

Electronic Supplementary Information for:

Copolymers of benzo[1,2-*b*:4,5-*b'*]dithiophene and bithiazole for high-performance thin film phototransistors

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Synthesis of P1. 2,6-Bis(trimethyltin)-4,8-didodecyloxybenzo[1,2-*b*:4,5-*b'*]dithiophene (**1**) and 5,5'-dibromo-4,4'-dihexyl-2,2'-bithiazole (**2**) were synthesized according to our previous work.⁵⁰ Compound **1** (265.8 mg, 0.3 mmol) and compound **2** (147 mg, 0.3 mmol) were dissolved in 50 mL of anhydrous toluene and deoxygenated with N₂ for 30 min. Pd(PPh₃)₄ (34.7 mg, 0.03 mmol) was then added under N₂. The mixture was stirred at reflux for 3 days. To end-cap the polymer chain, tributyl(thiophen-2-yl)stannane (11.2 mg, 0.03 mmol) was added under nitrogen and the mixture was stirred at reflux for 10 h. 2-Bromothiophene (9.7 mg, 0.06 mmol) was then added under nitrogen, and the mixture was stirred at reflux for 10 h. After the reaction mixture was cooled to room temperature, the polymer was precipitated by addition of 100 mL of methanol. The precipitate was filtered. Finally, the polymer was purified by size exclusion column chromatography over Bio-Rad Bio-Beads

S-X1 eluting with chloroform. The polymer was recovered as a purple solid from the chloroform fraction by rotary evaporation (160 mg, 60%). ^1H NMR (400 MHz, CDCl_3): δ 6.93 (br, 2H), 4.32 (br, 4H), 3.11 (br, 4H), 1.91 (br, 4H), 1.25 (br, 48H), 0.87 (br, 12H). GPC: M_n 3584; M_w 8711; M_w/M_n 2.4. Anal. Calcd for $(\text{C}_{52}\text{H}_{78}\text{N}_2\text{O}_2\text{S}_4)_n$: C, 70.06; H, 8.82; N, 3.14. Found: C, 65.73; H, 8.39; N, 2.84%.

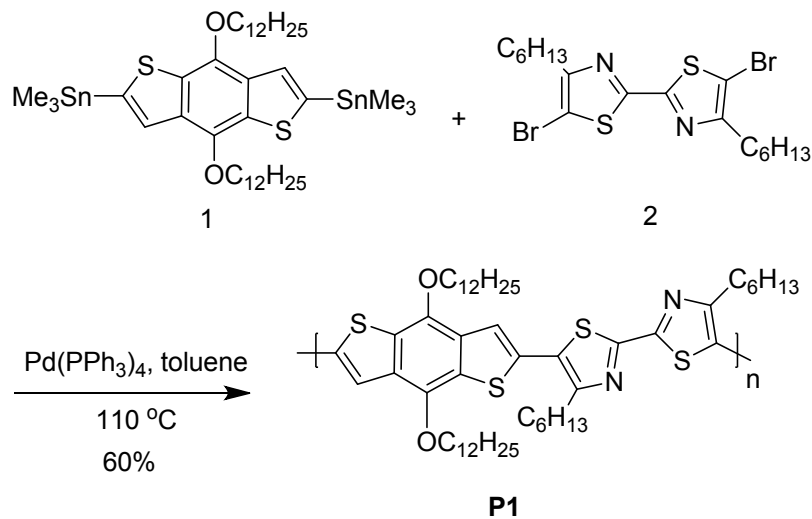


Fig. S1 Synthetic route of **P1**.

