#### **Electronic Supplementary Information**

### Naphthodipyrrolidone (NDP) Based Conjugated Polymers with High Electron

#### **Mobility and Ambipolar Transport Properties**

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#### Materials

3,8-Di(4-bromophenyl)-2,7-dioxo-1,2,3,6,7,8-hexahydronaphtho[1,2-b:5,6-

b']dipyrrole were prepared as described in the literature.<sup>[1]</sup> 4,8-bis(2ethylhexyloxy)benzo[1,2-b:4,5-b]dithiophene-2,6-diyl-bistrimethylstannane (**BDT**) was supplied by Dr. Wenjun Yang.<sup>[2]</sup> NBS, 2,2'-bithiophene, tetrakis(triphenylphosphine)palladium(0) (Pd(PPh<sub>3</sub>)<sub>4</sub>), and the solvents (tetrahydrofuran, dichloromethane, hexane, toluene, chlorobenzene) were obtained from Sigma-Aldrich. Anhydrous tetrahydrofuran (THF) was distilled over sodium and freshly used.

#### **Methods and Instrumentation**

UV/vis absorption spectra were recorded using a Hewlett Packard Model 8453 UV/vis spectrophotometer. 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 (5 mg/ml polymer in chloroform on glass substrate, 1500 rpm for 2 min). <sup>1</sup>H-NMR spectra were obtained using a Mercury 300 spectrometer. The thermal gravimetric analysis (TGA) was performed under nitrogen atmosphere (20 ml/ min) using a TA Instrument Model Q500 (heating rate: 10 °C/min). Molecular weights were determined upon gel permeation chromatography (GPC, HLC-8320GPC) equipped with Styragel columns. The calibration standard is polystyrene. All GPC measurements were carried out in

chloroform at 45 °C. Cyclic voltammograms were recorded by using an electrochemical station from CH Instruments (CHI 608E) inside an Ar-filled glove box. The thin films of polymers were prepared by casting polymer solution on an ITO electrode and cycled in acetonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>). Reference and counter electrodes were platinum. All potentials were corrected using ferrocene reference. The scan rate of CV is 100 mV s<sup>-1</sup> and the temperature is 20 °C.

#### **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 nF·cm<sup>-2</sup>). After cleaning the substrate with Piranha (H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> = 3/1), 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 µm and the channel width is1000 µm. The patterned substrate was then put in a glass Petri dish for active materials deposition. 4 mg/ml polymer solution (chlorobenzene) was heated at 70 °C for two hours in an Ar-filled glove box to ensure the complete dissolution of the polymer. Two to three drops of polymer solution were applied in the middle of the transistor gap through a syringe

(with PTFE filter, 0.45 µm, from VWR). The glass Petri dish was then covered for evaporating the solvent slowly at room temperature for two hours. Subsequently, the device was heated at 70 °C for 2 hours to ensure the complete removal of chlorobenzene. The device is then measured as "as prepared" device. The thermal annealing was conducted in a Ar-filled glove box on a hotplate. The transistor device was annealed at 140 °C for 5 min. Then the device was measured again as "annealed" device. The devices were characterized under vacuum in a six-arm Janis probe station with a HP/Agilent 4155A semiconductor analyzer. The field effect mobility was calculated using  $I_{SD} = (W/2L) \cdot \mu C_i (V_G - V_T)^2$ , 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;  $I_{SD}$ 

#### **GIWAXS Measurements**

Out-of-plane and in-plane profiles were integrated from line-cuts of grazing incidence wide-angle X-ray scattering (GIWAXS) patterns collected on Pilatus 1M pixel arraydetector at Beamline 8-ID-E [2] of the Advanced Photon Source (APS) at Argonne National Laboratory (ANL) at incident angle of  $0.14^{\circ}$ , slightly lower than the critical angles of total external reflection for the silicon wafer ( $0.165^{\circ}$ ), so as to maximize the scattering signals from the structures of the entire polymer film. Highly coherent X-ray beam with energy of 10.86 keV was collimated by slits with height of 20 µm and width of 200 µm, and the camera length is 228.165 mm. GIWAXS data were analyzed using the GIXSGUI package, and data are corrected for X-ray polarization, detector sensitivity, geometrical solid-angle, etc.<sup>[3]</sup>

