# Synthesis and Characterization of New Thermally Stable Poly(naphthodithiophene) Derivatives and Applications for High-Performance Organic Thin Film Transistors

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**Supporting Information** 

**ABSTRACT:** A series of new p-type polymers, PNDT-T and PNDT-TT, with enforced coplanar structure for effective  $\pi$ electron delocalization, having naphtho[2,1-b:3,4-b']dithiophene and thiophenes as main core units, were successfully synthesized by Stille coupling reaction. The naphtho[2,1-b:3,4-b']dithiophene unit of the polymer main chain enhances charge carrier mobility by extending  $\pi$ conjugation length and rigidly enforced coplanar structure. Both polymers, PNDT-T and PNDT-TT, have high thermal stability up to 250 °C with a high  $T_g$  of 402 °C. On the basis of



AFM and XRD results, it was found that PNDT-TT showed relatively more highly ordered intermolecular structures than did PNDT-T, with thiophene unit and high field-effect mobility, because the bithiophene unit provides crystallinity with increasing planarity and enough space for interdigitation of the long alkyl side chains for high order. These new p-type polymers PNDT-T and PNDT-TT exhibit high carrier mobilities of 0.01 and 0.076 cm<sup>2</sup>/(V s) and on/off ratios of  $4 \times 10^5$  and  $7 \times 10^6$ , respectively. The above results indicate that the plate structure with a sulfur-containing fully aromatic system, which has the upper direction extended, could enhance the thermal stability and charge transport characteristics for OTFT applications.

# INTRODUCTION

With increased interest among both academic and industrial institutions in organic semiconductors, considerable research efforts have been devoted to the improvement of polymerbased organic thin film transistors (OTFTs) produced by solution processes, which have potential advantages of low cost, light weight, and flexibility for electronic circuit; potential fields of use include such area as drivers for electronic paper displays, radio-frequency identification (RFID) tags, sensors, and flexible displays on flexible substrates.<sup>1–8</sup>

Among the organic materials being considered for use in active layers in solution-processed OTFTs, polythiophenes, which have been extensively investigated to date, have provided essential guidance for designing materials. Polythiophene is attractive due to its extended  $\pi$ -conjugated length and its coplanar structure, which allows for effective  $\pi$ -electron delocalization.<sup>9</sup> Recently, to enhance the charge carrier mobility of OTFTs based on polythiophene derivatives, many research groups have focused on the study of the relationship between OTFT performance and the molecular structure of polythiophene derivative. For example, Toney and co-workers have

reported a thieno[3,2-*b*]thiophene unit in a polymer (0.3 cm<sup>2</sup>/ (V s));<sup>10</sup> Ong and co-workers have reported a poly(2,6-bis(3-alkylthiophen-2-yl)dithieno-[3,2-*b*;2',3'-*d*]thiophene) (PBTDT) (0.3 cm<sup>2</sup>/(V s)) with processing stability.<sup>11</sup> Malliaras and co-workers reported poly(2,5-bis(thiophene-2-yl)-(3,7-didecanyltetrathienoacene) (P2TDC10FT4) (0.087 cm<sup>2</sup>/(V s)) with varied conjugation sizes of fused thiophene rings and side chain effects.<sup>12,13</sup> More recently, naphthodithiophene derivatives are being intensively studied because of their extended conjugation system, which leads to strong intermolecular orbital overlap.<sup>14</sup> Takimiya and co-workers reported naphthodithiophene (NDT)-based polymers (0.77 cm<sup>2</sup>/(V s)) with enhanced coplanarity, *π*-stacking, and steric impact of isomeric polymer.<sup>14a</sup> In this study, we aimed to develop a new p-type OTFT material that would have a sulfur-containing fully aromatic system and upper direction extended *π*-conjugation along the main chain for effective *π*-electron delocalization.

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Figure 1. Structures of P3HT and thiophene-based polymeric semiconductors.

Recently, interest in air-stable materials for solutionprocessable organic semiconductors has increased due to issues of oxidative doping by atmospheric oxygen and water, which processes limit polymer performance and application.<sup>15</sup> Generally regionegular poly(3-hexylthiophene) (rr-P3HT), which is a widely studied prototype conjugated semiconducting polymer, has provided guidance for oxidative stability, owing to its high highest occupied molecular orbital (HOMO) level (about -4.9 eV). Many research groups have reported new materials to enhance the stability of thiophene-based conjugated polymers, through the use of more fused thiophene, which lowers the HOMO.<sup>15,16</sup> An additional requirement of OTFT materials is that they must have sufficient thermal stability because OTFT performance is degraded by the relatively low glass transition temperature of the polymers and by possible morphology changes at the process temperature (150 °C).<sup>17,18</sup> However, stability at high temperatures has received less attention because conjugated polymers are generally believed to be incapable of withstanding high temperatures. However, semiconducting polymers capable of withstanding high temperatures will be needed to enable the fabrication of novel organic-inorganic hybrid devices because, typically, inorganic electronic devices carried out at high temperature as well as the heat generated during operation of integrated devices.<sup>19</sup>

