## SUPPORTING INFORMATION

# Tuning antiaromatic character and charge transport of pentalene-based antiaromatic compounds by substitution

Jianglin Wu<sup>ab</sup>, Yao Chen<sup>b</sup>, Jueshan Liu<sup>a</sup>, Zhenguo Pang<sup>a</sup>, Guoping Li<sup>b</sup>, Zhiyun Lu<sup>a</sup>, Yan Huang<sup>\*a</sup>, Antonio Facchetti<sup>\*bc</sup> and Tobin J. Marks<sup>\*b</sup>

<sup>a</sup> Key Laboratory of Green Chemistry and Technology (Ministry of Education), College of Chemistry, Sichuan University, Chengdu 610064, P. R. China.

<sup>b</sup>Department of Chemistry, Center for Light Energy Activated Redox Processes (LEAP), Materials Research Center (MRC), Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA.

<sup>c</sup> Flexterra Inc. 8025 Lamon Avenue, Skokie, IL60077, United States.

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## 1. Materials synthesis and instrumentation

All reagents are commercially available and were used without further purification unless otherwise stated. The dichloromethane (DCM), dimethylformamide (DMF), 1,4-dioxane were dried via distillation from  $P_2O_5$ , MgSO<sub>4</sub>, and Na, respectively.



Figure S1. Synthetic routes to key intermediate (compounds 3 and 7)

#### 2-Bromo-3-iodothiophene (1)<sup>1</sup>

A mixture of 3-iodothiophene (10.0 g, 47.6 mmol), *N*-bromosuccinimide (8.47 g, 47.6 mmol) in 100 mL DMF was heated at 100 °C under Ar for 1.5 h, then the reaction mixture was cooled to room temperature. The reaction mixture was poured into 200 mL water and was extracted with  $CH_2Cl_2$  (50 mL $\diamond$ 3). The organic phase was washed with brine and dried over anhydrous  $Na_2SO_4$  and filtered. After removal of the filtrate solvent in vacuo, the residue was purified by column chromatography in silica gel (eluate: PE) to afford 1 as a colorless oil (12.0 g, 87.3%).<sup>1</sup>H NMR(CDCl<sub>3</sub>, 400 MHz, ppm)  $\delta$  :7.23 (d, *J* = 5.6 Hz, 1H, ArH), 6.95 (d, *J* = 5.6 Hz, 1H, ArH).

2-Bromo-3-((4-pentylphenyl)ethynyl)thiophene (2)<sup>2</sup>

A mixture of compound **1** (5.0 g, 17.3 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (61 mg, 0.086 mmol) and copper(I) iodide (33 mg, 0.173 mmol) in triethylamine (150 mL) was stirred under Ar at room temperature. Next, 4-pentyphenylacetylene (3.28 g, 19.03 mmol) was added to the solution slowly. After stirring at room temperature for 12 h, the mixture was filtered and the filtrate was collected. After removal of the solvent in vacuo the residue was purified by chromatography on silica gel (eluent : hexane) to give the product as a colorless liquid (5.13 g, 89%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz, ppm)  $\delta$  : 7.46 (d, *J* = 8.4 Hz, 2H, ArH), 7.20 (d, *J* = 5.6 Hz, 1H, ArH), 7.16 (d, *J* = 8.4 Hz, 2H, ArH), 7.01 (d, *J* = 5.4 Hz, 1H, ArH), 2.61 (t, *J* = 7.6 Hz, 2H, CH2), 1.65-1.57 (m, 2H, CH2), 1.28-1.24 (m, 4H, CH2), 0.89 (t, *J* = 6.8 Hz, CH3, 3H).

