

## Supporting Information

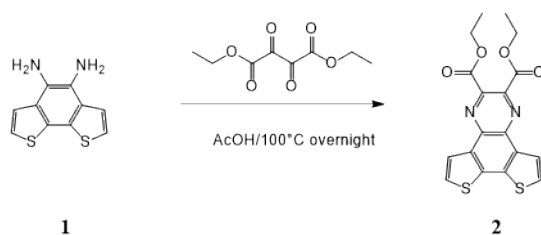
### **Dithieno-Fused Quinoxalineimide-Based All-Acceptor Polymers for n-Type Organic Semiconductors**

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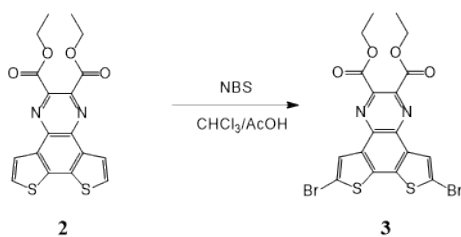
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## 1. Monomer and Polymers Synthesis



### Synthesis of diethyl dithieno[3,2-f:2',3'-h] quinoxaline-2,3-dicarboxylate(2)

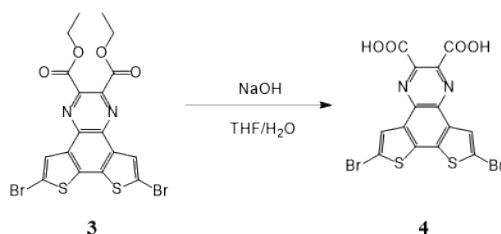
**1** (680 mg, 3.08 mmol) and diethyl 2,3-dioxosuccinate (1.24 mg, 6.2 mmol) were added to an oven-dried 50 mL round-bottomed flask, which was evacuated and filled with nitrogen three times. Then AcOH (80 mL) was added. The reaction was stirred at 110°C for 18 hours. The reaction mixture was then cooled to ambient temperature. Then the reaction mixture was poured into water and extracted with EA (100 mL×3), then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The EA solution was concentrated under vacuum, and the residue was purified by column chromatography on silica gel (DCM) provide the desired product (**2**) as an orange solid (1.28 g) in 50% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.39 (d, *J* = 3.8 Hz, 2H), 7.63 (d, *J* = 6.8 Hz, 2H), 4.57 (q, *J* = 7.1 Hz, 4H), 1.50 (t, *J* = 7.1 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.26, 142.22, 137.67, 137.61, 134.32, 125.65, 124.83, 77.24, 62.65, 14.16.



### Synthesis of diethyl 6,9-dibromodithieno[3,2-f:2',3'-h]quinoxaline-2,3-dicarboxylate(3)

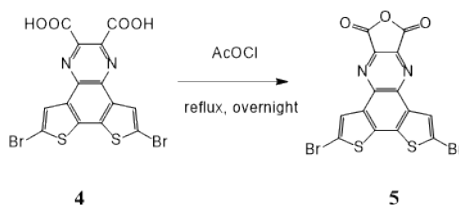
To a solution of diethyl dithieno[3,2-f:2',3'-h]quinoxaline-2,3-dicarboxylate (1.0 g, 2.56 mmol) in 15mL of chloroform/acetic acid (2:1, v/v) at room temperature was added NBS (3.58 g, 20.32 mmol). The resulting mixture was stirred at 80°C overnight. The reaction was brought to room temperature. The resulting mixture was quenched with the solution of Na<sub>2</sub>SO<sub>3</sub> and extracted with DCM. The organic layer was evaporated under reduced pressure after washing three times with deionized water and drying over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure, and the mixture was

purified by column chromatography on silica gel (PE: DCM = 1:3 v/v) to afford 1.30 g of pure product as an orange solid (yield: 92%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.35 (s, 2H), 4.56 (q,  $J = 7.2$  Hz, 4H), 1.49 (t,  $J = 7.2$  Hz, 6H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  164.88, 142.81, 134.35, 127.29, 114.79, 62.80, 14.15.



