Supporting information

Direct Arylation Polycondensation for Efficient Synthesis of Narrow-Bandgap Alternating D-A Copolymers Consisting of Naphthalene Diimide as Acceptor

Jinjun Shao, Guojie Wang, Kai Wang, Cangjie Yang, Mingfeng Wang*

School of Chemical and Biomedical Engineering, Nanyang Technological University,

62 Nanyang Drive, Singapore 637459, Singapore.

E-mail: mfwang@ntu.edu.sg;

Fax: +65 6794 7553; Tel: +65 6316 8746

Table of contents

1.	Synthesis of intermediates
2.	GPC traces for polymer P1, P2 and P3
3.	DSC curves for polymer P2 and P3
4.	Transfer and output characteristics of OTFT with P2 thin films annealed at 160 °C
	and tested in ambient conditions
5.	Transfer and output characteristics of OTFT with P3 thin films tested in ambient
	conditions at various thermal annealing temperatures
6.	Summary of OTFT characters of P2 and P3 thin films transistors in ambient
	conditions at various thermal annealing temperatures
7.	XRD data of P1, P2, P3 thin films test on silicon wafers in ambient conditions at
	various thermal annealing temperatures
8.	AFM images of P1, P2, P3 thin films test on silicon wafers in ambient conditions
	at various thermal annealing temperatures
9.	NMR spectra for new compounds and polymers

1. Synthesis of intermediates



(4-(2-ethylhexyl)thiophen-2-yl)trimethylstannane (3)

To a 100 mL of round bottom flask equipped with a magnetic stirring bar, Mg (0.316 g, 13 mmol) and one piece of I_2 were immersed in anhydrous THF (3 mL), the oil bath was kept at 50°C, then 2-Ethylhexyl bromide (1.931g, 10 mmol) in anhydrous THF (30 mL) were added dropwise into the mixture to keep the reaction mixture boiling all the time. The mixture was kept at 50°C for another 2h after the addition. When cooling to room temperature, and as prepared Grignard regent was ready for use. In another 100 mL of round bottom flask equipped with a magnetic stirring bar, 3bromothiphene (10 mmol) and catalyst NiCl₂(dppf)₂ (87 mg, 2%) were dissolved in anhydrous THF (20 mL), the mixture was cooling to 0°C in an ice bath. 10 min later, as prepared Grignard regent before was injected into the reaction mixture slowly. After the addition, the reaction mixture was increased to room temperature, and kept stirring for overnight. The mixture was quenched with HCl (10%, aq), and extracted with Hexane (200 mL \times 2). The combined organic phase was washed with NaHCO₃ (200 mL \times 2) and brine (200 mL \times 1). The organic phase was dried over anhydrous Na₂SO₄, and the organic solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, $CHCl_3$:Hex = 1:50) to afford compound 3-(2-ethylhexyl)thiophene as colorless liquid (1.785 g, 91%).

A mixture of 3-(2-ethylhexyl)thiophene (1.963 g, 10 mmol) and THF (20 mL) were charged into a 100 mL RBF under Ar(g), the mixture was cooling to -78°C, and LDA (1M, 12 mmol) was injected dropwise, after the addition of LDA, the reaction mixture was kept at -78°C for another 2 h. Later trimethyltin chloride in THF (1M, 10 mmol) was added in one portion at -78°C, the reaction was allowed to warm to room temperature slowly, and kept stirring for overnight. The mixture was quenched with HCl (10%, aq), and extracted with Hexane (150 mL \times 2). The combined organic phase

was washed with brine (150 mL \times 3). The organic phase was dried over anhydrous Na₂SO₄, and the organic solvent was removed under reduced pressure. The crude product was achieved as light yellow liquid (3.350 g, 93%).

¹H NMR (300 MHz, CDCl₃, 300 K): δ ppm = 7.18 (d, J = 0.9Hz, 1H), 6.98 (d, J = 0.9Hz, 1H), 2.60 (d, J = 6.9 Hz, 2H), 1.60-1.51 (m, 1H), 1.34-1.26 (m, 8H), 0.92-0.87 (m, 6H), 0.37 (s, 9H).



To a mixture of 2,5-dibromothiophene (14.280 g, 100 mmol) in concentrated sulfuric acid (95%, 150 mL) and Oleum (50 mL) at 0°C, KNO₃ (48 g, 400 mmol) was added slowly. The reaction was allowed to warm to room temperature slowly, and stirring at 45oC for overnight. After cooling to room temperature, the reaction mixture was poured into ice (500 g), and stirring for another 30min. the crude product was obtained by vacuum filtration. Later the pure 2,5-dibromo-3,4-dinitrothiophene was achieved by recrystallization in MeOH/CHCl₃ (1:10) as light yellow crystal (22.000 g, 66%).

A mixture of 2,5-dibromo-3,4-dinitrothiophene (3.319 g, 10 mmol), 2-(Tributylstannyl)thiophene (6.173 g, 25 mmol, 2.5 eq) and catalyst $PdCl_2(PPh_3)_2$ (350 mg, 5% mmol) in anhydrous DMF (3 mL) and THF (30 mL) was degassed by three freeze–pump–thaw cycles. The mixture was heated to 85 °C under argon overnight. The mixture was cooled to room temperature and extracted with ethyl acetate (100 mL × 2). The combined organic phase was washed with HCl (10%, aq, 100 mL × 2) and brine (100 mL × 1). The organic phase was dried over anhydrous Na₂SO₄, and the organic solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, CHCl₃:Hex = 1:2) to afford 3',4'-dinitro-2,2':5',2"terthiophene as yellow solid (3.120 g, 92%).

