

# Supporting Information

## New Selenophene-Based Semiconducting Copolymers for High Performance Organic Thin-Film Transistors

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## Synthesis

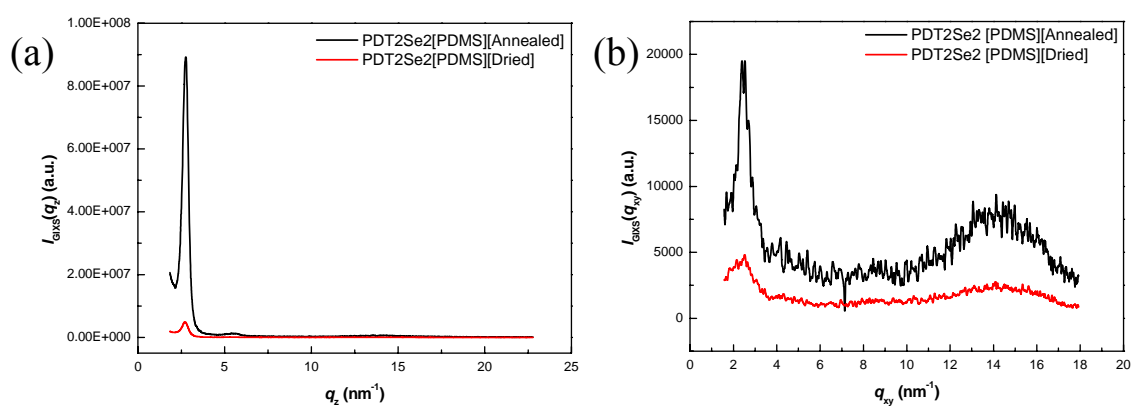
**2,2'-Biselenophene (1).** The compound was synthesized according to the previously published procedures.<sup>1</sup> <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.85 (d, 2H), 7.25 (d, 2H), 7.21 (dd, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 144.8, 130.2, 129.7, 126.7.

**5,5'-Dibromo-4,4'-didodecyl-2,2'-bithiophene (3).** The compound was synthesized according to the previously published procedure.<sup>2</sup> Yield: 2.73 g (86%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 6.75 (s, 2H), 2.50 (t, 4H), 1.56 (m, 4H), 1.29 (m, 36H), 0.87 (t, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 142.9, 136.2, 124.4, 107.9, 31.9, 29.67, 29.64, 29.61, 29.5, 29.4, 29.3, 29.2, 22.7, 14.1; MS (MALDI-TOF) (m/z) 660 [M<sup>+</sup>]; Anal. calcd for C<sub>32</sub>H<sub>52</sub>Br<sub>2</sub>S<sub>2</sub>: C 58.17, H 7.93, S 9.71; found: C 58.56, H 7.65, S 9.86.

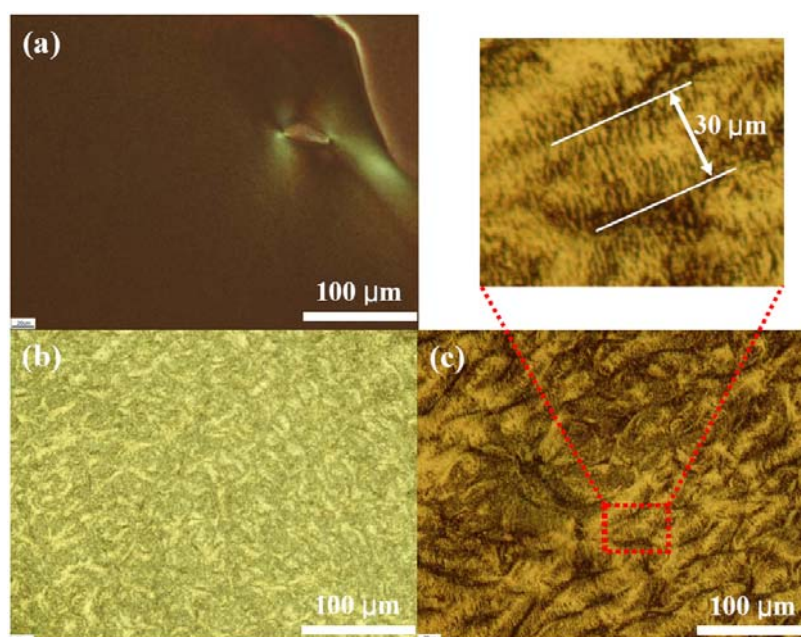
**2-(3-Dodecylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (4).** The synthesis of the compound was based on a procedure reported.<sup>3</sup> Yield: 3.72 g (57%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.46 (d, 1H), 7.01 (d, 1H), 2.89 (t, 2H), 1.59 (m, 2H), 1.33 (m, 30H), 0.89 (t, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 154.63, 131.21, 130.21, 83.44, 31.91, 31.81, 30.11, 29.68, 29.65, 29.62, 29.45, 29.34, 29.29, 24.75, 22.66, 14.07.