Here, we designed new poly(4,5-bis(2-octyldodecyloxy)naphtho[2,1-*b*:3,4-*b*']dithiophene—thiophene) (PNDT-T) and poly(4,5-bis(2-octyldodecyloxy)naphtho[2,1-b:3,4-b']dithiophene-bithiophene) (PNDT-TT), which are alternating copolymers composed of thiophenes and naphthodithiophene, for use in high-performance solution-processed OTFTs. The rigidly enforced planarity of naphthodithiophene confers effective  $\pi$ -electron delocalization with the extended  $\pi$ conjugation in the upper direction when incorporated into the conjugated polymer backbone. Furthermore, the enlarged aromatic form will lead to the further enhancement of air and thermal stability. In addition, the introduction of electrondonating 2-octyldodecyloxy groups can tune the electronic properties of naphthodithiophene and increase the solubility of the polymer. Although linear alkyl groups generally perform better than large branch alkyl groups at increasing the stacking characteristics through easy interdigitation, we found that polymers with linear alkoxy (dodecyloxy, 2,6-dimethylheptoxy) groups in the naphthodithiophene with thiophene units showed very poor solubility in common organic solvents. In order to increase the solubility, we used a long branched alkoxy side chain. To enhance the intermolecular  $\pi - \pi$  stacking, unsubstituted thiophene units were introduced. This property led to

many interesting characteristics, and the OTFT fabricated using PNDT-TT polymer showed a high hole mobility of 0.076 cm<sup>2</sup>/ (V s) and on/off ratio of  $7.6 \times 10^6$ . Moreover, the high thermal characteristics of PNDT-TT were stable after exposure to temperatures as high as 250 °C.

# EXPERIMENTAL SECTION

Measurements. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with a Bruker Advance-300 spectrometer. The thermal analysis were performed on a TA TGA 2100 thermogravimetric analyzer in a nitrogen atmosphere at a rate of 10 °C/min. Differential scanning calorimeter (DSC) was conducted under nitrogen on a TA Instruments 2100 DSC. The sample was heated with 10 °C/min from 30 to 300 °C. UV-vis absorption spectra were measured by UV-1650PC spectrophotometer. Molecular weights and polydispersities of the copolymers were determined by gel permeation chromatography (GPC) analysis with polystyrene standard calibration (Waters highpressure GPC assembly model M515 pump, u-Styragel columns of HR4, HR4E, HR5E, with 500 and 100 Å, refractive index detectors, solvent CHCl<sub>3</sub>). Cyclic voltammetry (CV) was performed on an EG and G Parc model 273 Å potentiostat/galvanostat system with a threeelectrode cell in a solution of 0.1 M tetrabutylammonium perchlorate (Bu<sub>4</sub>NClO<sub>4</sub>) in acetonitrile at a scan rate of 50 mV/s. The polymer films were coated on a square carbon electrode by dipping the electrode into the corresponding solvents and then dried under nitrogen. A Pt wire was used as the counter electrode, and an Ag/ AgNO<sub>3</sub> (0.1 M) electrode was used as the reference electrode. The atomic force microscope (AFM) (Multimode IIIa, Digital Instruments) was operated in tapping mode to acquire images of the surfaces of conjugated polymer. X-ray measurements were carried out using D8 DISCOVER with GADDS (Bruker AXS). DFT calculations were carried out with the Spartan 08 computational programs.<sup>2</sup>

OTFT Device Fabrication. To fabricate PNDT-T- and PNDT-TT-based OTFTs, we used heavily N-doped silicon substrate and thermally deposited SiO<sub>2</sub> 300 nm as dielectric layer. To determine the device performance for each material, we have employed bottom-gate top-contact geometry. Prior to treating the silicon oxide surface with ODTS (octadecyltrichlorosilane), the wafer was cleaned in piranha solution for 15 min at 200 °C and rinsed with abundant distilled water. PNDT-T semiconducting materials usually deposited onto each modified dielectric surface via spin-casting at 2000 rpm from 0.5 wt % chloroform solution. Films of PNDT-TT organic semiconductors were spin-coated at 4000 rpm from 0.5 wt % chloroform solution. Au as source and drain electrodes was thermally evaporated onto the semiconducting layer of 100 nm thickness, and to make pattern and channel region of 1000  $\mu$ m length and 100  $\mu$ m width, a shadow mask was used. All the OTFTs based on the polymers PNDT-T and PNDT-TT were found to exhibit typical p-channel characteristics. The electrical characteristics of the fabricated FETs were measured in air using both Keithley 2400 and 236 source/measure units. Field-effect mobilities were extracted in the saturation regime from the slope of the source-drain current.