#### 4,8-Bis(4-pentylphenyl)pentaleno[1,2-b:4,5-b']dithiophene (P1)<sup>2</sup>

A mixture of compound **2** (3.6 g, 10.8 mmol), hydroquinone (2.38 g, 21.6 mmol), Cs<sub>2</sub>CO<sub>3</sub> (7.04 g, 21.6 mmol), CsF (3.28 g, 21.6 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (197.8 mg, 0.216 mmol), [(*t*-Bu)<sub>3</sub>PH]BF<sub>4</sub> (188 mg, 0.65 mmol) in anhydrous 1,4-dioxane (80 mL) was heated at 140 °C under Ar for 48 h. After cooling to room temperature, the mixture was filtered and the solid was washed thoroughly with chloroform. The filtrate was collected and evaporated to dryness. The residue was purified by chromatography on silica gel (eluent : PE) to give the titled product as a brown solid (0.40 g, 14.6%).<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz, ppm)  $\delta$ : 7.53 (d, *J* = 8.0 Hz, 4H, ArH), 7.24 (d, *J* = 8.0 Hz, 4H, ArH), 6.81 (d, *J* = 4.8 Hz, 2H, ArH), 6.70 (d, *J* = 4.8 Hz, 2H, ArH), 2.64 (t, *J* = 8.0 Hz, 4H, CH2), 1.68-1.61 (m, 4H, CH2), 1.59-1.31 (m, 8H, CH<sub>2</sub>), 0.91 (t, *J* = 7.6 Hz, 6H, CH3). %).13H NMR (CDCl<sub>3</sub>, 100MHz, ppm)  $\delta$ :148.16, 144.80, 142.57, 139.04, 137.00, 130.60, 128.83, 127.64, 127.17, 121.25, 35.96, 31.55, 30.97, 22.55, 14.03. MALDI-TOF MS: Calcd for C50H52N2S2 (M+): 506.2102, Found (M+H+): 507.2177

#### 2,6-Dibromo-4,8-bis(4-pentylphenyl)pentaleno[1,2-b:4,5-b']dithiophene (3)<sup>2</sup>

*N*-Bromosuccinimide (232 mg, 1.30 mmol) was added to the solution of compound **P1** (0.30 g, 0.592 mmol) in chloroform (60 mL) and acetic acid (20 mL) at 0 °C. The mixture was stirred for 0.5 h at 0 °C and then was quenched with water. The mixture was then extracted with CH<sub>2</sub>Cl<sub>2</sub> (20 mL×3). The combined organic layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub> and then filtered. The solvent was removed from the filtrate under reduced pressure, and the residue was purified by recrystallization from acetone to afford a dark orange solid (0.25 g, 63.6%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz, ppm)  $\delta$ : 7.38(d, *J* = 8.4 Hz, 4H, ArH), 7.24 (d, *J* = 8.0 Hz, 4H, ArH), 6.64 (s, 2H, ArH), 2.64 (t, *J* = 8.0 Hz, 4H, CH2), 1.68-1.61 (m, 4H, CH2), 1.39-1.34(m, 8H, CH2), 0.91 (t, *J* = 7.6 Hz, 6H, CH3).

#### **Compound 4**

A three-necked reaction vessel was charged with 2-methyl-5-bromophenol (5.0 g, 26.7 mmol) and 50 mL dimethylformamide (DMF). Then, 2.56 g (50% dispersion in mineral oil; 53.4 mmol) NaH was added in three portions while stirring at 0 °C, and then the mixture was warmed to room temperature. After 1h, 9-(bromomethyl)nonadecane (11.58 g, 32.04 mmol) was added in one portion and the reaction was stirred for an additional 5 h at 50°C. Next, the reaction mixture was poured into 100 mL water and extracted with DCM. The combined organic phases were filtered and the solvent evaporated under vacuum to afford the crude product, which was run through a silica gel plug with hexane to afford the product (11.23 g) as a colorless oil. Yield: 90.0%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz, ppm)  $\delta$ : 7.01-6.94 (m, 2H, ArH), 6.91(d, J = 1.6 Hz, 1H, ArH), 3.80(d, J=5.6Hz, 2H, CH2), 2.15(s, 3H, CH3), 1.82-1.73(m, 1H, CH), 1.49-1.20(m, 36H, CH2), 0.88(t, J=7.2Hz, 6H, CH3).

