# Electronic Supplementary Information

for

# An n-Type Narrow-Bandgap Organoboron Polymer with Quinoid Character Synthesized by Direct Arylation Polymerization

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#### 1. Characterization

General. <sup>1</sup>H, <sup>13</sup>C, and <sup>19</sup>F NMR spectra of organic molecules and polymer were measured with a Bruker AV-500 spectrometer at 25 °C. Elemental analysis was performed on a VarioEL elemental analyzer. Gel permeation chromatography (GPC) was carried out at 150 °C with a PL-220-type GPC. 1,2,4-Trichlorobenzene (TCB) was used as the eluent and mono-disperse polystyrene was used as the reference. Thermal gravimetric analysis (TGA) was performed under an N<sub>2</sub> flow at a heating rate of 10 °C/min with a Perkin-Elmer-TGA 7 system. The absorption spectra were measured using a JAS.CO V-770 spectrophotometer with a home-built closed quartz colorimeter for protecting the samples from the air exposure during absorption measurement. Cyclic voltammetry (CV) was performed in a solution of 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> in acetonitrile with a CHI660a electrochemical analyzer system using a glassy carbon working electrode, a platinum gauze counter electrode and an Ag/AgCl reference electrode. The polymer was casted on the working electrode for measurement. The redox potentials were calibrated with ferrocene as an internal standard. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels of the materials were estimated by the equations: HOMO/LUMO = -(4.80)+ E<sub>onset</sub><sup>ox</sup>/E<sub>onset</sub><sup>red</sup>). The thickness of pristine or doped films were measured with a Bruker 3D Optical Profilometer Contour GT-I. Electron paramagnetic resonance (EPR) spectra were recorded with a Bruker EMXnano EPR spectrometer running the Xenon software at room temperature (The microwave power was 1 mW; the modulation amplitude was 0.2 G; the modulation frequency was 100.00 kHz; the time constant was 1.28 ms; and the sweep time was 45.04 s). The X-band EPR spectrum of polymers were recorded at 9.615 GHz with a modulation amplitude of 0.02 mT and a microwave power of 1 mW. The configuration optimizations of the two polymers were conducted by Density functional theory (DFT) calculations using the Gaussian 09 program at the B3LYP/6-31G\*\* level of theory on the neutral state and at the U $\omega$ B97XD/6-31G\* level on the negatively charged state.<sup>1</sup> All of the long alkyl chains have been replaced by methyl groups for simplification.

#### 2. Materials and synthetic procedures

**Materials.** All reactions were performed under an argon atmosphere, unless stated otherwise. Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Dry toluene was distilled via standard method.



Scheme S1. Synthetic routes to PBN-TP.

**Dibromo-substituted BNBP (1):** The synthesis of the monomer 1 is according to our previous work.<sup>2</sup> <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.20 (d, J = 1.5 Hz, 2H), 7.67 (d, J = 1.5 Hz, 2H), 3.48 (d, J = 7.1 Hz, 4H), 1.72 (s, 2H), 1.45 – 1.12 (m, 98H), 0.91 – 0.85 (m, 12H).

**2,5-dibromo-3,4-dinitrothiophene (2.2):** Into a dried three-necked flask containing a mixture of concentrated sulfuric acid (33.0 mL), fuming sulfuric acid (50.0 mL), and fuming nitric acid (28.0 mL), cooled with an ice bath, 2,5-dibromothiophene **2.1** (18.8 g, 77.7 mmol) was added slowly in a dropwise fashion to maintain a temperature of 15 °C. After complete addition, the reaction mixture was stirred at 30 °C for 3 h and then poured into 300 g of ice.

Upon melting of the ice, the yellow solid residue was collected by vacuum filtration and washed with water for three times. Finally, the coarse product was recrystallized from methanol to give the product **2.2** as buff crystal (10.3 g, 40%).<sup>13</sup>C NMR (126 MHz, DMSO)  $\delta$  139.65, 116.70.

**3,4-Diaminothiophene Dihydrochloride (2.3):** Concentrated HCI (135 mL, 37%) and 2,5-dibromo-3,4-dinitrothiophene **2.2** (7.5 g, 22.6 mmol) were combined in a thoroughly dried flask and cooled in an ice bath. Tin metal (18.7 g, 157.5 mmol) was slowly added within 30 min to maintain a temperature of 25-30 °C. After complete addition, the reaction was stirred at 30 °C for 6 h until all the tin was consumed, and the flask was then kept in a refrigerator overnight. The solid precipitate was recovered by vacuum filtration and washed with diethyl ether and acetonitrile to give the product **2.3** as white solid (4.0 g, 95%). <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  8.24 (s, 6H), 7.06 (s, 2H).