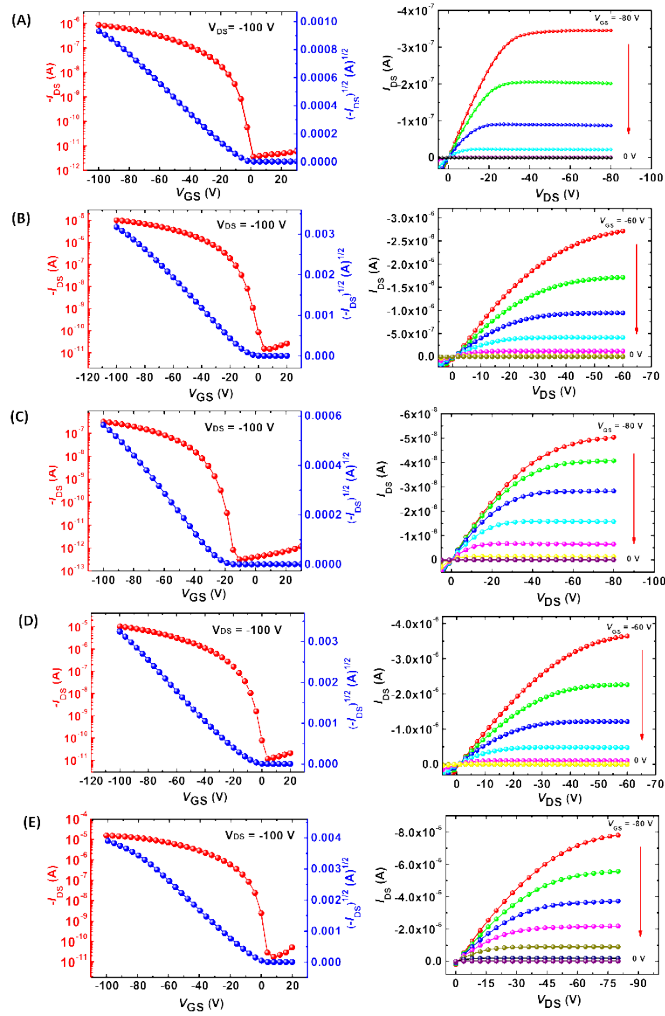


Fig. S2 Transfer and output characteristics of thin film transistors based on (A) P1; (B) P2; (C) P3; (D) P4; (E) P5.

