Supporting Information

Conjugated Polymers Based on Thiazole Flanked Naphthalene Diimide for Unipolar n-Type Organic Field-Effect Transistors

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1. General materials and characterizations

All reagents were purchased from commercial sources (Aldrich, Acros, and J&K) and used as received without further purification. The reference polymer N2200 with a number average molecular weight ($M_n$) of 54.0 kDa and a molar-mass dispersity ($D_M$) of 2.3 was purchased from Derthon Optoelectronic Materials Co. (3,4-difluorothiophene-2,5-diyl)bis(trimethylstannane) (2FT), 2,5-bis(trimethylstannyl)thiophene (T), 2,5-bis(trimethylstannyl)selenophene (Se), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (2T) were purchased from Suna Tech. Compound 1 and 2 were synthesized according to previous reported literatures. The $^1$H and $^{13}$C NMR were measured on a Bruker AV-500 MHz spectrometer with tetramethylsilane (TMS) as the internal reference. The high temperature $^1$H NMR was measured on a Bruker AVANCE AV 400 with deuterated 1,2-dichlorobenzene as the solvent at 120 °C. Molecular weights of the polymers were determined using an Agilent Technologies PL-GPC 220 high-temperature chromatograph in 1,2,4-trichlorobenzene at 150 °C using a calibration curve of polystyrene standards. The elemental analysis (EA) data was acquired on a varioELcube elemental analyzer. The geometry was optimized with density functional theory (DFT) using B3LYP hybrid functional with basis set 6-31g*. Quantum-chemical calculation was performed with the Spartan 10 software and the alkyl substituents being replaced by methyl group were used for calculations. Thermogravimetric analysis (TGA) was carried out with a NETZSCH (TG209F3) apparatus at a heating rate of 20 °C min$^{-1}$ under a nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements were performed on a NETZSCH (DSC200F3) apparatus under a nitrogen atmosphere with a heating/cooling rate of 20/40 °C min$^{-1}$ for the first cycle and a heating/cooling rate of 10/20 °C min$^{-1}$ for the second cycle, respectively. UV-vis absorption spectra of the polymer in ortho-dichlorobenzene solutions and in films were recorded on a SHIMADZU UV-3600 spectrophotometer. The electrochemical cyclic voltammetry (CV) measurements were conducted
on a CHI 600D electrochemical workstation in a solution of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, 0.1 M) in acetonitrile at a scan rate of 50 mV s⁻¹. An ITO electrode coated with polymer film, a platinum wire and a standard calomel electrode (SCE) were used as the working electrode, counter electrode, and reference electrode, respectively. The thin film X-ray diffraction (XRD) patterns were acquired by a Panalytical X-Empyrean with a Cu Kα (1.54060 Å) source, using current I = 40 mA and accelerating voltage V = 40 kV. Tapping-mode AFM images were obtained by using a Bruker Multimode & Microscope.

2. OFETs device fabrication and characterization

Top gate and bottom contact (TGB) OFETs were used to evaluate the charge transport properties of the polymers. The glass substrates were washed by an ultrasonic cleaner with deionized water, acetone and isopropanol, dried under a nitrogen flow and heated at 120 °C for 10 min. Au (30 nm) was deposited on the glass substrate as source and drain electrodes with W/L = 70 (W = 5600 µm, L = 80 µm). The polymer films (~25 nm) were spin coated from hot o-DCB solutions with a concentration of 4.0 mg mL⁻¹ at 1000 rpm. Then the films were annealed at 200 °C for 10 min. The dielectric layer (~600 nm) was spin coated from butyl acetate solution (80 mg mL⁻¹) of poly(methyl methacrylate) (PMMA, M_w = 120 kDa) at 1300 rpm and then annealed at 100 °C for 40 min. Finally, as gate electrode, Al (80 nm) was vacuum-evaporated on top. All the spin coating processes were conducted in a glove box and OFETs were measured under ambient conditions with two Keysight B1500A source/measure units. Field-effect mobility in linear and saturation regime were calculated by using the following equation: 

\[ I_{DS} = (\mu C_i W/L)(V_G - V_T)V_{DS}, \]

\[ I_{DS} = (\mu C_i W/2L)(V_G - V_T)^2, \]

respectively, in which \( I_{DS} \) is the drain-source current, \( \mu \) is the field-effect mobility, \( C_i \) is the capacitance per unit area of the dielectric layer, \( V_G \), \( V_D \) and \( V_T \) are the gate voltage, drain voltage and threshold voltage, respectively.