**2,3-dimethylthieno[3,4-b] pyrazine (2):** A mixture of dimethylglyoxal (0.83 g, 9.7 mmol), 3,4diaminothiophene dihydrochloride **2.3** (1.75 g, 9.4 mmol), and triethylamine (48 mL) in dichloromethane (85 mL) and ethanol (85 mL) was stirred at 50 °C for 8 h. After cooling, the reaction mixture was extracted with dichloromethane/water. The organic layer was collected and dried with sodium sulfate. The organic solvent was evaporated and the crude product thus obtained was further purified using silica gel flash column chromatography (chloroform/ethyl acetate, 4:1) to give the product **2** as light-tan solid (0.43 g, 28%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ 7.79 (s, 2H), 2.63 (s, 6H).

**Direct arylation polycondensation of PBN-TP:** A mixture of **1** (122.5 mg, 0.10 mmol.), **2** (16.4 mg, 0.10 mmol), Pd(OAc)<sub>2</sub> (1.1 mg, 0.005 mmol), KOAc (58.9 mg, 0.60 mmol), Bu<sub>4</sub>NBr (64.5 mg, 0.20 mmol) and degassed toluene (2.0 mL) was vigorously stirred at 115 °C under argon atmosphere for 24 hours. After cooling down, the resulting mixture was poured into methanol (100 mL) and the precipitate was collected by filtration. The crude polymer was washed in a Soxhlet apparatus first with acetone and then with n-hexane and finally with chloroform (CF). The CF fraction was concentrated and poured into methanol. The polymer was recovered by filtration and dried in vacuum overnight (35.0 mg). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  9.12 (s, 2H), 8.59 (s, 2H), 3.73 (s, 4H), 2.80 (s, 6H), 2.03 (s, 2H), 1.71 – 1.01 (m, 98H), 0.90 – 0.78 (m, 12H). <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -144.65 (s). Anal. Calcd. for C<sub>74</sub>H<sub>124</sub>B<sub>2</sub>F<sub>4</sub>N<sub>6</sub>S: C, 72.41; H, 10.18; N, 6.85; S, 2.61. Found: C, 72.02; H, 9.98; N, 6.67; S, 2.55. GPC (TCB, polystyrene standard, 150 °C): *M*<sub>n</sub> = 28.3 kDa, PDI = 2.36.

Polymer	Catalyst	Ligand	Base	additive	concentration	<i>M</i> <sub>n</sub>	PDI
						[kDa]	
1	Herrmann's cat 5%	P(o-MeOPh) <sub>3</sub>	$Cs_2CO_3$		1 mmol/30 mL	7.6	1.65
2	Herrmann's cat 5%	P(o-MeOPh) <sub>3</sub>	$Cs_2CO_3$		1 mmol/10 mL	12.0	1.96
3	Pd(OAc) <sub>2</sub> 5%		KOAc		1 mmol/30 mL	17.1	2.32
4	Pd(OAc) <sub>2</sub> 5%		KOAc	Bu₄NBr	1 mmol/30 mL	20.8	2.18
5	Pd(OAc) <sub>2</sub> 5%		KOAc	Bu₄NBr	1 mmol/10 mL	28.3	2.36

Table S1. Reaction conditions and results of direct arylation polycondensation toward PBN-TP.

#### 3. Molecular weights and molecular weight distribution



Figure S1. Gel permeation chromatography (GPC) elution curve of PBN-TP with 1,2,4-trichlorobenzene as the eluent at 150 °C.

#### 4. Thermal property

The thermal property of the PBN-TP was determined by thermal gravimetric analysis (TGA) under N<sub>2</sub> flow. It shows good thermal stability with the thermal decomposition temperature ( $T_d$ ) at 5% weight loss of 371 °C.



Figure S2. Thermogravimetric analysis (TGA) curve of PBN-TP.

#### 5. Density functional theory (DFT) calculations

Calculated spin density distributions of the four repeating units of PBN-TP and PBN-T at  $U\omega B97XD/6-31G^*$ level on the negatively charged state. All of the long alkyl chains have been replaced by methyl groups for simplification. Compared with PBN-T, PBN-TP shows longer polaron, which is beneficial to efficient charge transfer.