#### Compound 5

To a magnetically stirred solution of compound **4a** (3.5 g, 7.27 mmol) in CCl<sub>4</sub> (80 mL) was added NBS (1.56 g, 8.72 mmol) and benzoyl peroxide (176.8 mg, 0.73 mmol). After refluxing for 8 h, the reaction mixture was filtered and the solvent evaporated to afford the crude product, which was then run through a silica gel plug with hexane to afford the product (2.18 g) as a colorless oil. Yield: 55.0%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz, ppm)  $\delta$ :7.17(d, *J* = 8.0 Hz, 1H, ArH), 7.03(dd, *J*<sub>1</sub> = 8.0 Hz, *J*<sub>2</sub> = 2.0 Hz, 1H, ArH), 7.00(d, *J* = 2.0 Hz, 1H, ArH), 4.48(s, 2H, CH2-Br), 3.88(t, *J* = 5.2 Hz, 2H, CH2), 2.07-2.01(m, 1H, CH), 1.85-1.79(m, 2H, CH2), 1.55-1.46(m, 2H, CH2), 1.45-1.38(m, 2H, CH2), 1.36-1.26(m, 30H, CH2), 0.89-0.86(m, 6H, CH3).

#### **Compound 6**

A three-necked reaction vessel was charged with compound **5a** (2.0 g, 3.66 mmol), 4methylmorpholine *N*-oxide (1.71 g, 14.6 mmol), 20 mL DCM, and 10 mL of acetonitrile. The reaction mixture was stirred at 50°C for 4 h, next quenched with water, and finally extracted with DCM (3× 20 mL). The combined organic fractions were dried over sodium sulfate, filtered, and concentrated. The crude product was purified by silica gel chromatography, eluting with hexanes and DCM (5:1), to afford 1.58 g of product as light yellow oil. Yield: 90 %. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz, ppm)  $\delta$ : 10.43 (s, 1H, CHO) , 7.69(dd, *J1* = 8.8 Hz, J2 = 0.4Hz, 1H, ArH), 7.70-7.30(m, 2H, ArH), 3.94(d, *J* = 5.6 Hz, 2H, CH2), 1.87-1.82 (m, 1H, CH), 1.48-1.38(m, 4H, CH2), 1.38-1.25(m, 28H, CH2), 0.88(t, *J* = 7.2 Hz, 6H, CH3)  $\circ$ 

#### **Compound 7**

A three necked reaction vessel was charged with compound **6a** (1.0 g, 2.0 mmol), bis(pinacolato)diboron (1.01 g, 4.0 mmol), Pd(dppf)<sub>2</sub>Cl<sub>2</sub> (73 mg, 0.1 mmol), AcOK (0.59 g, 6.0 mmol), and 20 mL 1,4-dioxane. The reaction mixture was stirred at 85°C for 10 h, next quenched with water, and finally extracted with DCM ( $3 \times 20$  mL). The combined organic fractions were

dried over sodium sulfate, filtered, and concentrated. The crude product was purified by silica gel chromatography, eluting with hexanes and DCM (4:1), to afford 898 mg of product as a light yellow oil. Yield: 85%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400MHz, ppm)  $\delta$ :10.55 (s, 1H, CHO), 7.80(d, *J* = 7.6 Hz, 1H, ArH), 7.43(d, *J* = 7.6 Hz, 1H, ArH), 7.38(s, 1H, ArH), 4.01(d, *J* = 5.2 Hz, 2H, ArH), 1.86-1.80(m, 1H, CH), 1.50-1.42(m, 4H, CH2), 1.36(s, 12H, CH3), 1.30-1.20(m, 28H, CH2), 0.88(t, *J* = 7.2 Hz, 6H, CH3).

