Electronic Supplementary Information

An Ultra-low Bandgap Diketopyrrolopyrrole (DPP)-based Polymer with Balanced Ambipolar Charge Transport for Organic Field-Effect Transistors

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Synthesis of M1

To a solution of 3,6-dithien-2-yl-2,5-di(2-decyltetradecanyl)-pyrrolo[3,4-c]pyrrole-1,4-dione (0.86 g, 1.0 mmol) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.61 mL, 0.56 g, 3.0 mmol) in dry THF (10 mL) under argon at 25°C was added drop-wise by lithium diisopropylamide (LDA) (1.2 mL of a 2 M solution in THF, 2.4mmol) over 5 minutes. After 30 min at this temperature, the resulting mixture was warmed to 0°C and stirred for 1 h before being quenched with a solution of HCl (10 mL, 0.1 M). The product was extracted with dichloromethane (3×25 mL), dried over MgSO₄ and then the solvent was concentrated. The crude mixture was dissolved in dichloromethane and poured into cold acetone. After filtration, the filtrate was washed with cold acetone and dried under low vacuum to give a dark pink powder (0.84 g, 0.75mmol, 75% yield).

¹H NMR (CDCl₃, 400MHz), δ (ppm): 8.89 (d, *J* = 3.2 Hz, 2H), 7.70 (d, *J* = 2.8 Hz, 2H), 4.04 (d, *J* = 6.0 Hz, 4H), 1.89 (br, 2H), 1.37 (s, 24H), 1.28-1.21 (m, 64H), 0.88-0.84 (m, 12H); MALDI-TOF Mass (*m/z*): Calcd for [M+H]⁺ C₆₆H₁₁₀B₂N₂O₆S₂: 1112.8, found: 1111.7.



Fig. S1 ¹H NMR spectra of copolymer pDTDPP-TTF