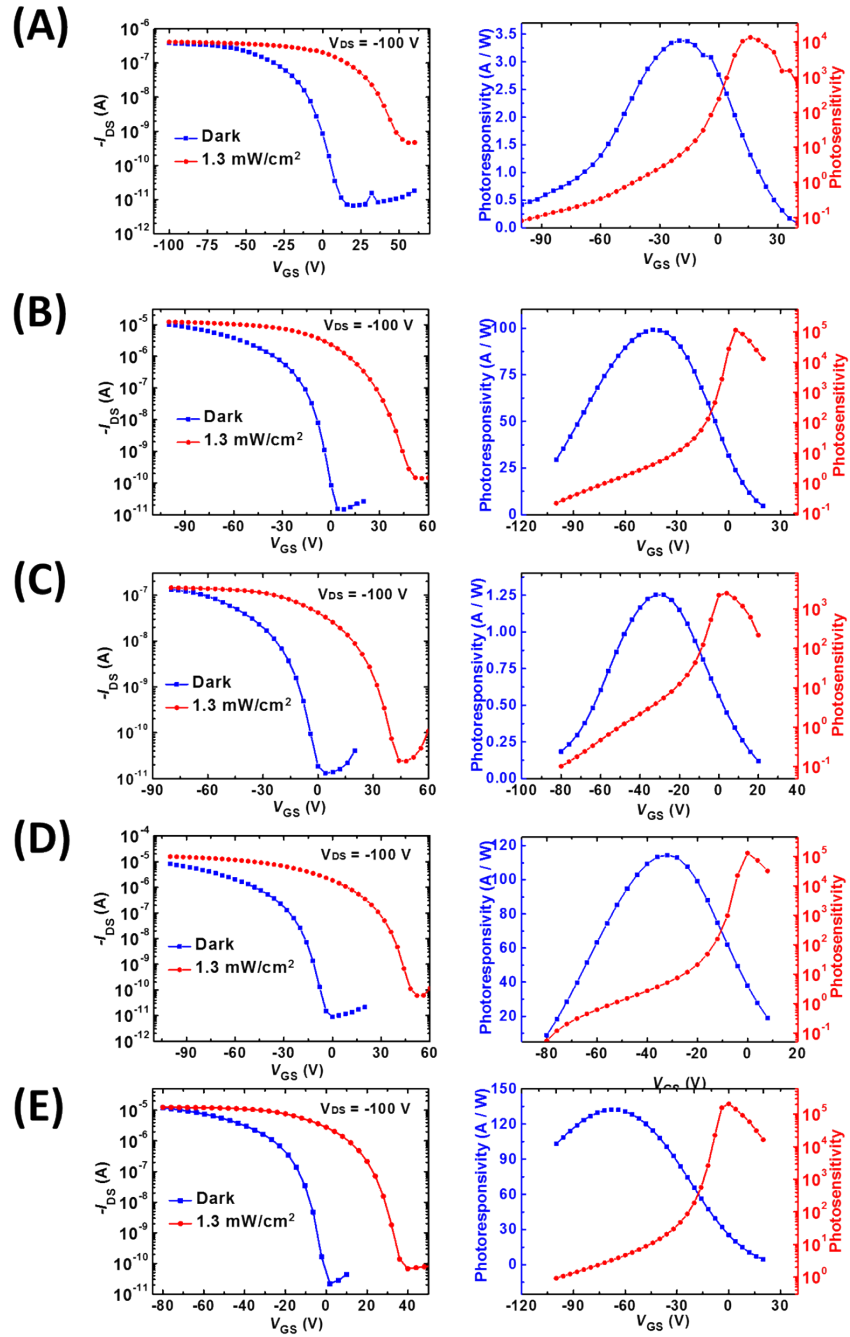


Fig. S3 Transfer characteristics, photoresponsivity, and photosensitivity of thin film phototransistors based on (A) P1; (B) P2; (C) P3; (D) P4; (E) P5.

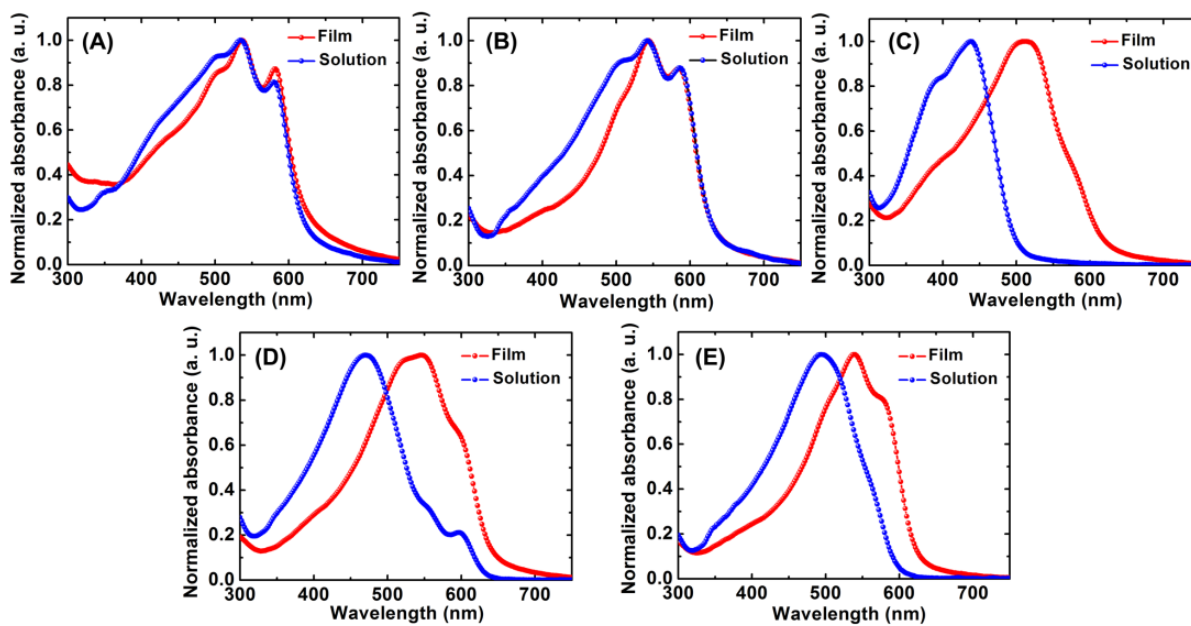


Fig. S4 UV-vis absorption spectra of (A) **P1**; (B) **P2**; (C) **P3**; (D) **P4** and (E) **P5** in solution and in thin films.