#### **Compound 8**

A three necked reaction vessel was charged with compound **3** (100 mg, 0.15 mmol), compound **7a** (326 mg, 0.6 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (15.83 mg, 0.015 mmol), K<sub>2</sub>CO<sub>3</sub> (2M) (0.45 mL, 0.9 mmol), 10 mL toluene, and 2 mL H<sub>2</sub>O. The reaction mixture was stirred at105°C for 24 h under Ar, next, quenched with water, and finally extracted with DCM ( $3 \times 20$  mL). The combined organic fractions were next over sodium sulfate, filtered, and concentrated. The crude product was purified by silica gel chromatography, eluting with hexanes and DCM (3:1), to afford 167 mg of compound 8 as a dark red solid, Yield: 85%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm)  $\delta$ :10.42(s, 2H, CHO), 7.79(d, J = 7.6Hz, 2H, ArH), 7.57(d, J = 8.0 Hz, 4H, ArH), 7.31(d, J = 8.0 Hz, 4H, ArH), 7.11(d, J = 7.6 Hz, 2H, ArH), 7.01(s, 2H, ArH), 6.96(s, 2H, ArH), 3.99(d, J = 5.6 Hz, 4H, CH2), 2.69(t, J = 7.8 Hz, 4H, CH2), 1.90-1.80(m, 2H, CH), 1.73-1.64(m, 4H, CH2), 1.52-1.40(m, 10H, CH2), 1.40-1.35(m, 16H, CH2), 1.32-1.25(m, 48H, CH2), 0.93(t, J = 6.8 Hz, 6H, CH3), 0.87(t, J = 7.2 Hz, 12H, CH3).

## 2. Materials characterization

1H spectra of all intermediates and P1 were recorded on a Bruker Avance AVII (400 MHz) instrument using CDCl<sub>3</sub> as solvent at room temperature. 1H spectra and 13C spectra of P2, P3, and P4 were recorded on a Bruker Ascend 600 MHz spectrometer using in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub> at 120 °C. The molecular mass of P1 and P2 was confirmed by using an ESI on the Bruker IMPACT II Mass Spectrometer, The molecular masses of P3 and P4 were confirmed by using an APPI on the Bruker IMPACT II Mass Spectrometer. Optical absorption spectra of the target compounds as  $5 \times 10^{-6}$  M chloroform solutions and as thin-films were measured using a Varian Cary 100 UV-vis spectrophotometer. The morphologies of the films were analyzed by AFM using a Dimension Icon scanning probe microscope (Bruker) in standard tapping mode. Grazing Incidence Wide-Angle Xray Scattering (GIWAXS) measurements were recorded at BeamLine 8-ID-E1 at the Advanced Photon Source (APS) at Argonne National Laboratory. CV experiments were performed using an LK2010 electrochemical workstation with a scan rate of 100 mV s<sup>-1</sup>. All CV measurements were carried out at room temperature with a conventional three-electrode configuration that employed a Pt disk as the working electrode, a Pt wire as the counter electrode, and Ag/AgNO<sub>3</sub> as the reference electrode. Dichloromethane was freshly distilled from phosphorus pentoxide ( $P_2O_5$ ) under dry argon. Tetrabutylammonium perchlorate (0.1 M) and the Fc/Fc<sup>+</sup> redox couple (with absolute energy of -4.80 eV under vacuum) were used as the supporting electrolyte and internal potential reference, respectively. The HOMO and LUMO energy levels of P1 to P4 were calculated from the peak of the first oxidation and reduction waves by comparison with the Fc/Fc+ redox couple according to the formula HOMO =  $-(E_{ox}+4.80)$  [eV] and the formula LUMO = - $(E_{\rm red}+4.80)$  [eV], respectively.



**P2:** 

P1:



**Figure S2.** ORTEP representations of the **P1** and **P2** crystal structures, drawn at a 50% probability level. Shown in red are the dihedral twist angles between the central core plane and the phenyl ring planes.



Figure S3. The layered structures of compounds P1 (a) and P2 (b) in the crystalline state showing the molecular packing. Dotted lines represent intermolecular contacts shorter than the sum of van der Waals radii. P1 without any weak secondary interactions has a disordered packing and weak  $\pi$ -edge interactions the distances of which are shown in (a). P2 has close  $\pi$ - $\pi$  interactions, selected distances of which are shown in (b).

