

Supporting Information

Electron-withdrawing quinone polymers with enhanced conjugated planarity for n-type organic thermoelectric

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1. Measurements and general methods

^1H NMR and ^{13}C NMR spectra were recorded using a Bruker AVANCE 500 NMR spectrometer in chloroform-d (CDCl_3) with tetramethylsilane as the internal reference. Gel permeation chromatography (GPC) measurements were conducted on Agilent PLgel 5um MIXED-C with chloroform as eluent. Optical absorption spectra were recorded by SHIMADZU UV-3600i Plus. The CV characterizations were performed on CHI660E in 0.1 M tetrabutylammonium hexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$) anhydrous acetonitrile solution electrolyte. Three electrodes configuration was utilized with glassy carbon electrode as the working electrode, a platinum wire as counter electrode, and saturated calomel electrode as reference electrode. The scan rate was 50 mV s^{-1} . The redox potential of ferrocene was measured as a standard control. X-ray photoelectron spectroscopy (XPS) analysis was conducted using the Thermo Scientific K-Alpha. The electron spin resonance test was performed using a Bruker ELEXSYS-II E500 instrument. of the material was drop cast on a glass slide, which was then placed into the measurement tube. Thermogravimetric analysis (TGA) was conducted on a Netzsch TG209 apparatus under nitrogen flow with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. Atomic force microscopy (AFM) measurements were performed in tapping mode on a Bruker MultiMode 8 instrument. The Hall effect measurements were conducted using the HMS-7000 instrument. Density functional theory (DFT) optimized molecular geometries and calculated energy levels were conducted by Gaussian 16 at the B3LYP/6-31G(d) level. The branched alkyl side chains were replaced by methyl groups to simplify the calculations.

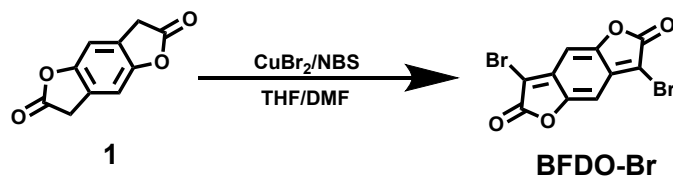
Fabrication and characterization of SCLC devices: The electron devices were constructed with the following architectures: ITO/ZnO/PBFDOT_h-T or PBFDOT_h-Se/PFN-Br/Ag. The hole devices were constructed with the following architectures: ITO/PEDOT:PSS/PBFDOT_h-T or PBFDOT_h-Se/MoO₃/Ag. Measurements for devices were conducted using a Keithley 236 source meter in the dark. The electron mobility was determined by fitting the dark current to the model of single-carrier space charge limited current (SCLC), as described by the equation:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3}$$

where J is the current density, μ is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the active layers, and V is the effective voltage. The effective voltage was obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the series resistance of the whole device except for the active layers from the applied voltage (V_{appl}), $V = V_{appl} - V_{bi} - V_s$. The electron mobilities and hole mobilities can be calculated from the slope of the $J^{1/2}$ - V .

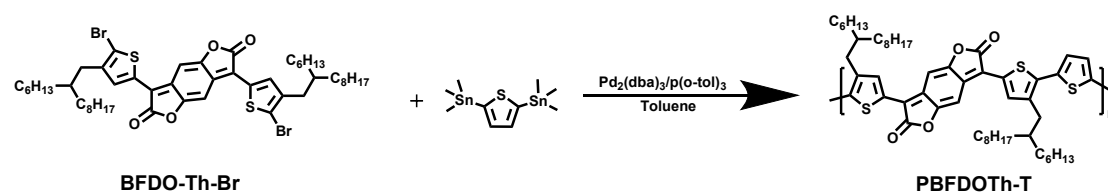
2. Materials and synthetic procedures

All air and water sensitive reactions were performed under argon and strictly followed the standard Schlenk technique. Unless otherwise noted, all chemical reagents were purchased from commercial sources such as Bidepharm, Energy Chemistry, and Jkchemical, and used as received. (4-(2-hexyldecyl)thiophen-2-yl)tributylstanne (97%) and 2,5-bis(trimethylstannyl)thiophene (97%) were purchased from Zhengzhou Alfa Chemical Co. Ltd. 2,5-Bis(trimethylstannyl)selenophene (97%) was purchased from Derthon Optoelectronics Materials Science Technology Co. LTD. 4-(1,3-Dimethyl-2,3-dihydro-1H-benzimidazol-2-yl)phenyl)dimethylamine (97%) was purchased from Merck KGaA.