**Materials.** 2,5-Bis(trimethylstannyl)thiophene and 5,5'-bis-(trimethylstannyl)-2,2'-bithiophene were prepared according to the reports.<sup>27</sup> 3-Thienylboronic acid (4) was purchased from Sigma-Aldrich, and tetrakis(triphenylphosphine)palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>) was purchased from Strem Chemicals Inc. The other materials were common commercial level and used as received. All solvents used were further purified prior to use.

**2-Octyldodecyl 4-Methylbenzenesulfonate (1).** *p*-Toluenesulfonyl chloride (63.8 g, 0.33 mmol) was added to 2-octyldodecanol (100 g, 0.33 mol) and pyridine (300 mL) at 0 °C under a nitrogen atmosphere. The reaction mixture was then stirred for 1 h in ice/water bath, and the mixture was stirred for another 2 h at room temperature. Afterward, the mixture was poured into aqueous 2 N HCl (300 mL) and extracted with ethyl acetate (EA). The combined organic layer was dried over magnesium sulfate (MgSO<sub>4</sub>) and concentrated. The crude oil was purified on silica gel (*n*-hexane/ethyl acetate 50:1). Yield: 90% as colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.82 (2H, d), 7.37 (2H, d), 3.94 (2H, d), 2.47 (3H, s) 1.57–1.61 (1H, m), 1.27 (32H, m), 0.92–0.88 (6H, t). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 144.90, 133.71, 130.13, 128.32, 73.30, 38.02, 32.30, 32.27, 31.02, 30.18, 30.01, 29.92, 29.88, 29.72, 29.65, 26.86, 23.04, 21.98, 14.47. HRMS (FAB+) *m*/*z* calcd for (C<sub>27</sub>H<sub>48</sub>O<sub>3</sub>S) 452.3324; found 452.3745.

**1,2-Bis(2-octyldodecyloxy)benzene (2).** From a mixture of catechol (15 g, 0.13 mol), 2-octyldodecyl 4-methylbenzenesulfonate (135.7 g, 0.3 mol), potassium hydroxide (30.6 g, 0.545 mol), and *N*,*N*-dimethylformamide (DMF) (400 mL), oxygen was removed by repeated evacuation followed by admission of nitrogen. The mixture was heated at 100 °C in a dry nitrogen atmosphere with stirring. After 24 h, water and diethyl ether were added. The organic layer was separated and dried over MgSO<sub>4</sub>. After removal of solvent, the crude oil was purified on silica gel (*n*-hexane/ethyl acetate 10:1). Yield: 69% as a colorless oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.89 (4H, s), 3.87 (4H, d), 1.82 (2H, s), 1.49–1.28 (64H, m), 0.90 (12H, t). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 150.16, 121.26, 114.51, 72.46, 38.67, 32.33, 31.81, 30.53, 30.14, 30.11, 30.07, 29.79, 27.34, 23.09, 14.48. HRMS (FAB+) *m*/*z* calcd for (C<sub>46</sub>H<sub>86</sub>O<sub>2</sub>) 670.6628; found 670.7289.

**1,2-Dibromo-4,5-bis(2-octyldodecyloxy)benzene (3).** Bromine (9.7 mL, 0.19 mol) in dichloromethane (DCM) (15 mL) was added to 1,2-bis(2-octyldodecyloxy)benzene (2) (63 g, 0.09 mol) in 200 mL of DCM. The mixture was stirred overnight at room temperature. After aqueous Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was added to the mixture, the organic layer was separated. The combined organic phases were washed with brine, dried over MgSO<sub>4</sub>, and concentrated. The crude oil was purified by silica gel column chromatography (*n*-hexane/dichloromethane 10:1). Yield: 87% as a light yellow oil. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.05 (2H, s), 3.82 (4H, d), 1.80 (2H, m), 1.46–1.28 (64H, m), 0.90 (12H, t). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 149.90, 118.27, 114.85, 72.67, 38.47, 32.32, 31.72, 30.45, 30.11, 30.07, 30.02, 29.76, 27.27, 23.08, 14.48. HRMS (FAB+) *m/z* calcd for (C<sub>46</sub>H<sub>84</sub>Br<sub>2</sub>O<sub>2</sub>) 828.4818; found 828.6124.