Compound	P1	P2
Empirical formula	C34H34S2	C50.5H53CIN2S2
Formula weight	506.73	787.52
Temperature	295.0(9)	110(14)
Crystal system	monoclinic	Triclinic
Space group	C2/c	P-1
a/Å	18.3889(3)	10.5300(3)
b/Å	7.75850(13)	13.3631(12)
c/Å	19.8905(4)	16.1775(14)
$\alpha$ /°	90.00	113.702(8)
β/°	109.506(2)	90.098(5)
$\gamma^{\prime \circ}$	90.00	94.981(5)
Volume/Å3	2674.90(9)	2074.8(3)
Z	4	2
$\rho_{calc}mg/mm^3$	1.258	1.261
$\mu/\mathrm{mm}^{-1}$	1.947	0.231
F(000)	1080.0	838
Crystal size/mm <sup>3</sup>	$0.45 \times 0.3 \times 0.2$	$0.196 \times 0.066 \times 0.006$
$2\theta$ range for data collection	9.434 to 143.136°	4.67 to 61.838°
	$-22 \le h \le 20$	$-13 \le h \le 14$
Index ranges	$-8 \le k \le 9$	$-18 \le k \le 15$
	$-21 \le 1 \le 24$	$-22 \le 1 \le 22$
Reflections collected	5922	29283
Independent reflections	2533[Rint=0.0271]	10245[R(int) = 0.0406]
Data/restraints/parameters	2533/0/164	10245/6/530
Goodness-of-fit on F <sup>2</sup>	1.038	1.038
Final R indexes $[I \ge 2\sigma(I)]$	$R1 = 0.0639, wR_2 = 0.1768$	R1 = 0.0607, wR2 = 0.1569
Final R indexes [all data]	$R1 = 0.0677, wR_2 = 0.1844$	R1 = 0.0873, wR2 = 0.1708
Largest diff.peak/hole/e Å <sup>-3</sup>	0.39/-0.42	1.057/-0.392
Final R indexes [I>= $2\sigma$ (I)] Final R indexes [all data] Largest diff.peak/hole/e Å <sup>-3</sup>	$R1 = 0.0639, WR_2 = 0.1768$ $R1 = 0.0677, WR_2 = 0.1844$ $0.39/-0.42$	R1 = 0.0607, WR2 = 0.1569 R1 = 0.0873, WR2 = 0.1708 1.057/-0.392

Table S1. Crystal data and structure refinement for P1 and P2.



Figure S4. Photographs of P1-P4 as CHCl<sub>3</sub> solutions.



Figure S5. Optical absorption spectra of P1 - P4 as thin films.



Figure S6. Cyclic voltammograms of the indicated compounds as dichloromethane solutions. The ferrocenium/ferrocene redox couple was used as internal potential reference.



Figure S7. Thermogravimetric analysis of the four polymers.



Figure S8. DSC scans of the four polymers.

Table S2. Summary of	of Thermal	properties	of <b>P1-P4</b>
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Compound	$T_{\rm g}$ (°C)	$T_{\rm m}$ (°C)/ $\Delta H_{\rm f}$ (J/g)	$T_{\rm c}$ (°C)/ $\Delta H_{\rm c}$ (J/g)
P1	300	171.2 (39.9J/g)	
P2	300	261.2 (28.7J/g)	240.5 (30.76J/g)
P3	320		
P4	306	189.2 (2.87J/g)	

## **3.** Electronic structure computation

#### **3.1 Computational Methods**

All calculations were performed using the Gaussian 09 program package. To reduce computational demands, the long side chains of all compounds were replaced by methyl group or methoxy group. The geometries of these molecules were first optimized at the B3LYP level of density functional theory (DFT) with the 6-311G(d) basis set. The absorption spectra were calculated by time-dependent density functional theory (TD-DFT) at the B3LYP/6-311+G(d) level of theory. Nucleus independent chemical shifts (NICS) calculations of **P1-P4** are at the B3LYP/6-31+G(d) computational level and were all carried out using the aroma 1.0 package according to published procedures.<sup>3</sup> The NICS-XY-scans are shown to contain the NICS $\pi$ ,ZZ values from the sigma only model. The ACID12 plots were generated with Gaussian09 using the CSGT method and AICD 2.0.0. ACID is a method to visualize conjugation and ring currents in molecules.