### Synthesis of 6,9-dibromodithieno[3,2-f:2',3'-h]quinoxaline-2,3-dicarboxylic acid(4)

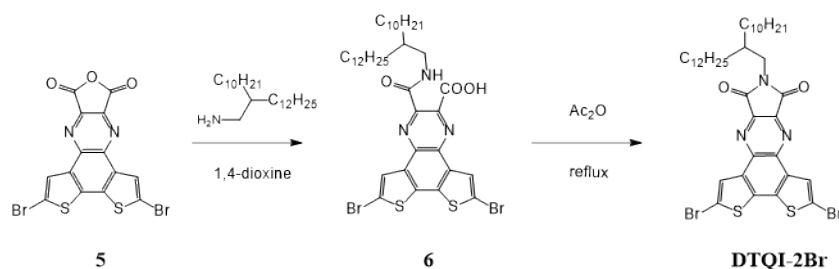
An oven-dried 100 mL round-bottomed flask equipped with compound **3** (1.00 g, 1.83 mmol) and KOH (218 mg, 5.56 mmol) was evacuated and filled with nitrogen three times. Then 30 mL  $\text{H}_2\text{O}$  and 30 mL THF were added. The reaction mixture was heated to 70  $^\circ\text{C}$  and stirred overnight. After cooled to room temperature, the THF was evaporated under a reduced pressure. The aqueous solution was cooled to room temperature. The THF was removed by vacuum rotary evaporation, the precipitate was collected by filtration and then washed with 30 mL water. After dried, a yellow solid was obtained as the product (**4**) (0.82 g, yield: 92%).  $^1\text{H}$  NMR (500 MHz, DMSO)  $\delta$  8.39 (s, 2H).  $^{13}\text{C}$  NMR (126 MHz, DMSO)  $\delta$  166.34, 144.08, 136.48, 135.78, 134.61, 127.26, 115.58.



### Synthesis of 2,5-dibromofuro[3,4-b]dithieno[3,2-f:2',3'-h]quinoxaline-8,10-dione(5)

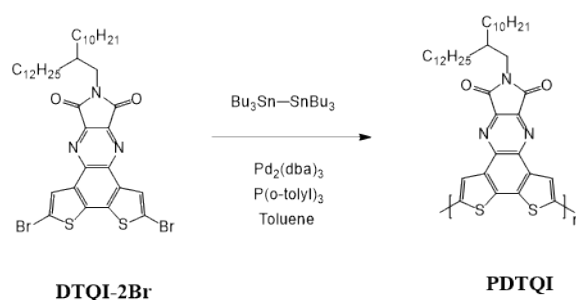
Compound **4** (1.19 g, 2.4 mmol) was stirred in 100 mL of acetic anhydride under reflux for 6 h. Upon cooling to 0  $^\circ\text{C}$ , the solid was collected by filtration, washed with hexane,

and dried in vacuo at 60 °C overnight. The resulting light yellow solid (0.93 g, 98% yield) was used without further purification.



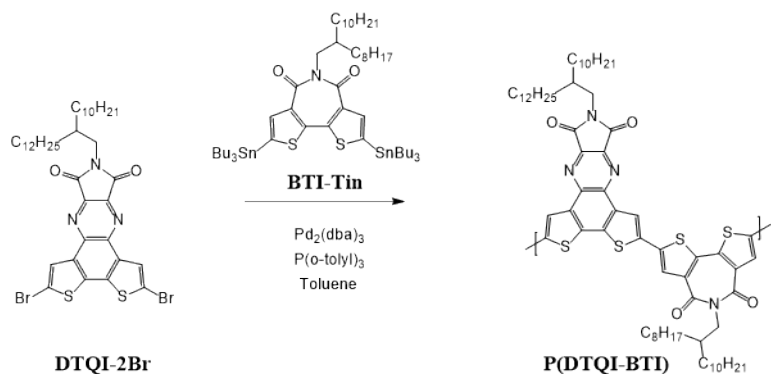
### Synthesis of DTQI-2Br

An oven-dried 100 mL two-necked flask equipped with compound **5** (0.47 g, 1 mmol) and 4-dimethylaminopyridine (0.18 g, 1.5 mmol) was evacuated and filled with nitrogen three times. Then 20 mL DCM and amine (446 mg, 1 mmol) were added. The reaction mixture was heated to 80 °C and stirred 12 h. Then, acetic anhydride (10 mL) was added to this solution and the solution was heated to 110 °C and stirred 3 h. After cooled to room temperature, the mixture was extracted with DCM three times and the combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed under a reduced pressure to afford a residue, which was purified by column chromatography on silica gel (PE: DCM = 5:1 v/v) to provide the desired product (**DTQI-2Br**) as a yellow solid (600 mg) with 74% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.48 (s, 2H), 3.82 (d, *J* = 7.3 Hz, 2H), 2.00 (s, 2H), 1.24 (d, *J* = 10.5 Hz, 41H), 0.87 (dt, *J* = 7.0, 3.5 Hz, 6H). <sup>13</sup>C NMR (126 MHz, DMSO) δ 164.56, 143.75, 138.90, 137.90, 135.11, 127.51, 115.51, 43.21, 37.18, 31.93, 31.50, 29.97, 29.73, 29.71, 29.70, 29.67, 29.63, 29.37, 26.27, 22.70, 14.14.