3,3'-(4,5-Bis(2-octyldodecyloxy)-1,2-phenylene)dithiophene (5). 1,2-Dibromo-4,5-bis(2-octyldodecyloxy)benzene (3) (68 g, 0.08 mol), 3-thiopheneboronic acid (23.1 g, 0.18 mol), Na<sub>2</sub>CO<sub>3</sub> (69.6 g, 0.65 mol), toluene (300 mL), ethyl alcohol (EtOH) (75 mL), and  $H_2O$  (75 mL) were added to the flask, and the solution was vigorously stirred during 1 h purge with nitrogen. Under a gentle nitrogen stream, Pd(PPh<sub>3</sub>)<sub>4</sub> (5.68 mg, 4.92 mmol) was added to the solution and heated at reflux for 18 h. After cooled to room temperature, the aqueous layer was extracted with ethyl acetate. The combined organic phases were washed with brine, dried over MgSO4, and concentrated. Chromatography of the crude material on silica gel (4:1 n-hexane/ dichloromethane) provided the product as colorless oil. Yield: 79%. <sup>1</sup>H NMR (300 MHz,  $CDCl_3$ ):  $\delta = 7.17 - 7.19$  (2H, dd), 7.04 (2H, d), 6.96 (2H, s), 6.78-6.80 (2H, dd), 3.92 (4H, d), 1.83-1.85 (2H, m), 1.28-1.50 (64H, m), 0.90 (12H, t). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 149.26, 142.60, 129.53, 128.29, 124.82, 122.61, 116.03, 72.55, 38.68, 32.36, 31.86, 30.56, 30.17, 30.14, 30.10, 29.80, 27.36, 23.10, 14.48. HRMS (FAB+) m/z calcd for (C<sub>54</sub>H<sub>90</sub>O<sub>2</sub>S<sub>2</sub>) 834.6382; found 834.7550.

4,5-Bis(2-octyldodecyloxy)naphtho[2,1-b:3,4-b']dithiophene (6) (NDT). A solution of 3,3'-(4,5-bis(2-octyldodecyloxy)-1,2phenylene)dithiophene (5) (5 g, 6 mmol) in dichloromethane (200 mL) was stirred vigorously under nitrogen as a suspension of iron(III) chloride (FeCl<sub>3</sub>) (2.14 g, 13.2 mmol) in nitromethane (MeNO<sub>2</sub>) (100 mL) was added dropwise. After the solution was stirred under nitrogen purging for 0.5 h, anhydrous methyl alcohol (MeOH) was added and stirred for 0.5 h. The solvents were removed, and the residue was taken up in dichloromethane and stirred vigorously with ammonium hydroxide NH<sub>4</sub>OH(aq). The aqueous layer was washed with dichloromethane, and the combined organics were washed with NH4OH and ammonium chloride (NH4Cl), dried, and removed. Purification on silica (n-hexane/dichloromethane 4:1) provided the product as a light yellow oil (40%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>2</sub>):  $\delta =$ 7.91 (2H, d), 7.69 (2H, s), 7.49 (2H, d), 4.09 (4H, d), 1.93-1.95 (2H, m), 1.28-1.63 (64H, m), 0.89 (12H, t). <sup>13</sup>C NMR (300 MHz,  $CDCl_3$ ):  $\delta = 149.79, 134.35, 130.74, 123.73, 123.12, 122.99, 107.03,$ 72.35, 38.65, 32.34, 31.92, 30.55, 30.15, 30.13, 30.09, 29.78, 27.42, 23.08, 14.48. HRMS (FAB+) m/z calcd for (C54H88O2S2) 832.6226; found 832.7335.

2,9-Dibromo-4,5-bis(2-octvldodecvloxv)naphtho[2,1-b:3,4b']dithiophene (7). N-Bromosuccinimide (NBS) (0.88 g, 4.96 mmol) in dichloromethane was added 2-octyldodecyloxynaphtho-[2,1-b:3,4-b']dithiophene (6) (2 g, 2.48 mmol) in dichloromethane (100 mL) under nitrogen, and the mixture was stirred at room temperature for 12 h. After aqueous sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>) was added to the mixture, the organic layer was separated. The aqueous layer was extracted with dichloromethane. The combined organic phases were washed with brine, dried over MgSO<sub>4</sub>, and concentrated. The crude product was purified by silica gel column chromatography (n-hexane/dichloromethane 3:1). The compound was further purified by recrystallization from acetone. Yield: 1.71 g, 72% as a white solid. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.85 (2H, s), 7.50 (2H, s), 4.06 (4H. d), 1.91–1.93 (2H, m), 1.27–1.61 (64H, m), 0.89 (12H, t). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ = 150.21, 134.15, 130.54, 125.91, 122.13, 112.49, 106.26, 72.21, 38.61, 32.33, 31.90, 30.53, 30.15, 30.12, 30.08, 29.80, 27.40, 23.08, 14.48. HRMS (FAB+) m/z calcd for (C54H86Br2O2S2) 990.4416; found 990.5056.

