

## Supporting Information

### $\pi$ -Conjugated Dithieno[3,2-b:2',3'-d]pyrrole (DTP) Oligomers for Organic Thin-Film Transistors

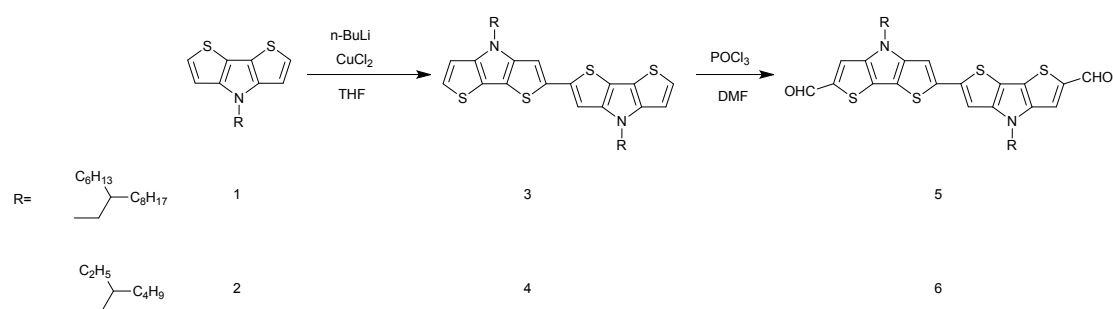
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#### Synthesis and characterization of intermediate products



**Figure S1.** Synthesis of intermediate products.

4,4'-bis(2-hexyldecyl)-4H,4'H-2,2'-bidithieno[3,2-b:2',3'-d]pyrrole (**3**): compound **1** (800 mg, 1.98 mmol) was dissolved in anhydrous THF (50 mL). After cooling to  $-78^{\circ}\text{C}$ , n-BuLi (1.98 mmol) was added slowly under an Argon atmosphere. After 2 stirring at this temperature, CuCl<sub>2</sub> (266 mg, 1.98 mmol) was added in one portion. The resulting mixture was warmed slowly to room temperature and stirred overnight. The reaction mixture was quenched with water, extracted with dichloromethane, washed with saturated brine solution, and dried over anhydrous sodium sulfate. The residual solvent was evaporated by rotary evaporation, and the crude product was purified by column chromatography on silica gel using hexanes/dichloromethane (10:1) as the eluent to give a yellow solid (215 mg, 27% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.12 (d, J=5.2 Hz, 2H), 7.05 (s, 2H), 6.96 (d, J=5.1 Hz, 2H), 4.05 (d, J=7.0 Hz, 4H), 2.02 (m, 2H), 1.61-1.05 (m, 48H), 0.93-0.81 (t, J=6.5 Hz, 12h); MS (MALDI-TOF): m/z 804.5 [M]<sup>+</sup>.

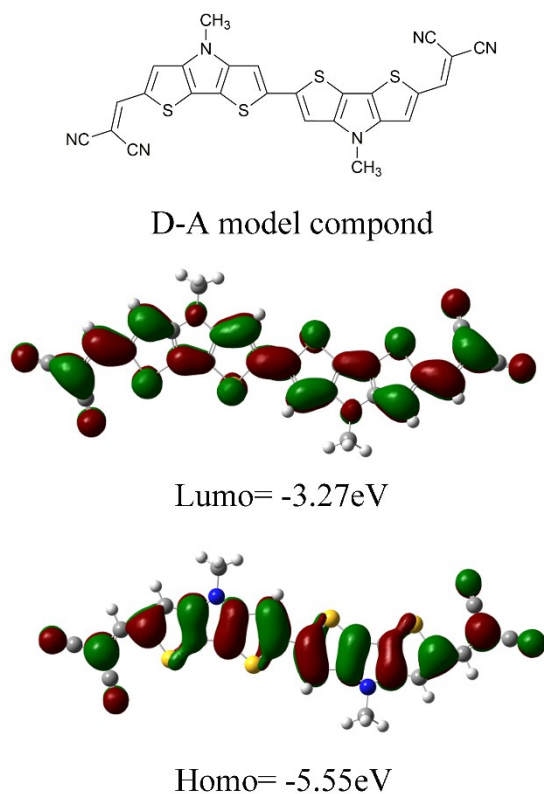
4,4'-bis(2-ethylhexyl)-4H,4'H-2,2'-bidithieno[3,2-b:2',3'-d]pyrrole (**4**) was synthesized according to a similar procedure of compound **3**. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.12 (d, J=5.0 Hz 2H), 7.06 (s, 2H), 6.97 (d, J=4.8 Hz, 2H), 4.06 (d, 4H), 1.97 (m, 2H), 1.21-1.54 (m, 16H), 1.01-0.83 (m, 12h); MS (MALDI-TOF): m/z 580.1 [M]<sup>+</sup>.