### Synthesis of polymers PDTQI

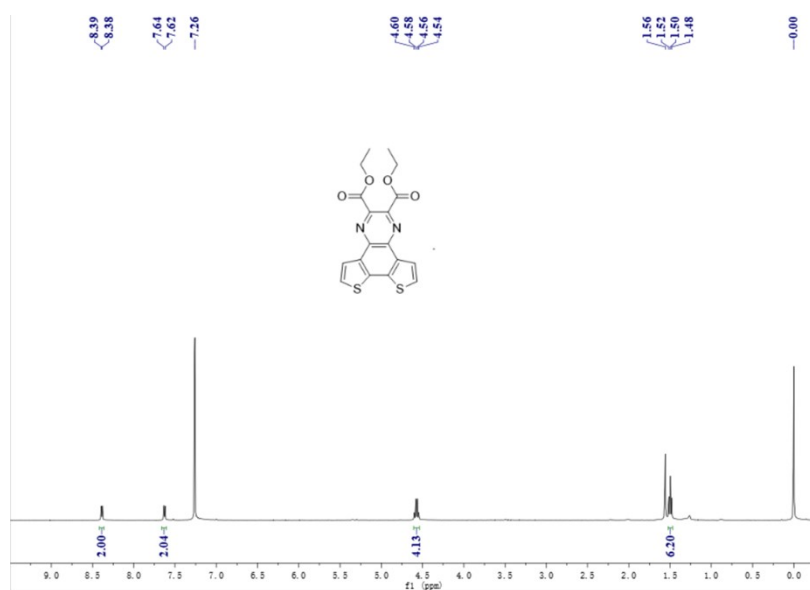
A glass tube was charged with the two monomers (0.1 mmol each), tris(dibenzylideneacetone)dipalladium (0) ( $\text{Pd}_2(\text{dba})_3$ ), and tris(o-tolyl) phosphine ( $\text{P}(\text{o-tolyl})_3$ ) (1:8,  $\text{Pd}_2(\text{dba})_3$ : $\text{P}(\text{o-tolyl})_3$  molar ratio; Pd loading: 0.03-0.05 equiv). The tube and its contents were subjected to 3 pump/purge cycles with argon, followed by the addition of 2.5 mL anhydrous toluene via syringe. The tube was sealed under argon flow and then stirred at 120 °C for 72 h. Then, 50  $\mu\text{L}$  2-(tributylstanny)thiophene was added and the reaction mixture was stirred at 120 °C for 0.5 h. Finally, 50  $\mu\text{L}$  2-bromothiophene was added and the reaction mixture was stirred at 120 °C for another 0.5 h. After cooling to room temperature, the reaction mixture was slowly dripped into 100 mL methanol (containing 0.5 mL 12 N hydrochloric acid) under vigorous stirring. After stirring for 1 h, the solid precipitate was transferred to a Soxhlet thimble. After drying, the crude product was subjected to sequential Soxhlet extraction with the solvent sequence of methanol, acetone, hexane, and dichloromethane. The dichloromethane fraction was concentrated by removing most of solvent under reduced pressure and then precipitated into methanol. The solid was collected by filtration and dried in vacuum to afford the polymer as a deep colored solid.



### Synthesis of polymers P(DTQI-BTI)

An glass tube was charged with the two monomers (0.1 mmol each), tris(dibenzylideneacetone)dipalladium (0) ( $\text{Pd}_2(\text{dba})_3$ ), and tris(o-tolyl) phosphine ( $\text{P}(\text{o-tolyl})_3$ ) (1:8,  $\text{Pd}_2(\text{dba})_3$ : $\text{P}(\text{o-tolyl})_3$  molar ratio; Pd loading: 0.03-0.05 equiv). The tube and its contents were subjected to 3 pump/purge cycles with argon, followed by the addition of 2.5 mL anhydrous toluene via syringe. The tube was sealed under argon flow and then stirred at 120 °C for 72 h. Then, 50  $\mu\text{L}$  2-(tributylstanny)thiophene was