Poly(4,5-bis(2-octyldodecyloxy)naphtho[2,1-b:3,4-b']dithiophene-thiophene), PNDT-T (8). 2,9-Dibromo-2octyldodecyloxynaphtho[2,1-b:3,4-b']dithiophene (7) (500 mg, 0.504 mmol) and 2,5-bis(trimethylstannyl)thiophene (199 mg, 0.504 mmol) were dissolved into toluene (20 mL) in a flask. Nitrogen was bubbled through this flask for 0.5 h. Tetrakis(triphenylphosphine)palladium(0) (29.19 mg, 0.025 mmol) was added to the mixture, and the reaction was maintained at 90 °C for 48 h. 2-Bromothiophene (0.2 mL) was injected to the reaction mixture for end-capping, and the mixture was stirred for 12 h followed by the addition of 2-(tributylstanny)thiophene (0.4 mL), after which it was stirred overnight. The reaction mixture was precipitated into a mixture of methanol (200 mL) and 2 N HCl hydrochloric acid (30 mL) and stirred for 1 h. The precipitate was filtered. The polymer was purified by silica gel column chromatography (toluene) and concentrated polymer was precipitated in methanol. The polymer was further purified by washing via Soxhlet extraction with methanol (24 h), acetone (24 h), and hexanes (24 h), then dissolved in chloroform and reprecipitated into methanol, and then dried in vacuo to give product PNDT-T as a red solid (0.39 g, 85%). <sup>1</sup>H NMR (500 MHz,  $CDCl_3$ ):  $\delta$  = 7.39 (4H, br), 6.97 (2H, br), 4.02 (4H, br s), 1.92 (2H, br s), 1.24 (64H, br), 0.81 (12H, br s).

Poly(4,5-bis(2-octyldodecyloxy)naphtho[2,1-b:3,4-b']dithiophene–bithiophene), PNDT-TT (9). 2,9-Dibromo-2octyldodecyloxynaphtho[2,1-b:3,4-b']dithiophene (7) (500 mg, 0.504 mmol) and 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (248 mg, 0.504 mmol) were dissolved into toluene (20 mL) in a flask. Nitrogen was bubbled through this flask for 0.5 h. Tetrakis(triphenylphosphine)palladium(0) (29.13 mg, 0.025 mmol) was added to the mixture, and the reaction was maintained at 90 °C for 48 h. 2-Bromothiophene (0.2 mL) was injected to the reaction mixture for end-capping, and the mixture was stirred for 12 h followed by the addition of 2-(tributylstanny)thiophene (0.4 mL), after which it was stirred

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Scheme 1. Synthetic Route of PNDT-T and PNDT-TT



overnight. The reaction mixture was precipitated into a mixture of methanol (200 mL) and 2 N HCl hydrochloric acid (30 mL) and stirred for 1 h. The precipitate was filtered. The polymer was purified by silica gel column chromatography (toluene) and concentrated polymer was precipitated in methanol. The polymer was further purified by washing via Soxhlet extraction with methanol (24 h), acetone (24 h), and hexanes (24 h), then dissolved in chloroform and reprecipitated into methanol, and then dried in vacuo to give product PNDT-TT as a dark red solid (0.46 g, 91%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.49 (4H, br), 7.08 (4H, br), 4.12 (4H, br s), 2.06 (2H, br s), 1.34 (64H, br), 0.89 (12H, br s).

# RESULTS AND DISCUSSION

**Synthesis and Characterization.** The structures and the synthetic route of the polymers are outlined in Scheme 1. The monomer was obtained by various organic reactions such as bromination, Suzuki coupling reaction, and oxidative cyclization. Especially, NDT was synthesized by thiophene-centered oxidative cyclization<sup>21,22</sup> to be a sulfur-containing fully aromatic and confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and MS. Both polymers were synthesized by Stille coupling reaction of 5,5'-bis-(trimethylstannyl)-2,2'-bithiophene or 2,5-bis-(trimethylstannyl)thiophene with dibrominated NDT. The number-average molecular weights ( $M_n$ ) of PNDT-T and

Table 1. Polymerization Results and Thermal Properties of Polymers

polymer	yield [%]	$M_{\rm n}^{\ a}$ [kg/mol]	$M_{\rm w}^{\ a}$ [kg/mol]	PDI <sup>a</sup>	$T_{d}^{b}[^{\circ}C]$
PNDT-T	85	18.5	40.7	2.20	402
PNDT-TT	91	23	57.9	2.51	402

<sup>*a*</sup>Determined by GPC in chloroform (CHCl<sub>3</sub>) using polystyrene standards. <sup>*b*</sup>The temperature of degradation corresponding to a 5% weight loss determined by TGA at a heating rate of 10  $^{\circ}$ C/min.



Figure 2. Normalized UV–vis absorption spectra of polymers in solution (CHCl<sub>3</sub>) and film. The PNDT-T and PNDT-TT films were annealing at 200 and 250  $^\circ$ C, respectively.