To a 100 mL of round bottom flask equipped with a magnetic stirring bar, dinitro compound (0.825 g, 2.5 mmol) was added into a mixture of THF (30mL), MeOH (15 mL) and HCl (conc. Aq. 15 mL), N₂(g) was purged into the mixture for 10min, then SnCl₂.2H₂O (6.769 g, 30 mmol, 12 eq) was added in one portion, later the mixture was kept stirring overnight at 50°C. After cooling to room temperature, the mixture was quenched with NaOH (10%, aq), and extracted with ethyl acetate (200 mL \times 2). The combined organic phase was washed with NaOH (10%, aq) (100 mL \times 3). The organic phase was dried over anhydrous Na₂SO₄, and the organic solvent was removed under reduced pressure. The crude product was achieved as dark liquid. After drying for 3h, PhNSO (0.672 mL), TMSCl (2.23 mL), anhydrous Et₃N (30 mL) and anhydrous CHCl₃ (30 mL) was added slowly. The reaction mixture was heated to 50°C for overnight. The mixture was cooled to room temperature and extracted with ethyl acetate (100 mL \times 2). The combined organic phase was washed with HCl (10%, aq, 200 mL \times 2) and brine (200 mL \times 1). The organic phase was dried over anhydrous Na₂SO₄, and the organic solvent was removed under reduced pressure. The crude product was purified by column chromatography (silica gel, $CHCl_3$:Hex = 1:20) to afford TTD 8 as purple blue solid (580 mg, 76%, based on dinitro compound 2.5 mmol). ¹H NMR (300 MHz, CDCl₃, 300 K): δ ppm = 7.54 (dd, J_1 = 0.9 Hz, J_2 = 3.75 Hz, 2H), 7.31 (dd, J_1 = 0.9 Hz, $J_2 = 5.1$ Hz, 2H), 7.09 (dd, $J_1 = 0.9$ Hz, $J_2 = 5.1$ Hz, 2H)



Potassium *tert*-butylate (13.19 g, 108 mmol) was added into a 250 mL round bottom flask with argon protection. A solution of 2-thiophenecarbonitrile (9.91 g, 90 mmol) in 75 mL *t*-amyl alcohol was then added into solution. The mixture was heated to 110 °C, and a solution of dimethyl succinate (4.38 g, 30 mmol) in 10ml *t*-amyl alcohol was added into solution dropwise in 1 hour. The reaction mixture was further heated at 120

°C for another 2 hours, and the colour changed to dark purple red. The solution was cooled to room temperature, and then poured into acidic MeOH (15 mL HCl in 300 mL MeOH). The suspension was then filtered and washed with hot MeOH and water to obtain dark purple solid (10.23 g, 76%). The product was used in the reaction in the following steps without further purification.

A 250 mL round bottom flask was charged with a stir bar, 3,6-di(thiophen-2-yl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3.000 g, 10 mmol), K₂CO₃ (4.140 g, 30.0 mmol) and DMF (100 mL) with argon flow. The reaction mixture was stirred at 120 °C before 2-ethylhexyl bromide (5.790 g, 30 mmol) was added to the reaction in 25 mL DMF dropwise in 30 min. After the reaction was stirred at 120 °C over night, the reaction mixture was then cooled to room temperature, poured into 400 mL water and filtered through a Büchner funnel. The filter cake was washed with water and the obtained crude product was further purified by flash chromatography (petroleum ether: dichloromethane = 4:1) to obtain purple solid (1.540 g, 29%).



Figure S1. GPC traces for polymer P1, P2 and P3



Figure S2. DSC curves for polymer P2 and P3

Figure S3. Transfer (a) and output (b) characteristics of OTFT with P2 thin films annealed at 160 °C and tested in ambient conditions.





Figure S4. Transfer and output characteristics of OTFT with **P3** thin films test in ambient conditions at 120 °C (a, b),160 °C (c, d), 200 °C (e,f) and 240 °C (g, h).

polymer	Annealing	$\mathbf{V_{th}}$ / \mathbf{V}	μ_h / cm ² V ⁻¹ s ⁻¹	$I_{on/off}$
P2	160 °C	-3.1	8.0 × 10-5	9.0×10^{2}
	120 °C	9.7	4.3×10^{-3}	2.25×10^3
D3	160 °C	11.8	4.6×10^{-3}	2.18×10^3
15	200 °C	13.0	1.1×10^{-4}	1.67×10^4
	240 °C	7.5	1.2×10^{-4}	55

Table S1. Summary of OTFT characters of **P2** and **P3** thin films transistors inambient conditions at various thermal annealing temperatures.



Figure S5. XRD data obtain from P1, P2, P3 thin films on silicon wafers annealed at different temperatures.

Figure S6. Tapping mode AFM images of **P1** and **P2** thin films test on silicon wafers in ambient conditions. Height (left) and phase (right) images are shown at a) **P1**, room temperature; (b) **P1**, 160 °C; (c) **P2**, room temperature; (d) **P2**, 160 °



Figure S7. Tapping mode AFM images of **P3** thin films test on silicon wafers in ambient conditions. Height (left) and phase (right) images are shown at a) 120 °C; (b) 160 °C; (c) 200 °C; (d) 240 °C.





Page S14

¹H NMR spectrum of



¹H NMR spectrum of











¹H NMR spectrum of





¹H NMR spectrum of **P1**