#### **Synthesis of Monomers**

#### **Monomer BTh**



Scheme S1: Synthesis route to BTh

#### 5,5'-dibromo-2,2'bithiophene (2)

In a 250 ml flask, 2,2'-bithiophene (1, 3.3 g, 20 mmol) was dissolved in chloroform (65 ml). NBS (10.68 g, 60 mmol) was slowly added to the solution under N<sub>2</sub> protection at room temperature. The reaction mixture was stirred for 12 h at room temperature. The mixture was poured into water and extracted with dichloromethane. The organic layer was washed with brine and dried by anhydrous magnesium sulfate. The solvent was removed at reduced pressure. The crude product was purified by column chromatography (silica gel with hexane:dichloromethane=6:1 as eluent) to yield 2 (5.52 g, 86 %). The obtained product was purified by crystallization from dichloromethane/ MeOH (4/1) twice to obtain 3.23 g white solid product (Yield: 51 %). <sup>1</sup>H-NMR (300 MHz, d<sub>1</sub>-CDCl<sub>3</sub>)  $\delta$  ppm: 6.96 (d, 2 H), 6.85 (d, 2 H). <sup>13</sup>C NMR:  $\delta$  ppm: 137.78, 130.64, 124.14, 111.52.

#### 5,5'-bis(trimethlstannyl)-2,2'bithiophene (BTh)

In a 250 ml flask, **2** (3.2 g, 10 mmol) was dissolved in anhydrous THF (100 ml). Under  $N_2$  protection, n-BuLi (10 ml, 2.5 M, 25 mmol) was added dropwise to the solution at -78 °C. After the reaction mixture stirring for 1 h at -78 °C, the reaction temperature

was slowly warmed up to room temperature for 15 min. Subsequently, trimethyltin chloride (6 ml, 30 mmol) was added into the mixture at -78 °C and the reaction was kept at this temperature for another 2 h. After 12 h reaction at room temperature, the mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water and dried by anhydrous magnesium sulfate. The solvent was removed at reduced pressure. The crude product was purified by crystallization from hexane/MeOH (3/1) three times to obtain 1.14 g white solid product (Yield: 23 %). <sup>1</sup>H-NMR (300 MHz, d<sub>1</sub>-CDCl<sub>3</sub>)  $\delta$  ppm: 7.27 (d, 2 H), 7.08 (d, 2 H), 0.38 (s, 18 H). <sup>13</sup>C NMR:  $\delta$  ppm: 143.29, 137.31, 136.09, 125.10, 124.83, -7.99.



Figure S1 <sup>1</sup>H NMR spectrum of monomer BTh.



Figure S2 <sup>13</sup>C NMR spectrum of monomer BTh.



**Monomer NDP** 

Scheme S2: Synthesis route to NDP.

#### 1,4-Bis(α-hydroxy(4-bromophenyl)acetylamino)naphthalene (5)

A mixture of 1,5-diaminonaphthalene ( $\mathbf{3}$ , 1.582 g, 10 mmol) and 4-bromomandelic acid ( $\mathbf{4}$ , 6.93 g, 30 mmol) in chlorobenzene (40 ml) is heated at 135 °C for 21 hours. On cooling to room temperature, the precipitate is filtered, washed with ethanol and dried in vacuo to yield the crude product (5.19 g, yield: 89 %). The crude product is

suspended in chlorobenzene (20 ml), heated to 135 °C and stirred for 20 minutes, and then is cooled to room temperature. The precipitated product is filtered off and washed with methanol. The product is dried in air giving a white solid (4.23 g, yield: 72 %). <sup>1</sup>H NMR (300 MHz, DMSO):  $\delta$  ppm 10.13 (s, 2H), 7.74 (d, J=8.1 Hz, 2H), 7.60 (d, J=8.4 Hz, 4H), 7.55 (d, J=8.4 Hz, 4H), 7.49 (t, J=8.0 Hz, 2H), 6.67 (d, J=4.8 Hz, 2H), 5.27 (d, J=4.5 Hz, 2H). <sup>13</sup>C NMR, (300MHz, CDCl<sub>3</sub>): 171.90, 140.89, 133.70, 131.56, 129.39, 129.31, 125.95, 122.80, 121.29, 120.72, 73.73.