4,4'-bis(2-hexyldecyl)-4H,4'H-[2,2'-bidithieno[3,2-b:2',3'-d]pyrrole]-6,6'-dicarbaldehyde (**5**): Phosphorus oxychloride (2.42 mL, 25.94 mmol) was added dropwise to DMF (2.54 mL, 33.06 mmol) at  $0^{\circ}\text{C}$  and the mixture was stirred for 1 h at room temperature. Compound **3** (205 mg, 0.25 mmol) was added and the mixture was stirred at  $100^{\circ}\text{C}$  for 12 h. After cooling to room temperature and addition of 30 mL of dichloromethane and 100 mL of a 1 M aqueous solution of sodium hydroxide, the mixture was stirred for 2 h at room temperature. The organic phase was then washed with water and dried over MgSO<sub>4</sub>. Solvent removal and column chromatography (silica gel eluent: dichloromethane) gave 183 mg (85%) of a red solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.87 (s, 2H), 7.57 (s, 2H), 7.08 (s, 2H), 4.08 (d, 4H), 2.02 (m, 2H),

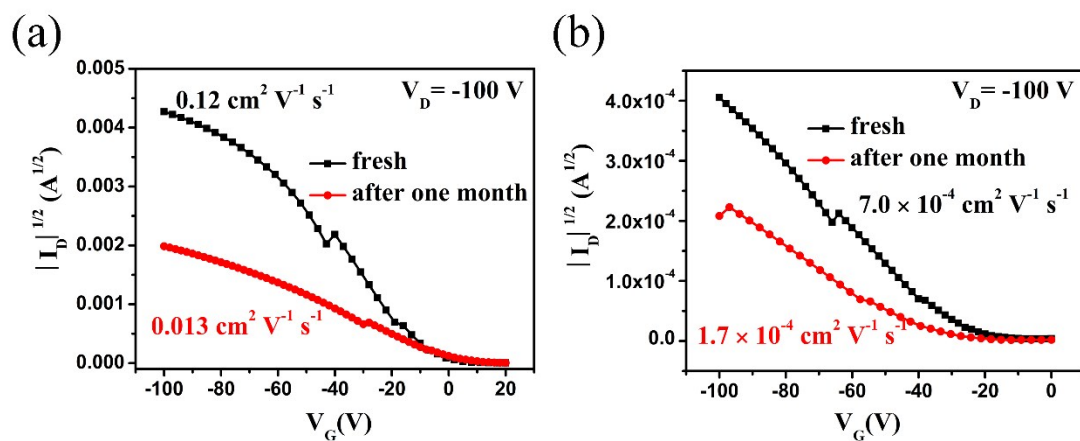
1.55-1.14 (m, 48H), 0.97-0.81(m, 12h);

4,4'-bis(2-ethylhexyl)-4H,4'H-[2,2'-bidithieno[3,2-b:2',3'-d]pyrrole]-6,6'-dicarbaldehyde (**6**) was synthesized according to a similar procedure of compound **5**.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ) 9.89 (s, 2H), 7.60 (s, 2H), 7.13 (s, 2H), 4.12 (d, 4H), 1.99 (m, 2H), 1.21-1.47(m, 16H), 0.97-0.89 (m, 12h).