3. Synthetic procedures and characterization
Synthesis of compound 3: Compound 1 (2.2 g, 2 mmol) and compound 2 (3.0 g, 8 mmol) were dissolved in toluene (30 mL). After being purged by argon twice, catalyst Pd(PPh₃)₄ (185 mg, 0.16 mmol) was added into the solution and then the reaction mixture was purged by argon twice again. The reaction was stirred at 110 °C overnight. After removal of the solvent, the product was purified by column chromatography of silica gel using ethyl acetate (EA): petrol ether (PE) =1:5 as the eluent to afford crude product, and then the product was further purified by recrystallization to give compound 3 (1.9 g, 87% yield) as yellow powder. H NMR (500 MHz, CDCl₃, δ): 8.96 (s, 2H), 8.08 (d, J=3.2, 2H), 7.69 (d, J=3.2, 2H), 4.08 (d, J=7.3, 2H), 1.94 (d, J=5.6, 2H), 1.47 – 1.11 (m, 80H), 0.89 (td, J=7.0, 3.2, 12H). C NMR (500 MHz, CDCl₃, δ): 164.65, 162.02, 142.62, 138.42, 135.38, 127.74, 125.99, 124.80, 122.07, 45.09, 36.44, 31.93, 31.92, 31.45, 30.04, 29.70, 29.69, 29.66, 29.64, 29.37, 29.36, 26.28, 22.69, 14.13. MS (MALDI-TOF): Calcd. for C₆₈H₁₀₄N₄O₄S₂: 1105.72. Found: 1106.84 [M+H].

Synthesis of compound 4: Compound 3 (553 mg, 0.5 mmol) and sodium carbonate anhydrous (500 mg, 5 mmol) were added into a solvent mixture of N,N-dimethylformamide (DMF, 2 mL) and chloroform (CF, 8 mL). Br₂ (1 mL) was added into the reaction mixture at 0 °C, and then the reaction was warmed to 40 °C. The reaction was monitored by thin layer chromatography. Sodium thiosulfate (5 g, 20 mL H₂O) solution was added into the reaction mixture and stirred for 30 min to remove Br₂. The mixture was washed with brine for serval times and the organic layer was extracted with dichloromethane, and then the organic layer was dried over MgSO₄. After removal of solvent, the product was purified by column chromatography of silica gel using dichloromethane as the eluent to afford crude product, and then the product was further purified by recrystallization to give compound 4 (300 mg, 48% yield) as red-orange solid. H NMR (500 MHz, CDCl₃, δ): 9.16 (s, 2H), 7.95 (s, 2H), 4.09 (d, J = 7.3 Hz, 4H), 1.95 (d, J = 6.1 Hz, 2H), 1.45 – 1.04 (m, 80H), 0.87 (td, J = 7.0, 3.3 Hz, 12H). C NMR (500 MHz, CDCl₃, δ): 164.72,
162.50, 161.93, 144.46, 138.28, 135.57, 127.69, 126.07, 123.62, 113.14, 45.12, 36.46, 31.92, 31.50, 30.04, 29.70, 29.68, 29.65, 29.36, 26.29, 22.70, 14.13. **MS (MALDI-TOF):** Calcd. for C_{68}H_{102}Br_{2}N_{4}O_{4}S_{2}: 1263.52. Found: 1264.57 [M+H].

**Polymerization of polymer PTzNDI-2FT:** To a degassed solution of compound 4 (126.4 mg, 0.1 mmol) and 3,4-difluorothiophene-2,5-diylbis(trimethylstannane) (44.6 mg, 0.1 mmol) in anhydrous o-xylene/DMF (2 mL/0.4mL) under argon protection, Pd_{2}(dba)_{3} (1.8 mg, 0.002 mmol) and P(o-Tol)_{3} (4.9 mg, 0.016 mmol) were added. Then the mixture was stirred at 110 °C for 24 hours. After that, 2-(tributylstannyl)thiophene and 2-bromothiophene were sequentially added to the reaction with 2 hours interval. After another 2 hours, the reaction mixture was diluted with chlorobenzene (CB), and refluxed with aqueous solution of sodium N,N-diethylcarbamodithioate trihydrate for 2 hours. After cooling to room temperature, the reaction mixture was precipitated in methanol and filtered through a Soxhlet thimble. The polymer was subjected to sequential Soxhlet extraction with methanol, acetone, hexane, dichloromethane, chloroform under argon protection, and the high molecular weight fraction was extracted with CB. The CB fraction was concentrated under reduced pressure and precipitated into methanol to obtain the polymer solid, and the solid was dried under vacuum to obtain resulting PTzNDI-2FT (112 mg, yield = 92%). \( M_n = 79.4 \) kDa, \( D_M = 1.8 \). EA found: C, 71.73%; H, 8.67%; N, 4.45%; S, 7.87% (calculated: C, 70.66%; H, 8.57%; N, 4.58%; S, 7.86%).