# *3,8-Di(4-bromophenyl)2,7-dioxo-1,2,3,6,7,8-hexahydronaphtho[1,2-b:5,6-b']dipyrrole (6)*

**5** (3,56 g, 6.1 mmol) is added to sulfuric acid (20 ml). After stirring at room temperature for 18 hours, the mixture is poured into ice water. The precipitate is filtered, washed with water and dried to yield the product (3.16 g, yield: 95 %). <sup>1</sup>H NMR (300 MHz, DMSO): δ ppm 11.27-11.58 (m, 2H), 7.44-7.55 (m, 4H), 7.00-7.12 (m, 4H), 6.72-6.83 (t, 2H), 6.52-6.61 (t, 2H), 3.98-4.78 (t, 2H). <sup>13</sup>C NMR, (300MHz, CDCl<sub>3</sub>): δ ppm 176.31, 175.48, 131.56, 130.74, 130.54, 130.26, 129.77, 129.64, 120.40, 108.78, 106.69. **3,8-Di-(4-bromophenyl)-2,7-dioxo-1,2,6,7-tetrahydronaphtho[1,2-b:5,6-b']dipyrrole** 

(7)

An aqueous solution of sodium hydroxide (2.11 ml, 5 N) is dropwisely added to a suspension of **6** (3.16 g, 5.8 mmol) in ethanol (18 ml). Then potassium persulfate (4.22 g, 15.7 mmol) in water (14 ml) is added. The resulting mixture is heated at reflux for 3 hours. The precipitate in the mixture is filtered, washed with water and ethanol, and dried to yield the product (2.88 g, yield: 91 %). The product is poorly soluble. NMR spectra cannot be measured.

#### 1-Iodo-2-decyltetradecane (8)

2-decyl-1-tetradecanol (7.4 g, 20.8 mmol), triphenylphosphine (6.53 g, 24.9 mmol) and imidazole (1.69 g, 24.9 mmol) were dissolved in dichloromethane (40 ml). The clear solution was cooled down to 0 °C and iodine (6.32 g, 24.9 mmol) was slowly added to the solution. After stirring for 15 min at this temperature, the reaction mixture was allowed to warm up to room temperature over 2 h. The reaction was quenched with 10 ml aqueous saturated sodium sulfite to reduce excess iodine. The solvent was removed by rotary evaporation. Subsequently the mixture was dissolved in 200 mL n-hexane, washed three times with 100 mL of water and once with 70 mL of brine. The raw product was passed through a 3 cm silica gel plug and dried over anhydrous magnesium sulfate. After filtration, the solvent was removed by rotary evaporation. The title product was obtained as colorless oil (9.65 g, yield: 95.3 %). 1H-NMR (300 MHz, d1-CHCl<sub>3</sub>)  $\delta$  ppm: 3.27 (d, J= 4.5 Hz, 2 H); 1.17-1.38 (m, 33 H); 0.88 (t, 6 H). <sup>13</sup>C NMR:  $\delta$  ppm: 38.74, 34.41, 31.91, 30.85, 29.84, 29.71, 29.67, 29.65, 29.63, 29.61, 29.57, 29.34, 26.49, 22.67, 16.68, 14.08.

## 3,8-di(4-bromophenyl)-1.6-bis(2-decyltetradecane)-2,7-dioxo-1,2,6,7-tetrahydronaphtho- [1,2-b:5,6-b']-dipyrrole (NDP)

In a mixture of 7 (2.73 g, 5 mmol) and  $K_2CO_3$  (2.43 g, 17.5 mmol) in DMF (80 ml), 8 was added (10.45 g, 22.5 mmol) under  $N_2$  protection. After stirred for 12 h at 60 °C in dark, the mixture was poured into water and extracted with dichloromethane. The organic layer was washed with brine and dried by anhydrous magnesium sulfate. The

solvent was removed at reduced pressure. The crude product was purified by column chromatography (silica gel with hexane:DCM=2:1 as eluent) to yield **NDP** (2.2 g, 36 %). The obtained product was purified by crystallization from dichloromethane/MeOH (1/2) twice to get 0.79 g black solid product (Yield: 13 %). <sup>1</sup>H-NMR (300 MHz, d<sub>1</sub>-CDCl<sub>3</sub>)  $\delta$  ppm: 7.66 (d, 4 H), 7.61 (d, 4H), 7.41 (d, 2 H), 7.16 (d, 2 H), 4.07 (d, 4 H), 1.94 (s, 2 H), 1.10-1.41 (br, 72 H), 0.87 (t, 12 H). <sup>13</sup>C NMR:  $\delta$  ppm: 169.7, 141.96, 134.20, 131.94, 130.99, 130.57, 123.11, 121.80, 119.10, 115.39, 38.31, 37.34, 31.90, 31.30, 29.98, 29.67, 29.63, 29.62, 29.54, 29.34, 29.32, 26.29, 22.66, 14.08.