### Theoretical Calculation

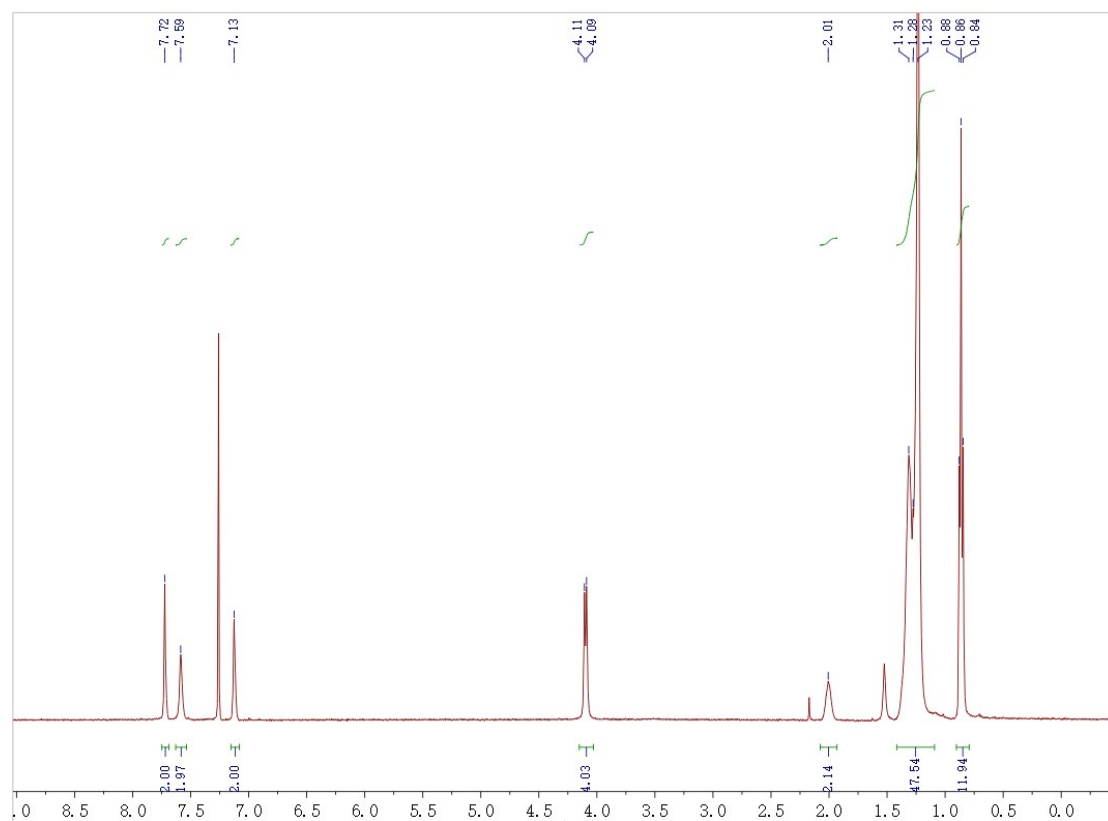


**Figure S2.** DFT-calculated (B3LYP/6-31G) HOMO and LUMO for D-A model compound.

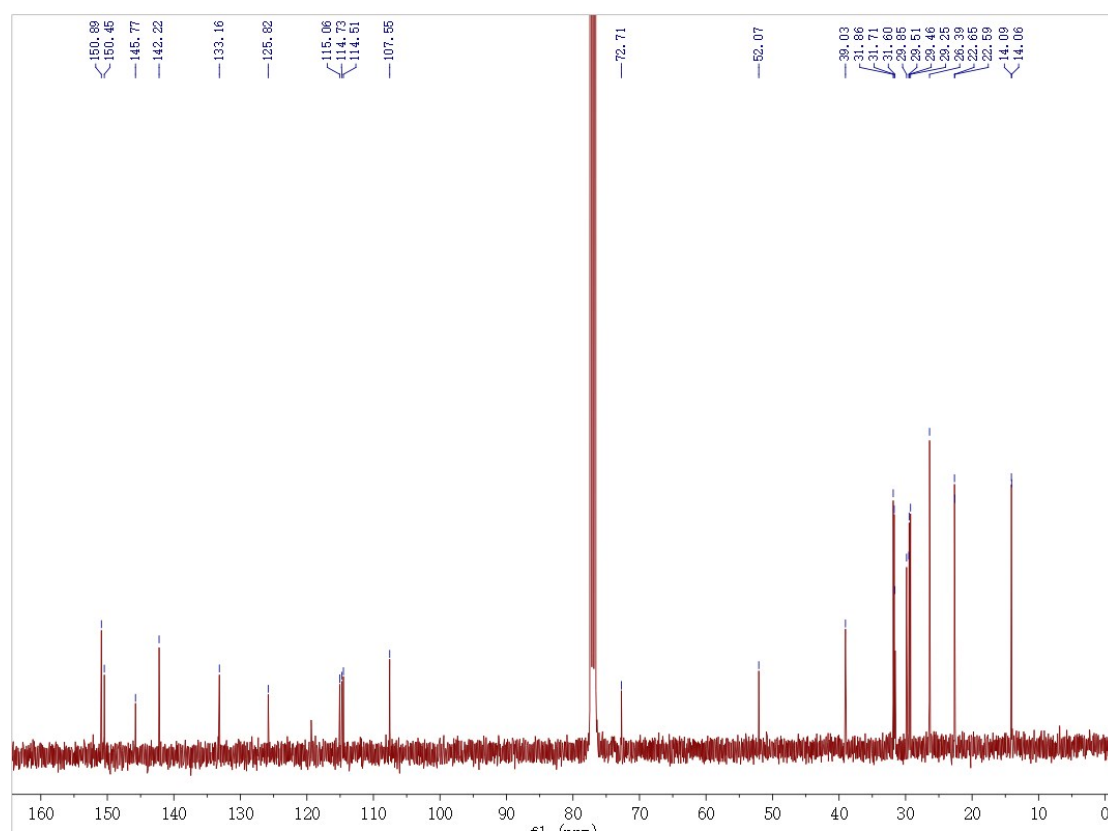


**Figure S3.** Air stability of (a) DTP-L and (b) DTP-S for FET.