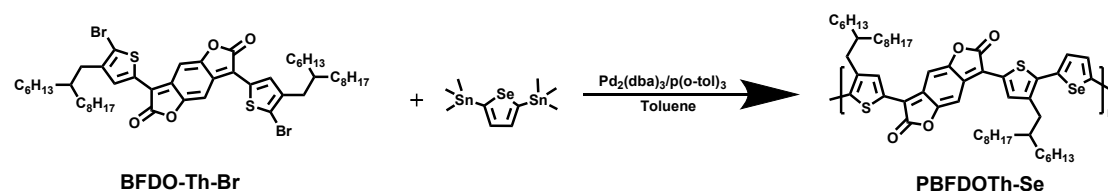


Synthesis of BFDO-Br. In a 500 mL two-necked flask, benzo[1,2-b:4,5-b']difuran-2,6(3H,7H)-dione (2 g, 10.52 mmol) and *N*-bromosuccinimide (4.68 g, 26.3 mmol) were added. Subsequently, tetrahydrofuran (200 ml) was added, and the two-necked flask was shielded from light. Then, cupric bromide (6 g, 26.3 mmol) was dissolved in *N,N*-dimethylformamide (100 ml). The solution was added dropwise into a two-necked flask. The reaction mixture was stirred for 48 h at room temperature. After

solvent was eliminated by rotary evaporation. The product was purified by column chromatography with dichloromethane: hexane (1:1, vol%) as the eluent. The product was then washed by methanol and dried under vacuum to obtain compound 3 (592 mg, yield: 83%). ¹H NMR (500 MHz, Chloroform-*d*, ppm) δ 7.69 (s, 2H), 6.92 (s, 2H), 2.55 (d, 4H), 1.35 – 1.22 (m, 50H), 0.87 (td, 12H). ¹³C NMR (126 MHz, Chloroform-*d*, ppm) δ 166.61, 153.79, 143.91, 132.82, 132.70, 132.64, 118.42, 118.36, 98.87, 38.56, 34.11, 33.34, 33.31, 31.92, 31.88, 29.99, 29.67, 29.61, 29.33, 26.51, 26.49, 22.69, 22.68, 14.13.



Synthesis of PBFDOTh-T. BFDO-Th-Br (200 mg, 0.208 mmol), 2,5-bis(trimethylstannyl)thiophene (85.5 mg, 0.208 mmol) and tri(*o*-tolyl)phosphine (12 mg, 8% mmol) were introduced into the Schlenk reaction tube. Subsequently, toluene (4 ml) was added to dissolve the reactants. The mixture was subjected to vacuum evacuation and argon replenishment three times. Following this, tris(dibenzylideneacetone)dipalladium (6 mg, 3% mmol) was added to the reaction mixture under argon protection. After 8 hours of reaction at 80 °C, the reaction solution was precipitated in methanol solution. The precipitate was filtered through a nylon filter and was subsequently purified via Soxhlet extraction for a duration of 8 h using acetone, followed by 12 h using hexane, and finally collected with chloroform. The chloroform was removed by rotary evaporation. The product was collected and vacuum dried to afford a dark solid. (179 mg, yield: ~ 85%).



Synthesis of PBFDOTh-Se. PBFDOTh-Se was obtained from BFDO-Th-Br (100.0 mg, 0.104 mmol) and 2,5-Bis(trimethylstannyl)selenophene (47.6 mg, 0.104 mmol) as a dark blue solid following the same procedure as that used to prepare

PBFDOTh-T. (80 mg, yield: 78%).

3. Device fabrication and characterization

Solution doping method. The polymer and dopant (N-DMBI) were dissolved separately in chloroform at a concentration of 10 mg ml⁻¹ in a glove box. The solution of dopant and polymer were mixed with different quantities, and then the mixed solutions were stirred at room temperature for 20 min.

Thermoelectric device fabrication and characterizations. The ultrasonic cleaner was used to wash the ultra-white glass sheets sequentially with deionized water, acetone, and isopropanol, and then dried under a stream of nitrogen followed by heating at 120 °C for 10 minutes. Polymer solutions of different doping levels were drop-coated onto the cleaned glass sheets in a nitrogen-filled glove box and then annealed at 100 °C for 1 h to allow successful deposition. The room temperature resistivity and Seebeck coefficients were measured using a Joule Yacht MRS-3RT instrument.

4. ^1H NMR and ^{13}C NMR spectra

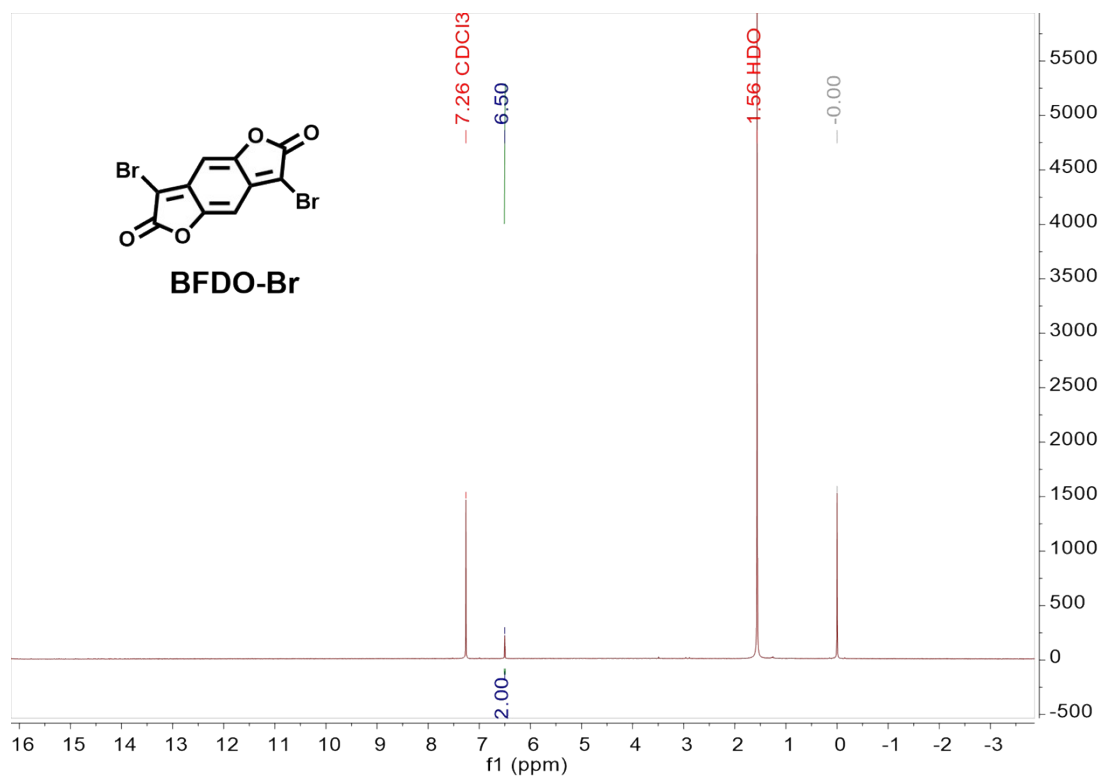


Figure S1. ^1H NMR spectrum of BFDO-Br.

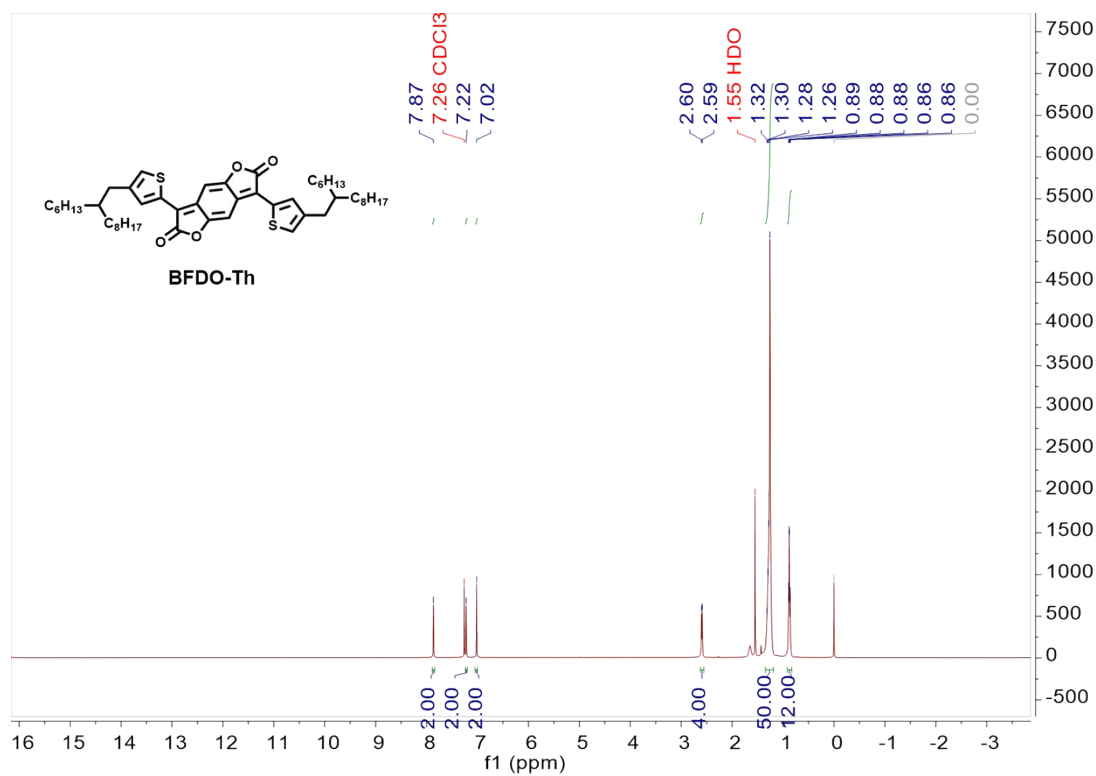


Figure S2. ^1H NMR spectrum of BFDO-Th.

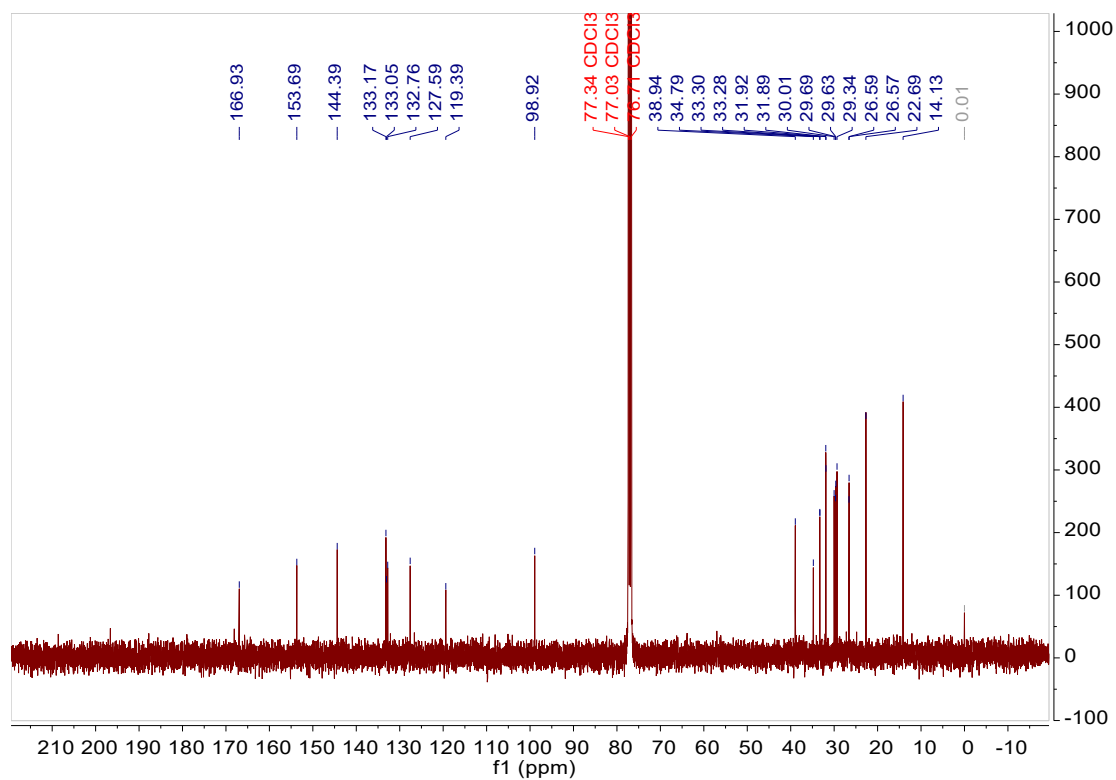


Figure S3. ^{13}C NMR spectrum of BFDO-Th.

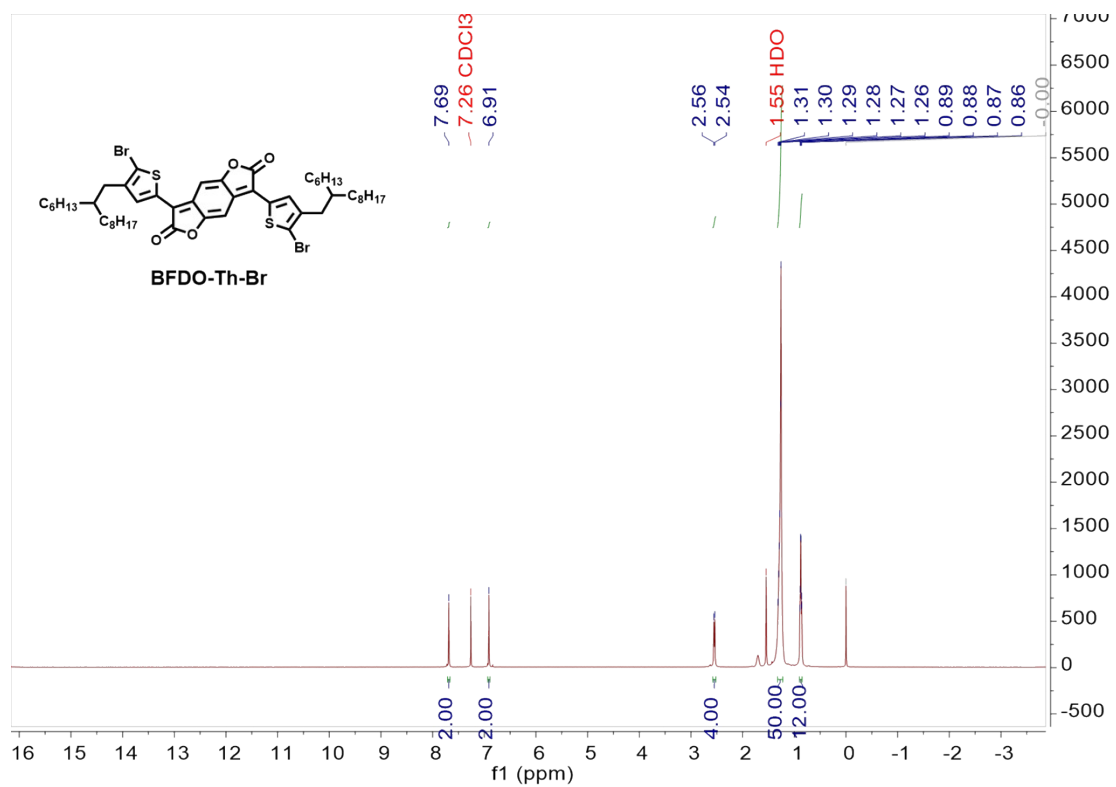


Figure S4. ^1H NMR spectrum of BFDO-Th-Br.

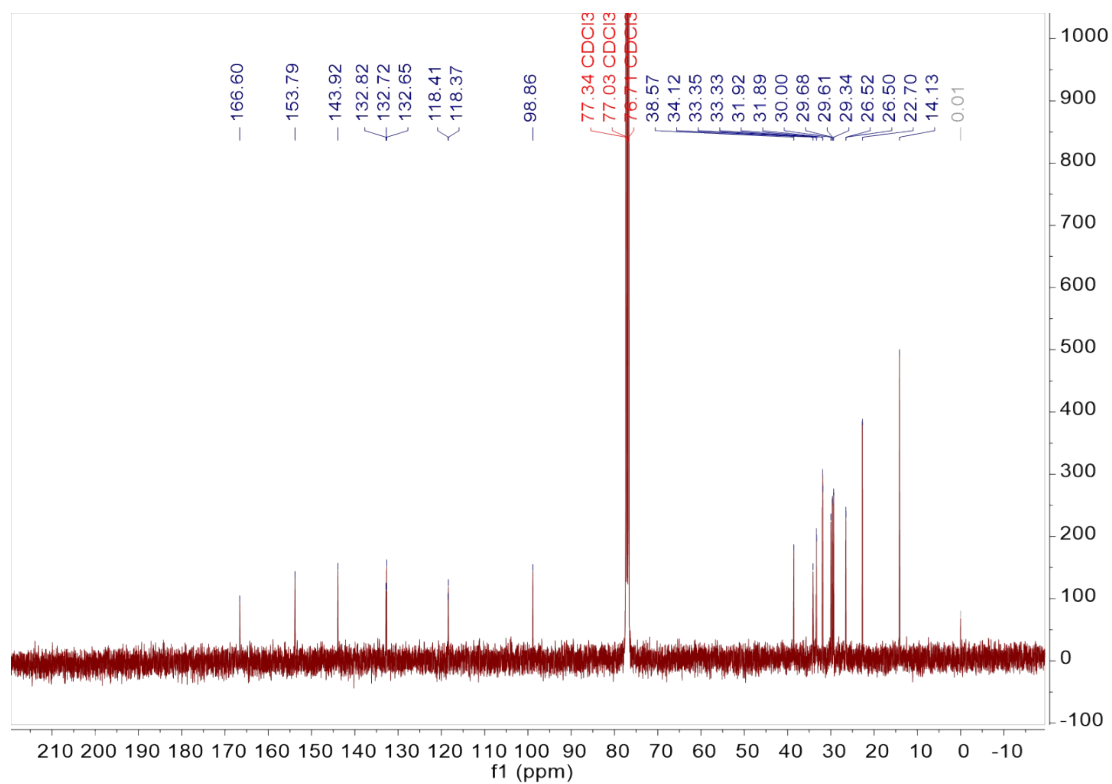
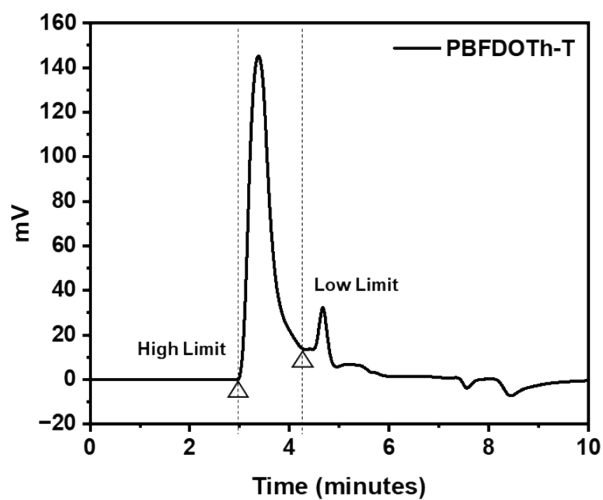


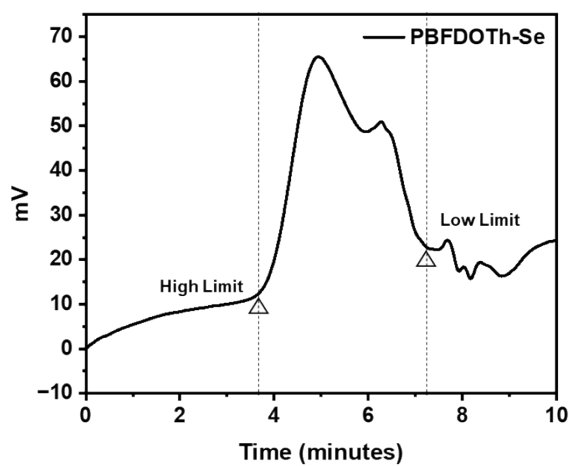
Figure S5. ^{13}C NMR spectrum of BFDO-Th-Br.

5. Supplementary figures and tables



Peak No	Mp	Mw	Mz	Mz+1	Mn	PD
1	117708	78087	107635	127991	48682	1.604

Figure S6. The GPC spectra of PBFDOTh-T.



Peak No	Mp	Mw	Mz	Mz+1	Mn	PD
1	33084	30681	61210	94076	12100	2.535

Figure S7. The GPC spectra of PBFDOTh-Se.

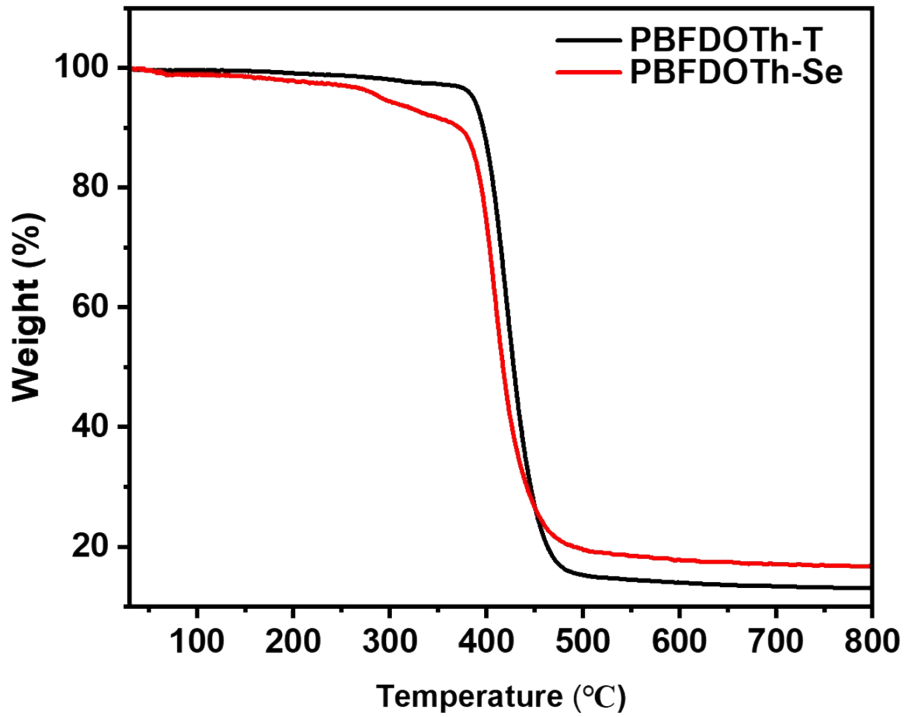


Figure S8. Thermogravimetric curve of PBFDOTh-T and PBFDOTh-Se.

Table S1. Carrier concentration and carrier mobility of PBFDOTh-T obtained from Hall effect tests at different doping concentrations.

PBFDOTh-T	5%	10%	15%	20%
Carrier concentration (cm^{-3})	1.26×10^{19}	2.55×10^{19}	6.88×10^{19}	9.93×10^{19}
Carrier mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	5.19×10^{-1}	1.10	5.42×10^{-1}	1.70×10^{-1}

Table S2. Carrier mobility and carrier concentration of PBFDOTh-Se obtained from Hall effect based tests at different doping concentrations.

PBFDOTh-Se	5%	10%	15%	20%
Carrier concentration (cm^{-3})	2.37×10^{19}	9.74×10^{19}	4.06×10^{20}	4.50×10^{20}
Carrier mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	5.86×10^{-1}	3.61×10^{-1}	1.2×10^{-1}	1.01×10^{-1}

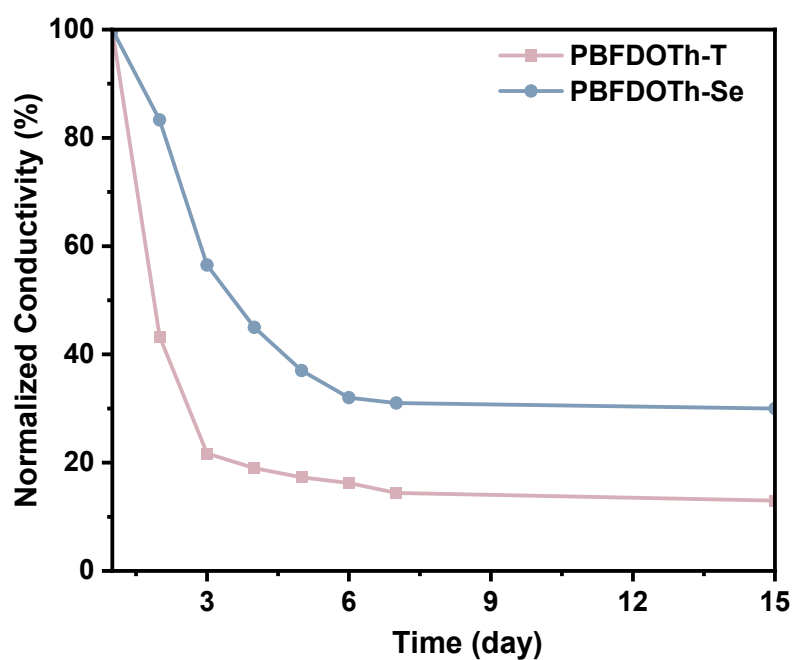


Figure S9. Device stability of PBFDOTh-T and PBFDOTh-Se after 15% N-DMBI doping under ambient environment (25°C, 80% relative humidity).

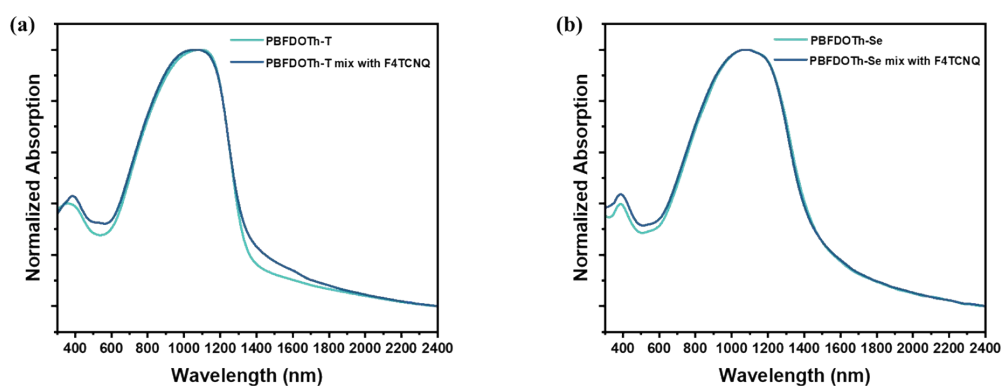


Figure S10. UV-vis-NIR absorption spectra of thin film of (a) PBFDOTh-T and (b)PBFDOTh-Se before and after mixing with F4TCNQ.

Table S3. Hole mobility and electron mobility of PBFDOTh-T and PBFDOTh-Se using device structures of ITO/ PEDOT:PSS or ZnO/PBFDOTh-T or PBFDOTh-Se/ MoO₃ or PFN-Br/Ag.

	Hole mobility (cm ² V ⁻¹ s ⁻¹)	Electron mobility (cm ² V ⁻¹ s ⁻¹)
PBFDOTh-T	4.02×10 ⁻⁴	1.13×10 ⁻³
PBFDOTh-Se	3.22×10 ⁻⁴	1.30×10 ⁻³

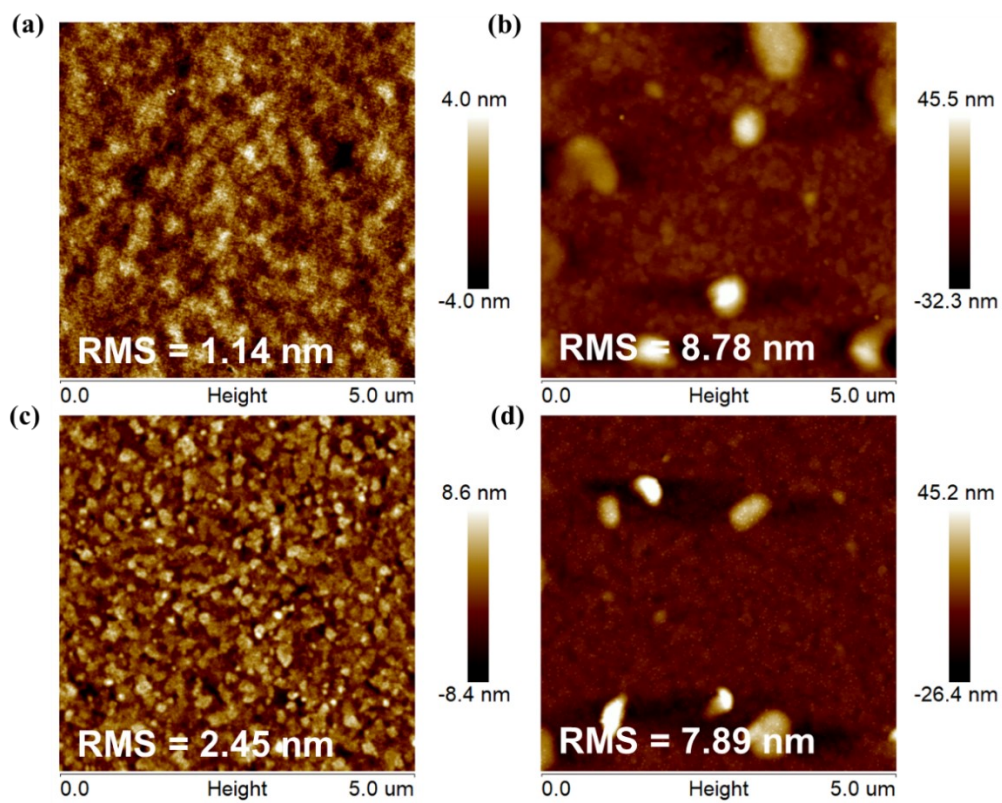


Figure S11. AFM height image of a) pristine PBFDOTh-T thin film; b) PBFDOTh-T thin film doped with N-DMBI ; c) pristine PBFDOTh-Se thin film; d) PBFDOTh-Se thin film doped with N-DMBI.

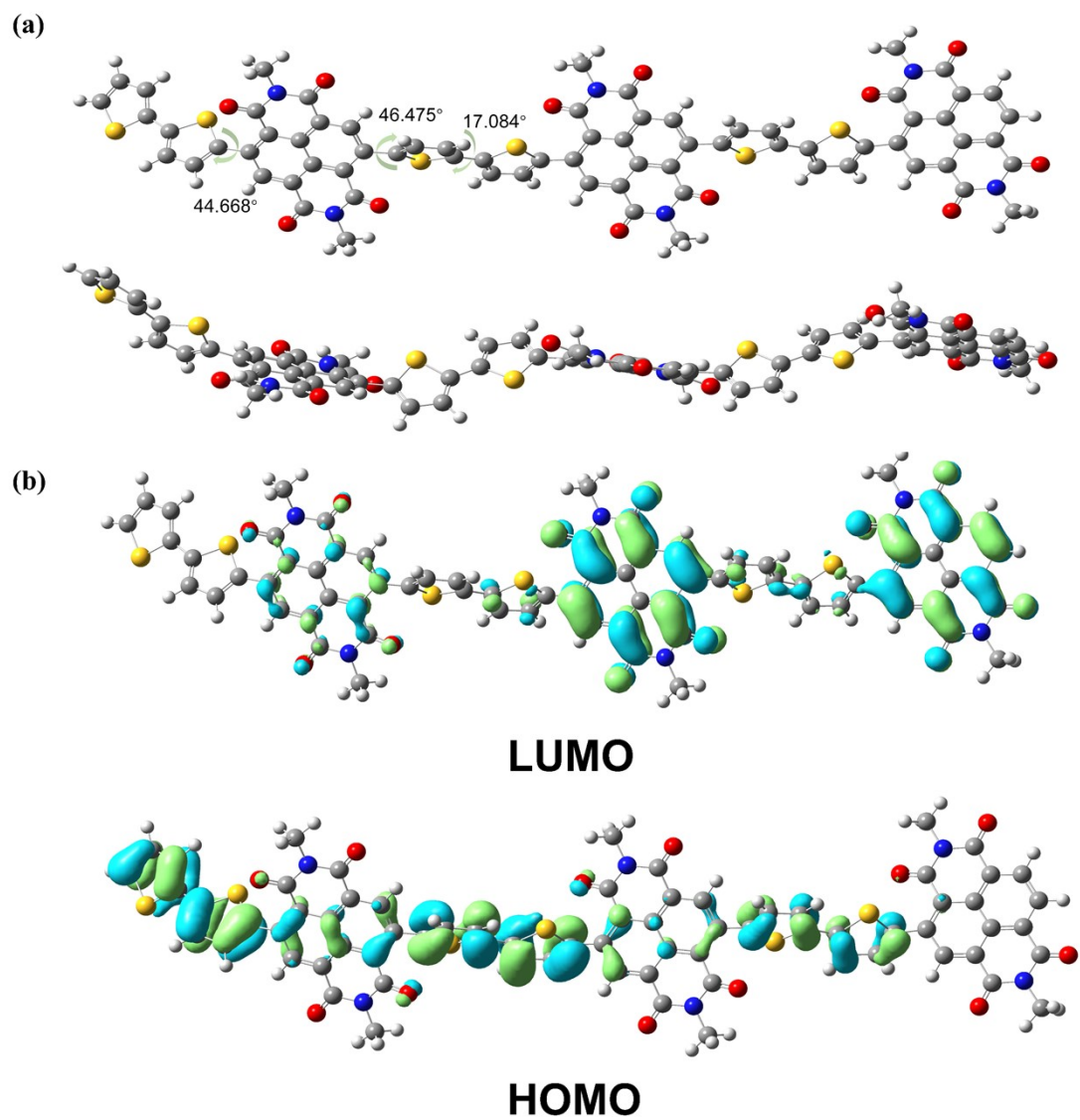


Figure S12. a) Optimized molecular geometries of trimers of N2200; b) Frontier molecular orbitals of trimers of N2200.