Figure S3 <sup>1</sup>H NMR spectrum of monomer NDP.



Figure S4<sup>13</sup>C NMR spectrum of monomer NDP.

#### **General Polymer Synthesis Procedure**

In a Schlenk flask, NDP (182.9 mg, 0.15 mmol), BTh (73.8 mg, 0.15 mmol) were dissolved in toluene/DMF = 4/1 (5 ml). The mixture was degassed for 5 min using ultrasonication under N<sub>2</sub> protection. Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mg, 0.004 mmol) was quickly added into the mixture under N<sub>2</sub> 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. 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 (128 mg, yield: 67 %). 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 (95 mg, yield: 49 %). Molecular weight (GPC, chloroform):  $M_w = 104.3$  KDa, PDI = 2.5. <sup>1</sup>H-NMR (500 MHz, d<sub>1</sub>-CHCl<sub>3</sub>) δ ppm: 7.56–7.89 (br, 10 H), 7.34–7.43 (m, 2 H), 7.13–7.24 (br, 4 H), 4.06 (s, 4 H), 1.93 (s, 2 H), 0.94–1.48 (br, 80 H), 0.85 (s, 12 H).



Figure S5 <sup>1</sup>H NMR spectrum of polymer P1.

**P2:** Monomer **BDT** instead of **BTh** was used in polymerization. Other steps follow the same procedure as **P1** (yield: 53 %). Molecular weight (GPC, chloroform):  $M_w = 149$  KDa, PDI = 2.8. <sup>1</sup>H-NMR (500 MHz, d<sub>1</sub>-CHCl<sub>3</sub>)  $\delta$  ppm: 7.31-7.96 (br, 12 H), 6.93-7.21 (br, 2 H), 3.99-4.29 (br, 8 H), 1.66–2.03 (br, 96 H), 0.83 (s, 24 H).



**Figure S6** <sup>1</sup>H NMR spectrum of polymer **P6**.



Figure S7 Structure of NDP



Figure S8 TGA of polymers under nitrogen



**Figure S9** Cyclic voltammogram of **P1** (a) and **P2** (b) as thin films on ITO-coated glass substrates. Solution: 0.1 M TBAPF<sub>6</sub>–acetonitrile. Potential calculated *versus* ferrocene. Scan rate: 100 mV s<sup>-1</sup>; T =20 °C. The insets are enlarged voltammogram of reduction.



**Figure S10** The output characteristics and transfer characteristics of as prepared P2 device (a, to d) and thermal annealed devices (e to h).



Figure S11 GPC spectrum of P1.



Figure S12 GPC spectrum of P2.

**Table S1:** The hole mobilities  $(\mu_h)$ , electron mobilities  $(\mu_e)$ , and on/off ratios  $(I_{on}/I_{off})$  of FET devices.

polymer	condition	$\mu_{\rm h}$ +	$V_{h,Th}$	$\mu_{e}$ +	$\mu_e \pm$	$V_{e,Th}$	$I_{on}/I_{off}$
		$(\text{cm}^2 \text{ V}^{-1} \text{s}^{-1})$	(V)	$(\text{cm}^2 \text{ V}^{-1} \text{s}^{-1})$	$(\text{cm}^2 \text{ V}^{-1} \text{s}^{-1})$	(V)	$(log_{10})$
P1	RT	0.037(0.042)	-0.4	0.375(0.392)	0.08(0.09)	23.7	5-6
P1	140 °C	0.058(0.069)	-3.02	0.597(0.667)	0.230(0.283)	25.8	5-6
P2	RT	0.013 (0.018)	1.6	0.158 (0.164)	0.012(0.015)	45.5	5-6
P2	140 °C	0.016 (0.021)	1.4	0.213 (0.227)	0.052(0.057)	42.8	5-6

All data were obtained at two conditions: as prepared (RT) and annealed (140 °C). The mobilities are provided in average (highest) form and the performance are based on more than 10 different FETs. +: mobility extracted by fitting the linear part of the plot of  $I_{DS}^{1/2}$  versus  $V_G$ . ±: mobility calculated on the basis of two points of the plot of  $I_{DS}^{1/2}$  versus  $V_G$  at  $V_{Th}$  and  $V_G = 100$  V using the equation  $I_{DS} = C_i \mu (V_G - V_{Th})^2 W/2L$ .

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