added and the reaction mixture was stirred at 120 °C for 0.5 h. Finally, 50  $\mu$ L 2-bromothiophene was added and the reaction mixture was stirred at 120 °C for another 0.5 h. After cooling to room temperature, the reaction mixture was slowly dripped into 100 mL methanol (containing 0.5 mL 12 N hydrochloric acid) under vigorous stirring. After stirring for 1 h, the solid precipitate was transferred to a Soxhlet thimble. After drying, the crude product was subjected to sequential Soxhlet extraction with the solvent sequence of methanol, acetone, hexane, and dichloromethane. The dichloromethane fraction was concentrated by removing most of solvent under reduced pressure and then precipitated into methanol. The solid was collected by filtration and dried in vacuum to afford the polymer as a deep colored solid.



**Figure S1.**  $^1\text{H}$  NMR of **6** in  $\text{CDCl}_3$

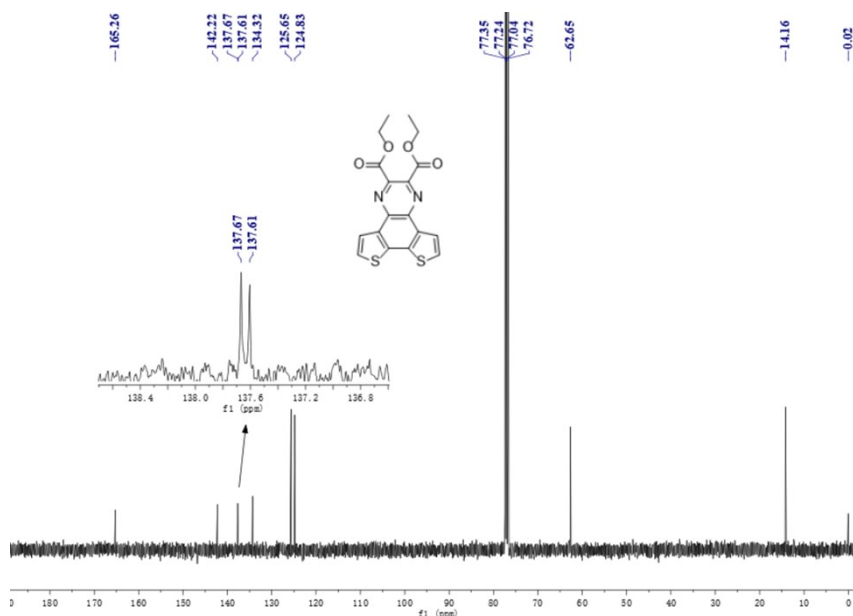


Figure S2.  $^{13}\text{C}$  NMR of 6 in  $\text{CDCl}_3$