**5,5'-Dibromo-2,2'-biselenophene (5).** The compound was synthesized according to the previously published procedures.<sup>1</sup> Yield: 2.45 g (87%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.12 (d, 2H), 6.85 (d, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ): 145.51, 133.60, 126.54, 114.93.; MS (MALDI-TOF) (m/z) 418 [M<sup>+</sup>]; Anal. calcd for C<sub>8</sub>H<sub>4</sub>Br<sub>2</sub>Se<sub>2</sub>: C 23.00, H 0.96; found: C 23.34, H 1.67.

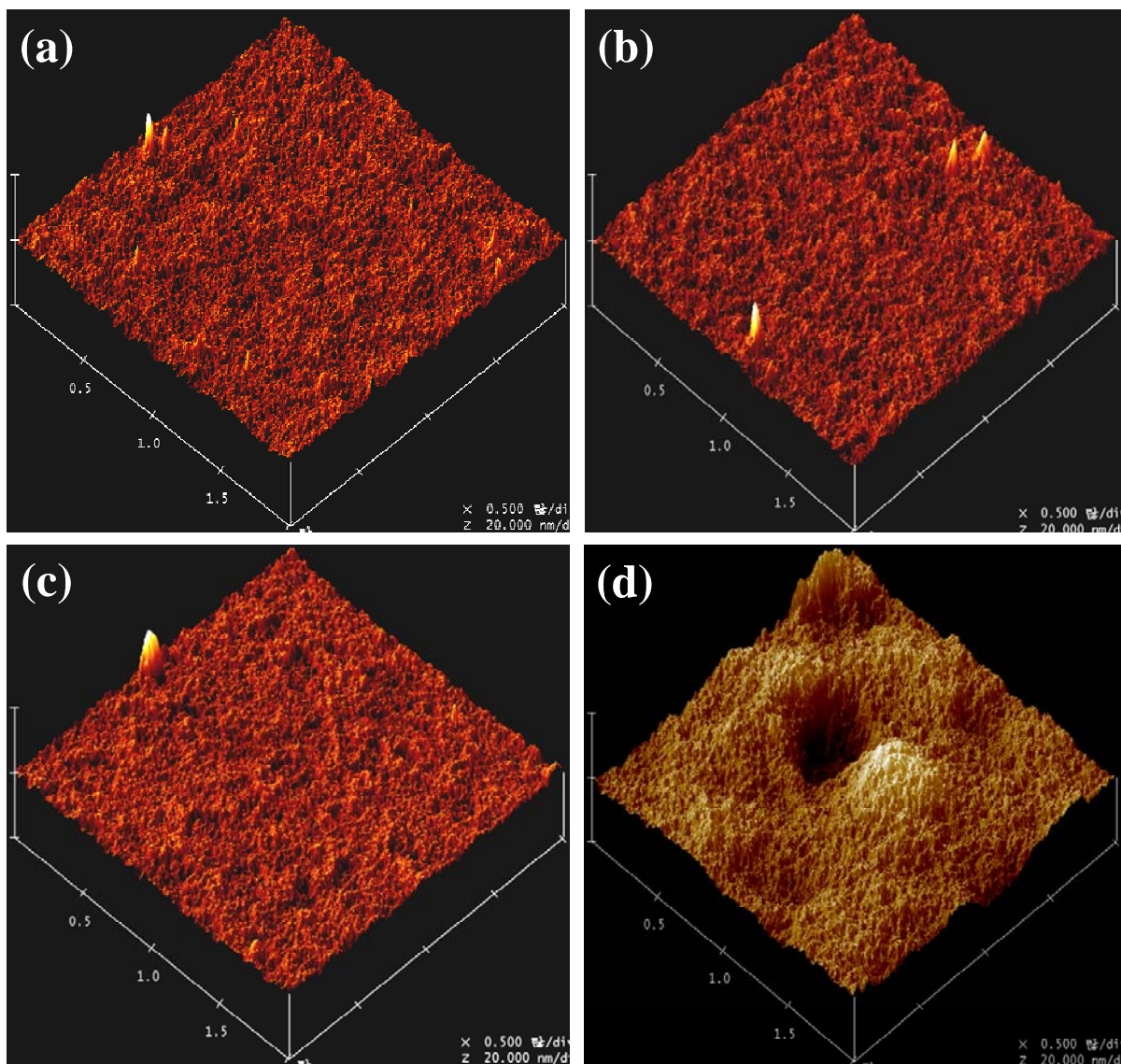
**2-Bromo-3-dodecylthiophene (7).** The compound was synthesized according to the previously published procedures.<sup>3</sup>