Molecule	Main view	Side view
P1	دي. دي قود دي قوي دي قري م د في ف د في ف د في د في د في	- <b>3</b>
Р2	مي مي مي مي مي مي مي مي مي مي مي مي مي م	ૢૢૢૢૢૢૢ <del>ૡૺૢૢૢૡ૾ૡ</del> ૻૡૻૡૻૡૢૺૢૻૡૻૺ૱૱ <i>ૡૺૡૢૺૡૺૺૢ</i> ૡૢૺ
Р3		
P4		ంల్లి స <u>్తిప్రస్తు ఆ చేస్తు</u> లు ఆటె రంతారా స్త్రాహ్

Table S3. Optimized configurations of the indicated compounds.



Figure S9. Excitation energies of antiaromatic compounds P1-P4 with oscillator strengths computed within the C2h point group using the B3LYP/6-311+G(d) level of theory.



Figure S10. The HOMO/LUMO topologies of P1-P4.

	c s a a b s c c	D b a a' b' D C C	A <sub>1</sub> b a' b S a' b' A <sub>1</sub> c	$A_2 \xrightarrow{b} a \xrightarrow{a'} b' A_2$	
ring	NICS (1)	NICS(1)	NICS (1)	NICS (1)	
а	18.2	20.4	15.3	14.8	
a'	18.2	20.4	15.3	14.8	
b	-11.5	-8.4	-8.0	-8.1	
b'	-11.5	-8.4	-8.0	-8.1	É.

**Table S4.** NICS values of the indicated compounds.



Figure S11. The NICS values and chemical structures of materials discussed here

## 4. OFET fabrication and characterization

Top-gate/bottom-contact (TG/BC) thin-film transistors with a structure of Cr/Au/TPNA-based polymers/PMMA/Al were fabricated to investigate the charge-transport properties of **P1** and **P3**. Corning Eagle 2000 glass substrates were cleaned by sonication in deionized water and isopropyl alcohol for 20 min. Source–drain electrodes (3 nm thick Cr adhesion layer and 30 nm thick Au electrodes) were thermally evaporated through a metal shadow mask (channel length 50  $\mu$ m, channel width 1000  $\mu$ m). The **P1** and **P3** active layers were spin-coated at 1500 rpm for 1 min from 4 mg mL<sup>-1</sup> chloroform solutions, and then they were tested as deposited or after thermal annealing on a hot plate at 130 °C, 150 °C, 180 °C, or 200 °C for 20 min. The PMMA dielectric layer was spin-coated at 1500 rpm for 40 s from 70 mg mL<sup>-1</sup> 2-butone solution and then dried at 80 °C for 3 h. Finally, 40 nm Al was evaporated on top as the gate electrode.

Bottom-gate top-contact (BGTC) TFTs of structure (Gate (Si)/dielectric (SiO<sub>2</sub>)/semiconductor/source-drain (Au) were fabricated with **P2**. The unpatterned 700  $\mu$ m thick heavily doped n-type silicon wafer (resistivity 0.005~ 0.02 $\Omega$ ·m) with 300 +/- 5% nm thermal oxide were used as the gate electrode and gate insulator, respectively. The silicon oxide substrates were immersed for an hour in 3 mM octadecyltrichlorosilane (OTS) in hexane at ~ 50% relative humidity in air, followed by sonication sequentially in hexane, acetone, and isopropanol. The resulting water contact angle was around 109°. The active semiconductor layer was formed by spin-coating a solution of the semiconductor compound dissolved in chloroform (4mg/mL CHCl<sub>3</sub>) and then annealing on a hot plate at 120 °C for 30 min, unless specified, to remove the solvent residues. Source/drain electrodes were defined by thermal evaporation of 40 nm thick gold film through shadow masks. The processing of semiconducting layer was performed inside of nitrogen-filled glove box unless specified. The channel lengths and widths are 50  $\mu$ m and 1000  $\mu$ m, respectively. The resulting capacitance of the silicon oxide dielectric with OTS treatment is about 10.5 nF/cm<sup>2</sup>