Table 2. Optical and Electrochemical Properties of PNDT-T and PNDT-TT

	UV-vis absorption spectrum			cyclic voltammogram		
polymer	$\lambda_{\max}$ (nm) solution <sup>a</sup>	$\lambda_{\max} \pmod{(nm)}{\operatorname{film}}$	$\lambda_{\text{onset}}$ $(\text{nm})$	$\left( \begin{array}{c} E^{\mathrm{g}}_{\mathrm{opt}} \\ \left( \mathrm{eV} \right)^{b} \end{array} \right)$	HOMO (eV)	LUMO (eV) <sup>c</sup>
PNDT-T	523, 554	532, 578	618	2.01	-5.33	-3.32
PNDT- TT	546, 579	546, 590	642	1.93	-5.26	-3.33

<sup>*a*</sup>Dissolved in CHCl<sub>3</sub>. <sup>*b*</sup>Calculated from the absorption edge wavelength in the films. <sup>*c*</sup>Calculated from HOMO and optical band gap.

PNDT-TT are 18.5 and 23 kg mol<sup>-1</sup>, with corresponding PDI of 2.20 and 2.51, respectively, determined by gel permeation chromatography (GPC) using CHCl<sub>3</sub> as eluent and the calibration curve of polystyrene as standards. Both polymers have excellent solubility in common organic solvents such as toluene, chloroform, chlorobenzene (CB), and dichlorobenzene (DCB) due to their bulky side chain. The good solubility of both the polymers makes possible the solution processed thin films for electronics such as OTFTs.

The thermal properties of PNDT-T and PNDT-TT were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. As shown in Figure S1 (Supporting Information) and Table 1, both polymers exhibit good thermal stability with 5% weight-loss temperatures ( $T_d$ ) of 402 °C. The glass transition temperatures ( $T_g$ ) or melting peaks of the copolymers were not observed up to 280 °C, as shown in Figure S2. TGA and DSC results revealed that neither PNDT-T nor PNDT-TT degrades



Figure 3. UV–vis absorption spectra of PNDT-TT thin films at various temperatures measured after exposure to elevated temperatures in a  $\rm N_2$  atmosphere.



**Figure 4.** Cyclic voltammetry (CV) of PNDT-T and PNDT-TT films deposited in 0.1 M  $Bu_4N^+ClO_4^-/acetonitrile$  solution at scan rate of 50 mV/s: PNDT-T (red line) and PNDT-TT (blue line), ferrocene curve for calibration (black line).



**Figure 5.** HOMO and LUMO of the oligomers at ab initio Hartree– Fock (HF) and density functional theory (DFT-B3LYP) methods with  $6-31+G^*$  and  $6-311+G^{**}$  basis sets using Spartan 08.



Figure 6. SAM images of PNDT-T (a, b, c) and PNDT-TT (d, e, f): (a, d) as-prepared samples; (b, e) annealed at 200 °C; (c, f) annealed at 250 °C. All annealing processes were taken for 15 min.

below 280 °C nor melt, which are properties desirable for polymer-based OTFT applications.

Optical and Electrochemical Properties. The UV-vis absorption spectra of both polymers in chloroform solution, and in thin films produced by spin-coating using polymer solutions (5 wt % in chloroform), are shown in Figure 2 and summarized in Table 2. In dilute chloroform solution, PNDT-T and PNDT-TT respectively show absorptions at 523 and 546 nm; the shoulder peaks appear at 554 and 579 nm, which appearances are associated with interchain interactions.<sup>23</sup> In the solid state, the shoulder peaks of PNDT-T and PNDT-TT show a significant red-shift at around 578 and 590 nm, respectively. This particular enhanced shoulder absorption in films generally indicates an effective  $\pi$ -conjugation length elongation and a strong intermolecular packing in the solid state, caused by the planar and rigid backbones of NDT and the thiophene unit.<sup>24</sup> Notably, although PNDT-T exhibited similar absorption shapes in thin film, PNDT-TT showed more distinctively strong absorption shoulder at 590 nm and a broader absorption spectrum. Evidently, compared to PNDT-T, PNDT-TT exhibited pronounced aggregation in the solid film because of the rigid bithiophene unit, which might further enhance its mobility.

To confirm the thermal stability of the polymers, Figure 3 and Figure S3 show the UV-vis absorption spectra of the polymer thin films annealed for 15 min at various temperatures

 Table 3. Field Effect Transistor Device Characteristics upon

 Annealing Temperature

polymer	annealing temp (°C)	mobility (cm²/(V s))	threshold voltage (V)	on/off ratio
PNDT-T	fresh	0.000709	-2.37	$2.13 \times 10^{4}$
	100	0.000735	-22.5	$8.11 \times 10^{4}$
	150	0.00151	-24.7	$7.20 \times 10^4$
	200	0.00490	-19.2	$3.39 \times 10^{5}$
	250	0.00812	-18.5	$9.14 \times 10^{5}$
	300	0.0102	-17.3	$4.19 \times 10^{5}$
PNDT-TT	fresh	0.0227	-2.52	$6.29 \times 10^{4}$
	100	0.0364	-7.72	$1.65 \times 10^{6}$
	150	0.0453	-8.86	$8.77 \times 10^{5}$
	200	0.0579	-9.75	$2.30 \times 10^{6}$
	250	0.0760	-10.3	$7.61 \times 10^{6}$
	300	0.0689	-13.0	$1.11 \times 10^{6}$

in N<sub>2</sub>. The  $\pi - \pi^*$  absorption spectrum of PNDT-TT is not affected by annealing temperatures up to 300 °C because of the rigidly enforced planarity of naphthodithiophene and bithiophene, while PNDT-T is stable up to 200 °C, as shown in Figure S3. These results indicate that the electronic band structure of PNDT-TT is stable up to an annealing temperature as high as 300 °C.<sup>17</sup>

The cyclic voltammetry measurements for PNDT-T and PNDT-TT thin films are shown in Figure 4, and the results are summarized in Table 2. The HOMO levels of both polymers can be estimated from the equation  $E^{\text{HOMO}} = -(E^{\text{OX}}$ ferrocene<sup>OX</sup>) - 4.8 eV, where  $E^{OX}$  is the onset oxidation potential of both polymers (PNDT-T: 0.97 eV; PNDT-TT: 0.9 eV) and ferrocene<sup>OX</sup> is the onset oxidation potential of the ferrocene (0.44 eV) as reference.<sup>25,26</sup> The lowest unoccupied molecular orbital (LUMO) values were calculated using the optical band gap  $(E^{g}_{opt})$  and the calculated highest occupied molecular orbital (HOMO). HOMO energy levels of PNDT-T and PNDT-TT were estimated to be -5.33 and -5.26 eV, respectively, which values are about 0.4 eV higher than that of regioregular P3HT (about 4.9 eV), thus showing greater stability against oxidation doping. In addition, the HOMO value of PNDT-TT (-5.26 eV) is higher than that of PNDT-T (-5.33 eV) because the bithiophene unit in PNDT-TT is more electron-rich, while the LUMO values of both polymers are quite similar.27,28

In addition, we calculated the electron distribution in the molecular structure using the density functional theory (DFT)



Figure 7. X-ray diffraction patterns of (a) PNDT-T and (b) PNDT-TT: as-spun (i), and annealed film at 100 °C (ii), and 150 °C (iii), and 200 °C (iv), and 250 °C (v).



Figure 8. Field effect transistor device characteristics under ambient air with PNDT-T (a, b, c) and PNDT-TT (d, e, f) semiconductors: (a, d) output characteristics; (b, e) transfer characteristics; (c, f) transfer curves at fresh, 100 °C, 150 °C, 200 °C, 250 °C, and 300 °C.

in order to study the electron delocalization on a molecule, which is two repeating units of the polymers; for the simplification of the calculation, long alkyl chains were replaced by a  $CH_3$  group in the molecule. The calculated electron density distributions of HOMO and LUMO are shown in Figure 5. Inspection of the HOMO densities for these systems shows that  $\pi$ -orbitals are delocalized along the NDT unit as well as along the conjugated backbone.

**Structural and Morphological Studies.** In order to investigate the microstructure of the polymer thin films in detail at different thermal annealing temperatures, we conducted tapping-mode atomic force microscopy (TM-AFM) and X-ray diffraction measurements. The films of PNDT-T and PNDT-TT were prepared using 0.5 wt % chloroform solution; they were then spin-cast at 2000 and 4000 rpm on molecularly functionalized ODTS-treated SiO<sub>2</sub> substrates, respectively. Before annealing, the as-cast films of both PNDT-T and PNDT-TT show no clear crystalline surface morphology, as can be seen in Figure 6 (and Figure S4).

However, after annealing at 150, 200, 250, and 300 °C, the AFM phase images of both polymers clearly demonstrate pronounced film morphology, and the rms roughness also increased for both. It is likely that the morphology of the polymers is indicative of the effective packing formation of polymer chains in the  $\pi-\pi$  stacking direction. In addition, as shown in the UV–vis spectra of the as-cast and annealed polymer films at different temperatures, the morphology of the PNDT-TT film in the AFM image is stable up to as high as 250 °C and PNDT-T is stable up to 200 °C. The structural study of the polymers was further confirmed with X-ray diffraction (XRD) by analyzing the relative crystallinities of the PNDT-T and PNDT-TT in the solid state at various annealing temperatures, as shown in Figure 7. The XRD spectra of

both polymers show no visible peak up to 100 °C. However, PNDT-T clearly shows a crystalline diffraction peak at the annealing temperature of 150 °C, and PNDT-TT shows a crystalline diffraction peak at the annealing temperature of 200 °C. Both polymers exhibited obvious diffractions at  $2\theta = 3.8^{\circ}$ (PNDT-T) and  $3.5^{\circ}$  (PNDT-TT), which correspond to the interlayer *d*-spacings of 23.2 and 25.2 Å, respectively. The primary diffraction peak of PNDT-TT was observed to exhibit the relatively higher intensity. This indicates that PNDT-TT has better crystallinity than PNDT-T because bithiophene increases the planarity and provides enough space for the interdigitation of the long alkyl side chains.<sup>29</sup>