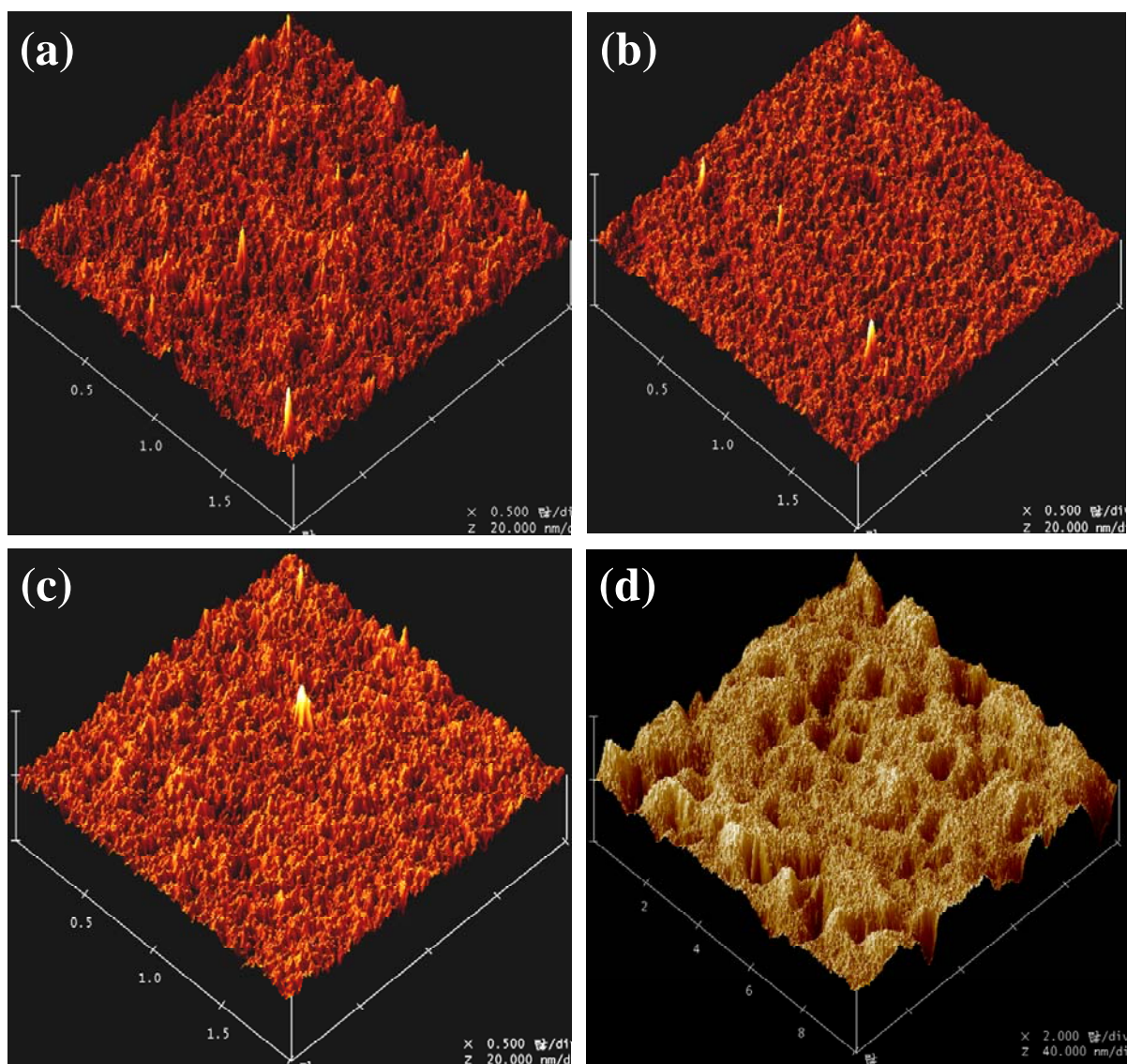
**Fig. S1** Two dimensional GIXRD patterns of **PDT2Se2** (a) out-of-plane and (b) in-plane on PDMS-modified substrates.