The other three polymers were obtained via the similar procedure as PTzNDI-2FT, and the molecular weights and the elemental analysis results of the polymers are as follows.

PTzNDI-T (94 mg, yield = 80%). \( M_n = 115.6 \) kDa, \( D_M = 1.8 \). EA found: C, 72.78%; H, 9.02%; N, 4.54%; S, 7.98% (calculated: C, 72.80%; H, 9.00%; N, 4.72%; S, 8.10%).
PTzNDI-Se (102 mg, yield = 83%). $M_n = 118.3$ kDa, $D_M = 1.5$. EA found: C, 70.66%; H, 8.76%; N, 4.41%; S, 5.18% (calculated: C, 70.04%; H, 8.65%; N, 4.54%; S, 5.19%).

PTzNDI-2T (80 mg, yield = 42%). $M_n = 96.6$ kDa, $D_M = 1.8$. EA found: C, 71.18%; H, 8.74%; N, 3.95%; S, 9.25% (calculated: C, 71.88%; H, 8.57%; N, 4.41%; S, 10.10%).

4. Additional figures and tables

Figure S1. $^1$H NMR spectrum of compound 3.
Figure S2. $^{13}$C NMR spectrum of compound 3.

Figure S3. $^1$H NMR spectrum of compound 4.
Figure S4. $^{13}$C NMR spectrum of compound 4.

Figure S5. $^1$H NMR spectrum of PTzNDI-2FT acquired at 120 °C.
Figure S6. $^1$H NMR spectrum of PTzNDI-T acquired at 120 °C.

Figure S7. $^1$H NMR spectrum of PTzNDI-Se acquired at 120 °C.
**Figure S8.** $^1$H NMR spectrum of PTzNDI-2T acquired at 120 °C.

**Figure S9.** GPC traces of the polymer PTzNDI-2FT (a), PTzNDI-T (b), PTzNDI-Se (c) and PTzNDI-2T (d) acquired with 1,2,4-trichlorobenzene as eluent at 150 °C.
Figure S10. Energy-minimized conformation and calculated frontier molecular orbitals of PTzNDI-2FT (a, b), PTzNDI-T (c, d), PTzNDI-Se (e, f), and PTzNDI-2T (g, h), respectively. Alkyl chain was substituted by methyl to simplify the calculation.
Figure S11. DSC thermograms of PTzNDI-2FT (a) and PTzNDI-T (b) with a heating/cooling rate of 20/40 °C min⁻¹ for the first cycle and a heating/cooling rate of 10/20 °C min⁻¹ for the second cycle, respectively.

Table S1. Electrochemical properties of the polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>(E_{\text{red}}) [V] (^a)</th>
<th>(E_{\text{ox}}) [V] (^a)</th>
<th>LUMO [eV] (^b)</th>
<th>HOMO [eV] (^b)</th>
<th>(E_{\text{CV}}) [eV] (^c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N2200</td>
<td>-0.62</td>
<td>1.46</td>
<td>-3.81</td>
<td>-5.89</td>
<td>2.08</td>
</tr>
<tr>
<td>PTzNDI-2FT</td>
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<td>1.81</td>
<td>-3.89</td>
<td>-6.24</td>
<td>2.35</td>
</tr>
<tr>
<td>PTzNDI-T</td>
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<td>1.58</td>
<td>-3.85</td>
<td>-6.01</td>
<td>2.16</td>
</tr>
<tr>
<td>PTzNDI-Se</td>
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<td>1.48</td>
<td>-3.83</td>
<td>-5.91</td>
<td>2.08</td>
</tr>
<tr>
<td>PTzNDI-2T</td>
<td>-0.63</td>
<td>1.30</td>
<td>-3.80</td>
<td>-5.73</td>
<td>1.93</td>
</tr>
</tbody>
</table>

\(^a\) Versus Fc/Fc\(^+\); \(^b\) LUMO = \(-e(E_{\text{re}} + 4.80 - E_{\text{Fc/Fc}^+})\), HOMO = \(-e(E_{\text{ox}} + 4.80 - E_{\text{Fc/Fc}^+})\), \(E_{\text{Fc/Fc}^+}=0.37\) V; \(^c\) \(E_{g\text{CV}}=\text{LUMO−HOMO}\).

References: