plate by drop-casting method; In CV measurement, its chlorobenzene solution was then deposited on platinum disk electrode by drop-casting method. Elemental Anal. Calcd.: C, 71.82; H, 8.72; N, 2.90; S, 13.25, Found: C, 72.34; H, 8.25; N, 2.75; S, 13.22.

1.3 Device fabrication and characterization

OFET devices were fabricated in a staggered bottom-gate, top-contact configuration. The polymers of P(40/1)-Boc, and P(100/0) were dissolved in dichlorobenzene at the concentration of 4 mg/mL. There are two alternative methods to obtain side chain-free or side-chain partly removed DPP polymer thin films for evaluating their FET performance: (1) by annealing *t*-Boc DPP polymer films in-situ and (2) by pre-annealing t-Boc DPP polymer bulk sample to obtain N-H containing DPP polymer, and then spin-coating its solution on substrate to achieve the target thin films. It is note that we have chosen method (1) to achieve polymer thin film because

of its simplified process. The channel semiconductor layers were deposited by spin coating. Thermally deposited (~40 nm) gold with fixed channel length of 80 μ m and channel width of 1500 μ m was used as source/drain electrode. The field-effect characterizations were conducted at room temperature in ambient conditions using a Keithley 2636B two channel Source/Meter. The field-effect mobility in the saturation regime was extracted from the $|I_{\rm DS}|^{1/2}$ vs $V_{\rm G}$ plot in the low gate voltage ($V_{\rm G}$) regime ($V_{\rm G}-V_{\rm th}\sim10$ V).

2. Figures and Table S1 in ESI



A linear DPP polymer

Type A: with identical side chains $(R_1=R_2=R_3=R_4=...)$ **Type B**: with composite side chains (e.g. $R_1=R_2$, $R_3=R_4$ and $R_1(R_2) \neq R_3(R_4)$; or $R_1(R_3) \neq R_2(R_4)$) **Type C**: with partial or none of side chains (e.g. $R_1=R_2=H$, $R_3=R_4\neq H$; or $R_1=R_2=R_3=R_4=...=H$)

Figure S1 The linear DPP polymer with the different type of side chains linked on

DPP cores. (Only two DPP cores were shown in it for simplicity).





t-Boc-containing precursor polymers

t-Boc-removed polymers



Figure S3 Literature overview of representative polymers obtained via *t*-Boc precursor approach in OFETs.







Type C3 (with adjustable DPP-H)

Figure S5 Constructing DPP polymers with "Type C" side chains



Figure S6 Comparison of the solubility of polymers in chlorobenzene. (Label 4:1, 10:1 and 40:1 refer to P(4/1)-Boc, P(10/1)-Boc and P(40/1)-Boc

respectively).

All the polymers showed poor solubility in chlorobenzene solution at room temperature. P(40/1)-Boc displayed good solubility (at least 4 mg/mL) in hot chlorobenzene (80 °C), while P(10/1)-Boc and P(4/1)-Boc showed limited solubility in parallel testing.



Figure S7 TGA characteristics of polymers with heating rate of 10 °C/min under N₂.



Figure S8 FT-IR spectra for reference polymer P(100/0) and t-Boc-removed polymers







Figure S10 HT-GPC test result of P(40/1)-Boc sample (TCB as eluent, 150 °C).



Figure S11 DFT calculations of three models.



Figure S12 Normalized UV-vis absorption spectra of (a) **P(100/0)** and (b) **P(40/1)-Boc** and annealed film of **P(40/1)-H** obtained from pre-annealing **P(40-1)-Boc** bulk sample.



Figure S13. Field-Effect Properties of P(40/1)-Boc and P(40/1)-H. (a) transfer curves of OFETs based on P(40/1)-Boc and P(40/1)-H; (b) corresponding square root of source-drain current, |I_{DS}|^{1/2}, vs. gate voltage; Output curves of OFETs with (c) P(40/1)-Boc and (d) P(40/1)-H, respectively.



Figure S14 XRD patterns of P(40/1)-Boc pristine film and its annealed film (P(40/1)-H) deposited on OTS-modified SiO₂/Si substrates.



Figure S15 AFM topography images of (a) P(100/0) annealed film and (b) P(40/1)-H film (P(40/1)-Boc as annealed film).

Table S1 Photophysical	and electrochemical	properties o	f polymers
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Polymer	Conditions	$\lambda_{_{ m max}}^{\scriptscriptstyle solution}$	$\lambda_{_{ m max}}^{\it film}$	$\lambda_{\scriptscriptstyle onset}^{\scriptscriptstyle film}$	E_g^{opt} a	$E_{_{ox}}^{_{onset}}$	Е _{номо}	E _{LUMO}
		(nm)	(nm)	(nm)	(eV)	(V)	^b (eV)	^c (eV)
P(100/0)	Pristine	811	807	970	1.28	0.92	5.28	-4.00
	Annealed		797	985	1.26			
P(40/1)-Boc	Pristine	814	787	960	1.29	0.96	5.32	-4.03
	Annealed ^d		794	970	1.28			
	Annealed ^e		802	995	1.25	1.12	5.48	-4.20

^a Calculated by the equation : $E_g^{opt} = 1240 / \lambda_{onset}^{film} eV$

b $E{HOMO} = -(E_{ox}^{onset} + E_{1/2}^{Fc/Fc+} + 4.8)eV$, $E_{1/2}^{Fc/Fc+} = 0.36eV$

$$_{\rm c} \ E_{_{LUMO}} = E_{_{g}}^{_{opt}} + E_{_{HOMO}}$$

^d Thin films were annealed at 230 °C for 10 minutes in vacuum.

^e **P(40/1)-Boc** sample was pre-annealed at 230 °C for 1 h in vacuum for gaining *t*-Boc-removed polymer (**P(40/1)-H**) and them its corresponding film were further annealed at 230 °C for 10 minutes in vacuum.

Polymer	Mobility (cm ² /Vs)	On/off ratio	Hysteresis (V)	R factor*
P(40/1)-Boc	0.16	4×10 ⁵	12.1	66%
Р(40/1)-Н	0.91	5×10 ⁵	9.9	22%
P(100/0)	0.56	9×10 ⁵	15.8	32%

 Table S2 FET (hole) mobility, current on/off ratio, and hysteresis of OFETs based on polymers films

^{*}The R factor (expressed in %) was calculated following the method proposed in *Nat*. *Mater.* **2018**,17, 2-7, which reflects the measurement reliability between the maximum mobility experimentally achieved in a FET (μ_{eff}) and the claimed mobility ($\mu_{claimed}$).

3. References

[1] V. S. Gevaerts, E. M. Herzig, M. Kirkus, K. H. Hendriks, M. M. Wienk, J. Perlich,
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[2] B. Fu, J. Baltazar, A. R. Sankar, P. H. Chu, S. Zhang, D. M. Collard and E. Reichmanis, *Advanced Functional Materials*, **2014**, 24, 3734-3744.