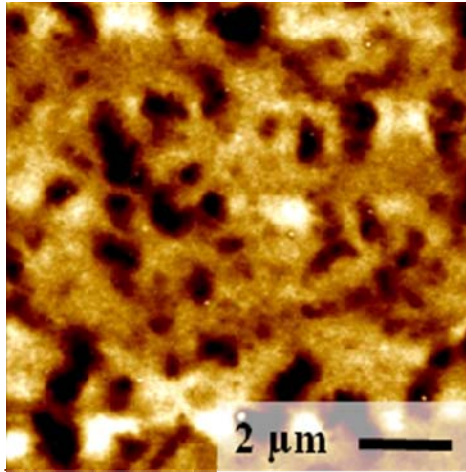
**Fig. S2** POM images of higher MW **PDT2Se2**. The film was (a) as-cast, (b) annealed at 90°C for 15 min and then slowly cooled to RT, and (c) annealed at 150°C for 30 min and then quickly quenched.



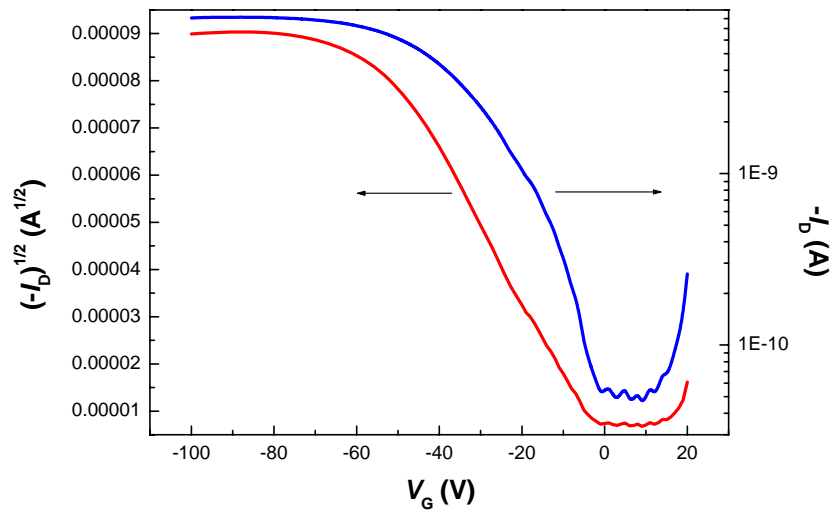
**Fig. S3** Z-range AFM topography images of the dried polymer films spin-coated onto ODTs-modified  $\text{SiO}_2/\text{Si}$  substrates: (a) lower MW **PDT2Se2** and (b) higher MW **PDT2Se2** obtained with Stille coupling, (c) **PDT2Se2** obtained with oxidative coupling, and (d) **PDT4Se2**.



**Fig. S4** Z-range AFM topography images of the annealed polymer films spin-coated onto ODTS-modified SiO<sub>2</sub>/Si substrates: (a) lower MW **PDT2Se2** and (b) higher MW **PDT2Se2** obtained with Stille coupling, (c) **PDT2Se2** obtained with oxidative coupling, and (d) **PDT4Se2**.



**Fig. S5** The enlarged  $10 \times 10 \mu\text{m}$  AFM image of annealed **PDT4Se2** film spin-coated onto ODTS-modified  $\text{SiO}_2/\text{Si}$  substrate.



**Fig. S6** TFT performance of **PDT4Se2** on ODTS-modified  $\text{SiO}_2/\text{Si}$  substrate: transfer characteristics at a constant source-drain voltage of  $-100 \text{ V}$  (semilogarithmic plot of  $-I_D$  vs  $V_G$  (blue line) and plot of  $(-I_D)^{1/2}$  vs  $V_G$  (red line)).

## References

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- 3 Dang, T. T. M.; Park, S.-J.; Park, J.-W.; Chung, D.-S.; Park, C. E.; Kim, Y.-H.; Kwon, S.-K. *J. Polym Sci. Part A* **2007**, *45*, 5277.