Figure S3. Calculated spin density distributions of the four repeating units of PBN-TP and PBN-T at  $U\omega B97XD/6-31G^*$  level on the negatively charged state. All of the long alkyl chains have been replaced by methyl groups for simplification.

#### 6. UV-vis-NIR absorption spectra

UV-vis-NIR absorption spectroscopy was used to evaluate the n-doping process of the two polymers for different doping duration. For PBN-T, the absorption spectra of the films has almost no change after TDAE steam treatment, suggesting that PBN-T has not been effectively n-doped. In contrast, the absorption spectra of PBN-TP films changed more obviously as the TDAE exposure time increases, implying a gradually increased n-doping level.



Figure S4. UV-vis-NIR absorption spectra of PBN-TP a) and PBN-T b) in thin films for different doping duration.

#### 7. Thermoelectric properties

**Device fabrication.** The borosilicate glass was sequentially cleaned using ultrasonication in deionized water (twice), acetone (twice), and isopropanol (once), 10 minutes for each time. The substrates were heated at 120 °C for 30 minutes and finally treated through UV-zone instrument for 15 minutes. The Au (~40 nm) was vacuum-deposited as electrodes, with a channel length of 200  $\mu$ m and a channel width of 1000  $\mu$ m for conductivity measurements and a channel length of 1000  $\mu$ m and a channel width of 5000  $\mu$ m for Seebeck coefficient measurements. The undoped polymer films were then spin-coated onto the substrate from chloroform solution (3 mg/mL) in a glovebox under nitrogen atmosphere. The n-doping was conducted in a nitrogen-filled glovebox by exposing these polymer films to the TDAE vapor inside an airtight glass bottle (12 mL in volume filled with 0.06 mL liquid TDAE) at 50 °C over different durations.

**Electrical conductivity measurements.** The measurements of thermoelectric properties are similar to our previous study.<sup>[3]</sup> The electrical conductivity ( $\sigma$ ) was measured with a probe station and Keysight B1500A under argon atmosphere. Conductivity ( $\sigma$ ) calculated by using the equation:  $\sigma$ =(I/V)×L/(w×d), where I is the current, V is the voltage, d is the thickness of the film, L and *w* are the length and width of the channel. The conductivities of four separate points were averaged to obtain the conductivity of one device.

**Seebeck coefficient measurements.** The Seebeck coefficient was measured under argon atmosphere and calculated by the formula:  $S = V_{therm}/\Delta T$ , where  $V_{therm}$  is the thermovoltage obtained by creating the temperature difference ( $\Delta T$ ) at the two ends of the channel. The  $V_{therm}$  was tested by Keithley 2000, and the temperature difference was created by two Peliter elements and tested by an infrared camera FLIR A300 (thermal sensitivity < 50 mK). To calibrate our setup, commercial constantan wire (127 µm from Omega) and high purity nickel wire were also measured.<sup>3</sup> The Seebeck coefficient measurement by using our home-built setup is quite reliable.



Figure S5. The I-V curves of films by the two-probes method a) and by the four-probes method b).



Figure S6. Thermal voltage as a function of  $\Delta T$  for TDAE doped PBN-TP.

#### 8. Photoluminescence spectrum

We studied the emission property of PBN-TP via measuring the photoluminescence (PL) spectrum and fluorescence quantum yield in CHCl<sub>3</sub>. PBN-TP shows a maximum fluorescence peak at 696 nm with fluorescence quantum yield of 0.068. Compared with PBN-T,<sup>2</sup> PBN-TP has a red-shifted fluorescence spectrum, which is ascribed to the quinoidal character and the more rigid skeleton of PBN-TP. However, the fluorescence quantum yield of PBN-TP is a little lower than that of PBN-T, the possible reason is that the relative lower bandgap of PBN-TP would increase the non-radiative transition rate.



Figure S7. Photoluminescence spectrum of PBN-TP in CHCl<sub>3</sub> (excited at 600 nm).

### 9. <sup>1</sup>H NMR,<sup>19</sup>F NMR and <sup>13</sup>C NMR spectra



<sup>1</sup>H NMR spectrum of  $\mathbf{1}$  in CDCl<sub>3</sub>



<sup>1</sup>H NMR spectrum of **2.3** in DMSO



<sup>1</sup>H NMR spectrum of  $\mathbf{2}$  in CDCl<sub>3</sub>



<sup>1</sup>H NMR spectrum of **PBN-TP** in  $CDCl_3$ 



<sup>&</sup>lt;sup>19</sup>F NMR spectrum of **PBN-TP** in CDCl<sub>3</sub>

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