OTFT characterization was performed under ambient conditions in the dark on a custom probe station using an Agilent 1500 semiconductor parameter analyzer. The mobilities of OTFTs were extracted from the saturated region based on the equation:

$$I_{SD} = \frac{WC_i}{2L} \mu (VG - VT)^2$$

where W is the width of the channel (1000  $\mu$ m), L the length of channel (50  $\mu$ m),  $I_{SD}$  the source–drain saturation current, C<sub>i</sub> the capacitance per unit area of the insulator,  $\mu$  the mobility, V<sub>G</sub> the gate voltage, and V<sub>T</sub> the threshold voltage.



Figure S12. Transfer curves of P1 for both n- and p-type modes.



Figure S13. The transfer curves (a) and output curves (b) of P2.



Figure S14. The output curves of P3 after different annealing temperatures

Active layer	T (°C)	$\mu_{\rm e} ({\rm cm}^2{\rm V}^{-1}{\rm s}^{-1})$	$V_t(V)$	$I_{ m on}/_{ m off}$
	RT	$0.014{\pm}0.004$	23.0±1.5	$\sim 2 \times 10^2$
	130	$0.028 {\pm} 0.006$	$20.7{\pm}1.0$	$\sim 5 \times 10^2$
P3	150	$0.029 \pm 0.004$	25.2±1.6	$\sim 2 \times 10^3$
	180	$0.030{\pm}0.004$	23.2±1.2	$\sim 2 \times 10^3$
	200	$0.026 \pm 0.006$	$28.1{\pm}1.0$	$\sim 7 \times 10^2$

Table S5. OTFT performance parameters of P3-based devices annealed at various temperatures (AT).

## 5. OPV characterization

Non-fullerene OSC devices were fabricated by using indium tin oxide (ITO)-coated glass as the substrates (sheet resistance =15  $\Omega$  sq<sup>-1</sup>) with an inverted structure of ITO/ZnO (30 nm)/PTB7/P3HT: P3 /MoO<sub>3</sub> (10 nm)/Ag (100 nm). The patterned ITO-coated glass substrates were cleaned in detergent, deionized water, and acetone, followed by methanol and then isopropanol using a sonicator for 20 min each. The substrate was treated with UV/ozone for 20 min before device fabrication. The cathode interfacial layer, ZnO, was deposited from a precursor solution of 0.5 M zinc acetate dihydrate and 0.5 M 2-aminoethanol in 2-methoxyethanol, which was spun-cast at 7000 rpm for 30 s and annealed at 170 °C for 20 min in air. Active layer solutions were prepared by dissolving PTB7:**P3** (2:1 weight ratios) in  $CHCl_3$  with a total concentration of 10 mg mL<sup>-1</sup> with vigorous stirring for 8 h at 50 °C in an argon-filled glovebox. Active layers were then spin-cast inside the glovebox (800 - 1200 rpm, 60 s). Finally, the substrates were transferred into the high-vacuum chamber where MoO<sub>3</sub> (10 nm) and Ag (100 nm) were deposited as the interfacial layer and top electrode at pressures of less than  $2 \times 10^{-4}$  Pa with a rate of 0.10 - 0.2 and 1.0 - 0.21.5 Å s<sup>-1</sup>, respectively. The active area of the OSC cells was 6 mm<sup>2</sup>. To obtain the average data related to device performance, three batches of devices (four cells per batch) for each set of conditions were fabricated and tested. The photovoltaic characteristics of devices were tested under ambient conditions. The current density-voltage (J-V) curves were obtained using a Keithley 2400 instrument under simulated AM 1.5 G irradiation (100 mW cm<sup>-2</sup>) using an Xe arc lamp of a Spectra-Nova 300 W Class-A solar simulator. The light intensity was calibrated using an NREL-certified monocrystalline Si photodiode coupled to a KG3 filter to bring the spectral mismatch to unity.



Figure S15. CV plots of P3, PTB7-Th, P3HT, PTB7 as films (a), and the *J*-V curve of PTB7:P3/P3HT:P3 based OSCs (b)/(c).

Table S6. OPV performance parameters of PTB7/P3HT:P3 based OSCs.

PTB7: <b>P3</b>	$J_{\rm sc}$ (mA cm <sup>-2</sup> )	$V_{\rm OC}$ (V)	FF (%)	PCE (%) <sup>a</sup>
2:1 (60 nm)	0.05	0.47	30	0.007 (0.01)
2:1 (70 nm)	0.13	0.46	32	0.02 (0.025)
2:1 (80 nm)	0.13	0.45	34	0.02 (0.02)
РЗНТ: <b>РЗ</b>	$J_{\rm sc}~({ m mA~cm^{-2}})$	$V_{\rm OC}$ (V)	FF (%)	PCE (%) <sup>a</sup>
1:1 (3000 rpm)	0.11	0.47	30	0.015 (0.013)
1:1 (2000 rpm)	0.13	0.46	28	0.017 (0.014)
1:1 (1500 rpm)	0.15	0.46	27	0.018 (0.015)

<sup>a</sup> The PCE values in brackets is the maxium PCE.

## 6. Film morphology characterization

Atomic force microscopy (AFM) was measured on a Dimension Icon scanning probe microscope (Bruker Dimension FastScan AFM) in standard tapping mode. The blend thin films were prepared in the same way as the photovoltaic devices and spun cast on Si substrates. The neat films were spun cast on Si substrates in chloroform 16 mg mL<sup>-1</sup> solutions. Grazing-incidence wide-angle x-ray scattering (GIWAXS) measurements were performed at beamLine 8ID-E at the Advanced Photon Source at Argonne National Laboratory. The samples were irradiated at incidence angles from 0.130° to 0.140° in vacuum at 10.915 keV for two summed exposures of 2.5 s each. Signals were collected with a Pilatus 1M detector located at a distance of 228.16 mm from the samples. Blend films for GIWAXS were prepared according to the procedure for photovoltaic devices. For neat films, 16 mg mL<sup>-1</sup> solutions of corresponding polymers in chloroform were used to cast on Si (20 mm x 20 mm).



Figure S16. AFM heigh images (a) and phase images (b) of P3 films annealed at the indicated temperatures.



Figure S17. The out-of-plane (OOP) and in-plane (IP) line-cuts for pristine and 180°c thermally annealed P3 films.

Table S7. GIWAXS diffraction parameters for pristine and 180oc thermal annealing P3 films.

Film	OOP (100)(Å <sup>-1</sup> )	d(100) (Å)	IP(010) (Å <sup>-1</sup> )	d(010) (Å)
<b>P3</b> (RT)	0.300	20.93	1.779	3.53
<b>P3</b> (180°C)	0.300	20.93	1.785	3.52

## 7. NMR/Mass spectral data



**Figure S19.** <sup>1</sup>H NMR of **P2** in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>(120°C)



**Figure S20.** <sup>1</sup>H NMR of **P3** in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>(120°C)



Figure S21. <sup>1</sup>H NMR of P4 in  $C_2D_2Cl_4(120^{\circ}C)$ 



Figure S23. <sup>13</sup>C NMR of P2 in C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>(120°C)





Figure S26. Mass spectrum of P1



Figure S27. Mass spectrum of P2



Figure S28. Mass spectrum of P3



Figure S29. Mass spectrum of P4

## 8. References

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