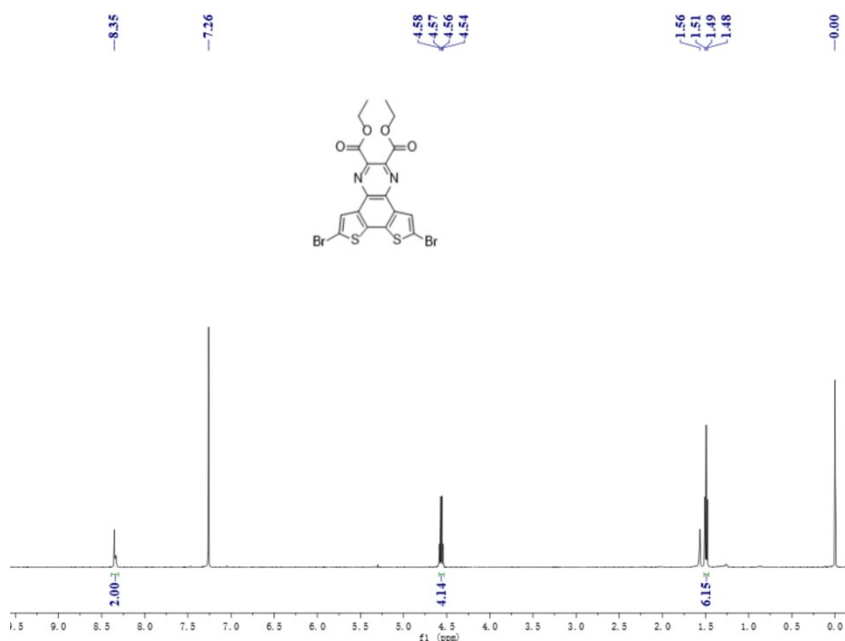


Figure S3.  $^1\text{H}$  NMR of 7 in  $\text{CDCl}_3$

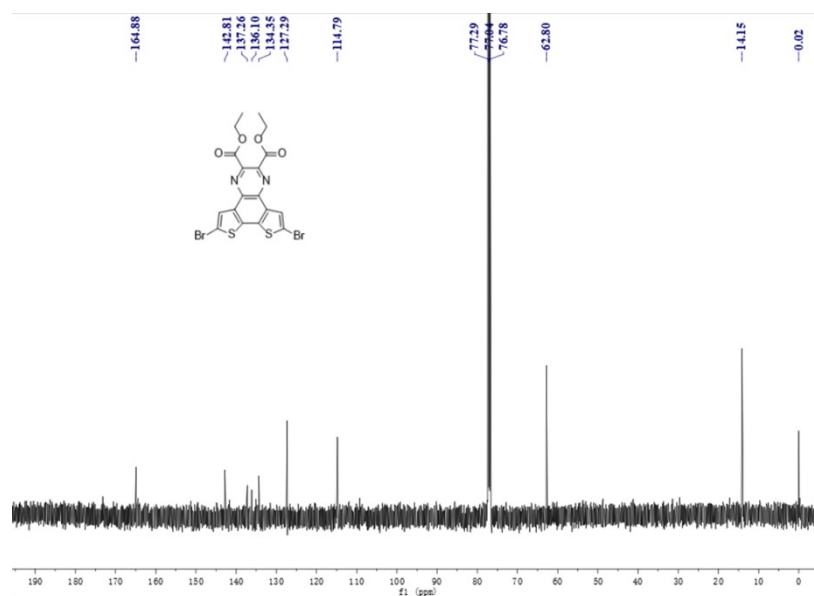


Figure S4.  $^{13}\text{C}$  NMR of **7** in  $\text{CDCl}_3$

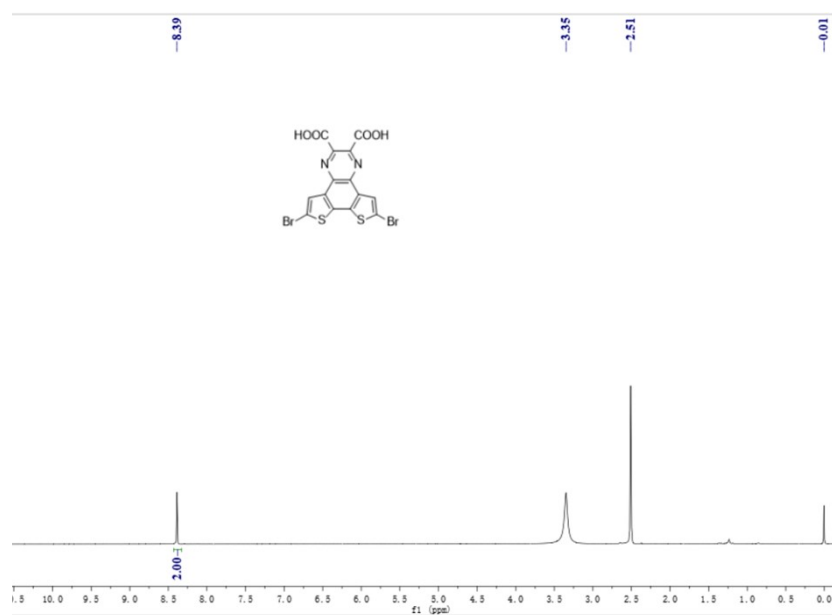


Figure S5.  $^1\text{H}$  NMR of **8** in DMSO



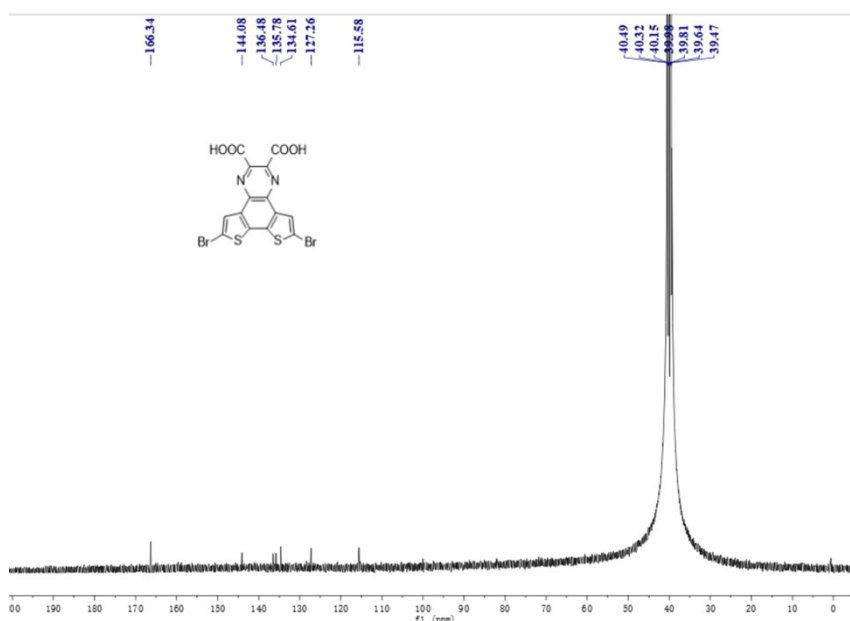


Figure S6. <sup>13</sup>C NMR of **8** in CDCl<sub>3</sub>

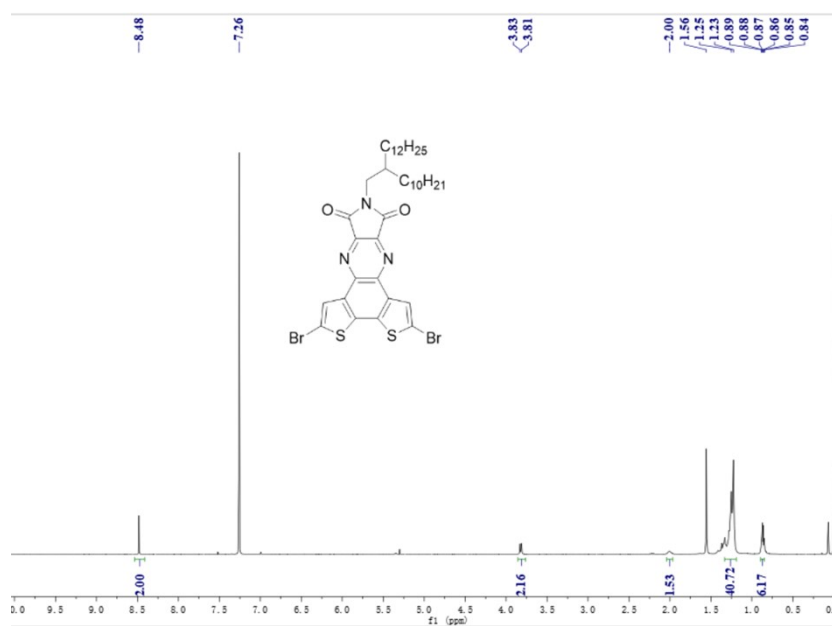
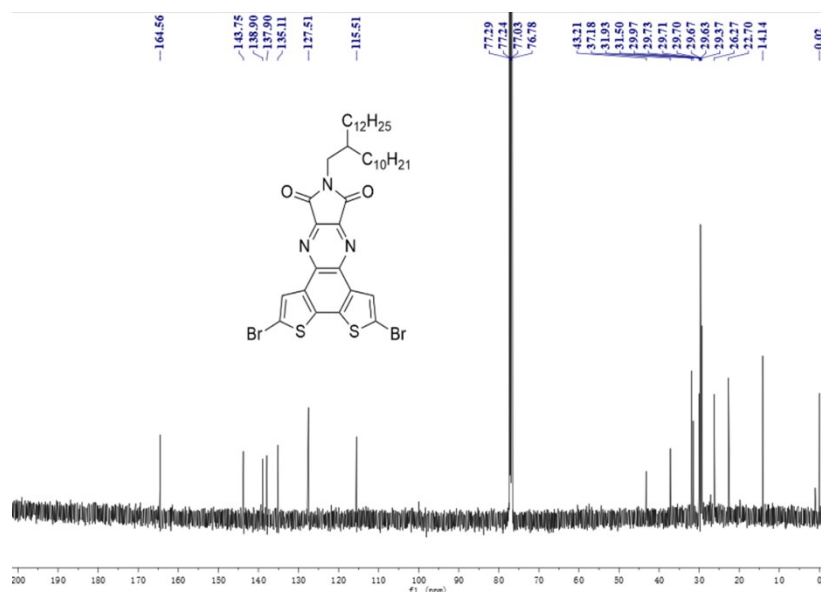
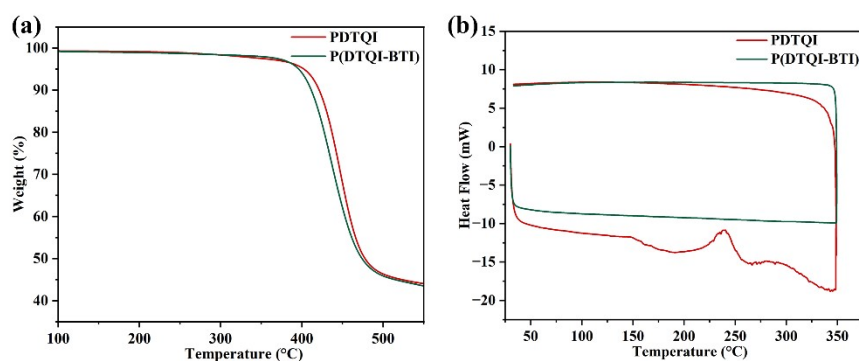


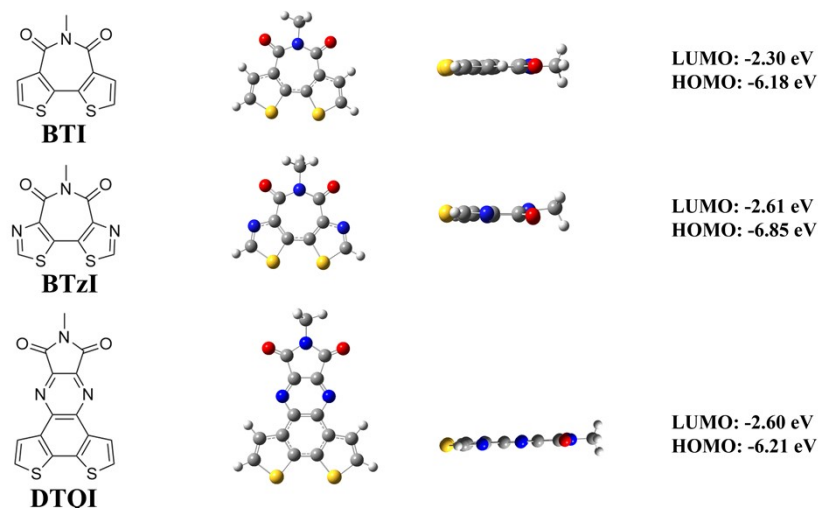
Figure S7. <sup>1</sup>H NMR of DTQI-2Br in CDCl<sub>3</sub>



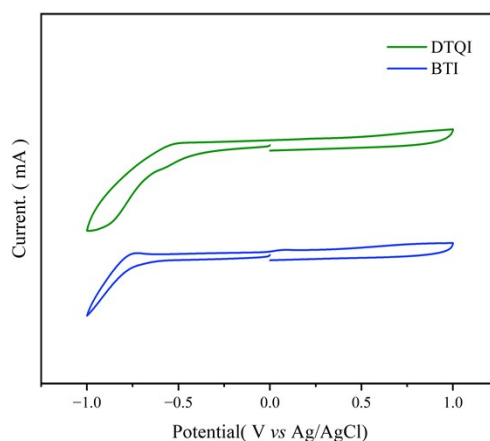
**Figure S8.**  $^{13}\text{C}$  NMR of DTQI-2Br in  $\text{CDCl}_3$



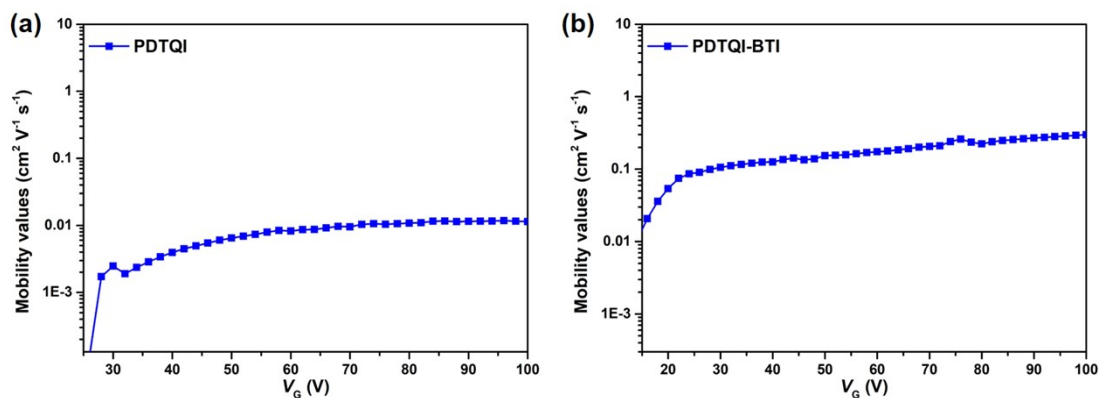
**Figure S9.** (a) Thermogravimetric analysis of polymers PDTQI and P(DTQI-BTI) at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ . (b) DSC thermograms of polymers PDTQI and P(DTQI-BTI). The DSC curves are from the second heating and first cooling scans with a ramp rate of  $10\text{ }^{\circ}\text{C min}^{-1}$ .  $\text{N}_2$  was used as the purge gas for both TGA and DSC measurements.



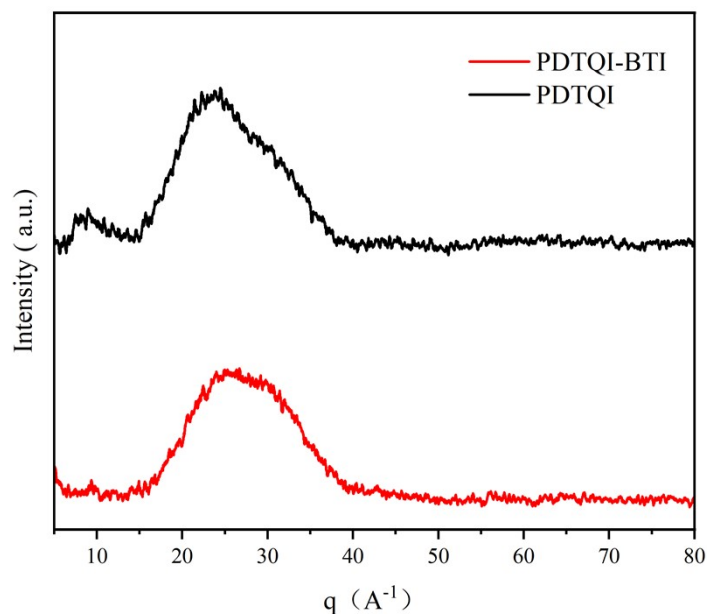
**Figure S10.** Chemical structures, optimized geometries and frontier molecular orbital energy levels for bithiophene imide (BTI), bithiazole imide (BTzI) and Dithieno-fused quinoxalineimide (DTQI). Calculations were carried out at the DFT//B3LYP/6-31G\* level.



**Figure S11.** Cyclic voltammograms of BTI and DTQI measured in 0.1 M tetrabutylammonium hexafluorophosphate dichloromethane solution with the Fc/Fc<sup>+</sup> redox couple as an external standard at a scanning rate of 0.05 V s<sup>-1</sup>.



**Figure S12.** Electron mobility vs  $V_g$  plots: (a) PDTQI; (b) P(DTQI-BTI).



**Figure S13.** XRD diffractogram patterns of P(DTQI-BTI) and PDTQI.

## 2. Organic thin-film transistors fabrication

The top-gate bottom-contact (TGBC) OTFTs based on the thin films of n-type polymers are fabricated to evaluate the charge-transport properties. A layer of 30 nm Au was deposited on a cleaned glass plate with thermal evaporation process as source and drain electrodes. Then the substrate was cleaned by sonication in deionized water, acetone and isopropanol for 15 minutes successively and finally was transferred into glove box with nitrogen atmosphere. The organic semiconductor layers were fabricated with spin-coating process of a 2000 rpm 50  $\mu\text{L}$  chloroform solution and annealed at 100  $^{\circ}\text{C}$  for 20 minutes. The dielectric layer was fabricated with spin-coating process of a 60  $\mu\text{L}$  polymethyl methacrylate (PMMA) butylacetate solution and annealed at 100  $^{\circ}\text{C}$  for 20 minutes. Finally, 100 nm Ag layer was deposited on the dielectric layer with thermal evaporation process as gate electrode.

The saturation charge-carrier mobility ( $\mu$ ) was calculated according to the equation:

$I_{DS} = (W\mu C_i/2L)(V_G - V_{th})^2$ , where the  $I_{DS}$  is the source-drain current,  $V_G$  and  $V_{th}$  are the gate voltage and threshold, respectively.  $W$  and  $L$  are the channel width and length of OFET,  $C_i$  is the capacitance per unit area of dielectric and  $C_i$  (PMMA) = 3 nF·cm<sup>-2</sup>.