**<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra**



**Figure S4.** <sup>1</sup>H NMR spectrum of DTP-L.



**Figure S5.** <sup>13</sup>C NMR spectrum of DTP-L.

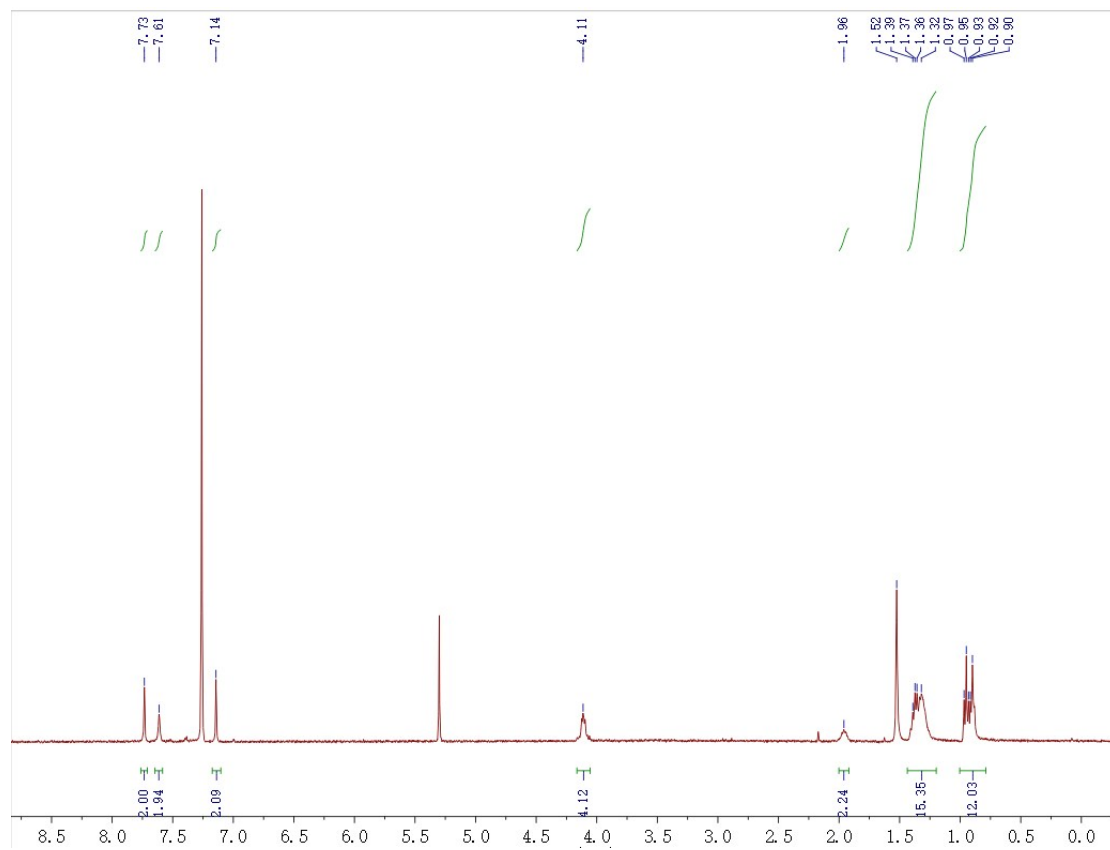


Figure S6. <sup>1</sup>H NMR spectrum of DTP-S.