OTFT Properties. Thin film transistors (TFT) based on both polymers were fabricated using bottom gate-top contact device geometry by spin-casting the polymer solution in chloroform. The carrier mobility was measured in the saturation regime using the relationship  $\mu_{sat} = (2I_{DS}L)/$  $(WC(V_{\rm g} - V_{\rm th})^2)$ , where  $I_{\rm DS}$  is the saturation drain current, C is the capacitance of the oxide dielectric,  $V_{\rm g}$  is the gate bias, and  $V_{\rm th}$  is the threshold voltage.<sup>30,31</sup> The slope of the plot was applied in the saturation region of the drain current 1/2 vs gate voltage curve of each of the polymers in order to calculate the mobility. The mobilities and on/off ratios of both polymers are summarized in Table 3. As shown in Figure 8, PNDT-T and PNDT-TT were found to exhibit typical p-type characteristics, and the output curves of the polymers showed linear shapes and very good saturation in each range of the drain voltage, which is common behavior for conjugated polymers.<sup>30,32</sup> PNDT-TT exhibited high hole mobility of 0.076  $\text{cm}^2/(\text{V s})$ and on/off ratio of  $7.61 \times 10^6$ . PNDT-T showed a hole mobility of 0.01 cm²/(V s) and on/off ratio of 4.19  $\times$   $10^5.$ Interestingly, as shown in Table 3, for both polymers the annealing temperature tends to affect the mobility. All devices based on both polymers were annealed at 100, 150, 200, 250, and 300 °C, and both polymers showed thermal stability on each device. PNDT-T and PNDT-TT devices at 250 °C were found to possess higher charge carrier mobility of 0.01 and 0.076 cm<sup>2</sup>/(V s), respectively. This behavior is explained by the enhanced intensity and the second-order peak in X-ray diffraction, indicating a higher order in the polymer films, as well as the morphological differences in the AFM images at the various annealing temperatures.

The FET devices using these polymers showed high on/off ratio (about 10<sup>6</sup>). In addition, PNDT-TT exhibited a higher mobility compared to that of PNDT-T. This result shows that, compared to that of PNDT-T, the high mobility of PNDT-TT resulted from the increased degree of crystallinity produced by the thermal annealing, as verified by AFM and X-ray diffraction, compared to those of PNDT-T. PNDT-TT polymer can be thought to be capable of developing thin film crystallinity during thermal treatment because the bithiophene provides enough space for the long alkyl side chains interdigitation and increases the planarity with enhanced  $\pi$ -stacking.

### CONCLUSION

We have synthesized and characterized two p-type conjugated polymers, PNDT-T and PNDT-TT, for use as active materials in OTFTs, by incorporating naphthodithiophene for more effective  $\pi$ -electron delocalization with upper direction extended  $\pi$ -conjugation. The PNDT-T polymer has a molecular weight of 18.5 kDa with a polydispersity index of 2.2, and the PNDT-TT has a molecular weight of 23 kDa with a polydispersity index of 2.51. The obtained polymers have good solubility with long alkyl side chains and HOMO levels of -5.33 eV (PNDT-T) and -5.26 eV (PNDT-TT), resulting in good oxidation stability. Both polymers have high thermal stability up to 250 °C with a high  $T_g$  of 402 °C, from TGA, UV, and AFM. These new polymers, PNDT-T and PNDT-TT, exhibit higher field-effect mobilities of 0.01 cm<sup>2</sup>/(V s) ( $I_{on/off}$  = 4.19  $\times$  10<sup>5</sup>) and 0.076 cm<sup>2</sup>/(V s) ( $I_{\rm on/off}$  = 7.61  $\times$  10<sup>6</sup>), respectively. The higher mobility of PNDT-TT was found to result from the increasing thiophene content of PNDTs, which effectively increases polymer crystallinity, as evident from XRD and AFM studies. Based on these results, main chain modifications for high crystallinity with NDTs are also expected to yield higher thermal stability and enhanced charge carrier mobility for high OTFT performance.

# ASSOCIATED CONTENT

#### **S** Supporting Information

Figures S1–S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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#### Notes

The authors declare no competing financial interest.

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