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Synthesis, Characterization, and Field-Effect Transistors Properties of Tetrathienoanthracene-Based Copolymers Using A Two-Dimensional π-Conjugation Extension Strategy: A Potential Building Block for High-Mobility Polymer Semiconductors

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Synthesis. The synthetic procedures for 2-(2-octyldodecyl)thiophene (1),[1] 3-tri-*n*-buthylstannyl-5-(2-octyldodecyl)thiophene (2),[1] 1,4-bis(2-thienyl)-2,5-dibromobenzene (3),[2] and 2,9,-dibromo-5,12-di(2'-octyldodecyl)trithieno[2',3':5,6:3',2':3,4:3',2':7,8]anthrax-[1,2,*b*]-thiophene (TTB-2Br)[2] are similar to the reported literatures.

2-(2-Octyldodecyl)thiophene (1)[1]**.** Under a N_2 atmosphere, *n*-butyl lithium (100 mmol, 40 ml 2.5 M in hexane) was added dropwise to a 500 mL dried three-neck round-bottom flask containing thiophene (8.4 g, 100 mmol) and 200 mL of dry THF at –78 ℃. The mixture solution was stirred at –78 ℃ for 2 h. After that, 9-(bromomethyl)nonadecane (105 mmol, 38 g) was added in one portion by syringe at –78 ℃. After complete addition the mixture was stirred at 60 ℃ overnight and then cooled to room temperature. The mixture was extracted with dichloromethane and dried over anhydrous Na_2SO_4. After concentration by rotary evaporation, the residue was purified by vacuum distillation to give the title compound as a colorless liquid (16.4 g, 45 %). ^{1}H NMR (400 MHz,

$CDCl_3$), δ (ppm): 7.11 (d, 1H), 6.93 (dd, 1H), 6.75 (d, 1H), 2.78 (d, 2H), 1.64 (m, 1H), 1.28 (m, 26H), 0.87 (m,12H)

3-Tributhylstannyl-5-(2-octyldodecyl)thiophene (2) [1]**.** A solution of *n*-BuLi (10 mmol) was added dropwise to a solution of 2-(2-octyldodecyl)thiophene (1) (3.65 g, 10 mmol) in 100 mL of dry THF at –78 ℃. Then the mixture was allowed to warm to 0 ℃ and stirred for 1 h. After cooling to –78 ℃ again, tri-*n*-butyltin chloride (3.25 g, 10 mmol) was added in one portion. The mixture was then warmed to room temperature and stirred overnight. The reaction mixture was extracted with diethyl ether, dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. A light yellow liquid was obtained and used directly without further purification. ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 6.98 (d, 1H), 6.84 (d, 1H), 2.77 (d, 2H), 1.61 (m, 1H), 1.26 (m, 26H), 0.88 (m,12H).

1,4-Bis(5-(2'-octyldodecyl)-2-thienyl)-2,5-bis(2-thienyl)benzene (4). Under a N_2 atmosphere, a mixture of 3 (4 g, 10 mmol), $Pd(PPh_3)_4$ (578 mg, 0.5 mmol), and DMF (40 mL) were added to a 250 mL dried three-neck round-bottom flask, then added compound 2 (16.3 g, 25 mmol) at once. Then the mixture was stirred at 110 ℃ for 48 h. After cooling to room temperature, the mixture was extracted with dichloromethane, dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (silica gel, hexane) to yield a white solid product (6.77 g, 70 %). ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.62 (s, 2H), 7.26 (d, 2H), 6.98 (m, 4H), 6.73 (d, 2H), 6.61 (d, 2H), 2.70 (d, 4H), 1.57 (m, 2H), 1.26 (m, 64H), 0.88 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 144.74, 141.00, 138.20, 132.38, 132.13, 131.97, 126.25, 125.98, 125.93, 125.16, 124.16, 38.99, 33.50, 32.18, 30.97, 29.05, 28.74, 28.73, 28.71, 28.69, 28.42, 28.40, 25.64, 21.75, 14.19. MALDI-TOF-MS: m/z = 966.66 (M^+).

1,4-Bis(5-(2'-octyldodecyl)-2-thienyl)-2,5-bis(5-bromo-2-thienyl)benzene (5). To a solution of 2 (4.84 g, 5 mmol) in THF (60 mL), NBS (1.96 g, 11 mmol) was added in three portions. In the dark, this mixture was stirred at room temperature for 12 h. Then the reaction solution was extracted with dichloromethane, dried with anhydrous Na_2SO_4 and filtered. The organic layer was concentrated by rotary evaporation and further purified by column chromatography (silica gel, Hexanes) to yield a light yellow sticking liquid (3.87 g, 80%). ^1H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.54 (s, 2H), 6.91 (d, 2H), 6.76 (m, 4H), 6.64 (d, 2H), 2.72 (d, 4H), 1.57 (m, 2H), 1.27 (m, 64H), 0.87 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 145.16, 142.51, 137.43, 132.40, 131.86, 131.58, 128.75, 126.42, 124.38, 112.12, 38.97, 33.51, 32.24, 30.99, 29.05, 28.75, 28.73, 28.71, 28.43, 28.41, 25.68, 21.75, 13.17. MALDI-TOF-MS: m/z = 1122.86 (M^+).

2,9-dibromo-5,12-di(2'-octyldodecyl)trithieno[2',3':5,6:3',2':3,4:3',2':7,8]anthrax[1,2,*b*]thiophene (TTB-2Br). Under a N_2 atmosphere, a solution of iron (III) chloride (2.43 g, 15.0 mmol) in nitromethane (10 mL) was added dropwise to a solution of 5 (2.81 g, 2.5 mmol) in dichloromethane (1000 mL). After being stirred for 20 min, methanol (200 mL) was added in one portion. The reaction solution was extracted with dichloromethane, dried with anhydrous Na_2SO_4 and evaporated in vacuum. The crude product was recrystallized from hexane to yield a yellow solid (1.26 g, 45 %). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 8.32 (s, 2H), 7.56 (s, 2H), 7.22 (s, 2H), 2.95 (d, 4H), 1.85 (m, 2H), 1.25–1.40 (m, 64H), 0.86 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 144.31, 134.24, 132.58, 131.40, 130.82, 124.73, 123.28, 122.49, 119.76, 116.05, 112.34, 112.21, 39.29, 34.41, 32.38, 31.03, 30.99, 29.17, 28.86, 28.81, 28.78, 28.47, 28.40, 25.79, 23.58, 21.78, 21.75, 13.21, 13.18. MALDI-TOF MS: m/z = 1120.65 (M^+).

Reference

[1] Ellinger, S.; Ziener, U.; Thewalt, U.; Landfester, K.; Möller, M. *Chem. Mater.*, **2007**, 19, 1070–1075.

[2] He, F.; Wang, W.; Chen, W.; Darling, S. B.; Strzalka, J.; Liu, Y.; Yu, L. P. *J. Am. Chem. Soc.*, **2011**, *133*, 3284–3287.

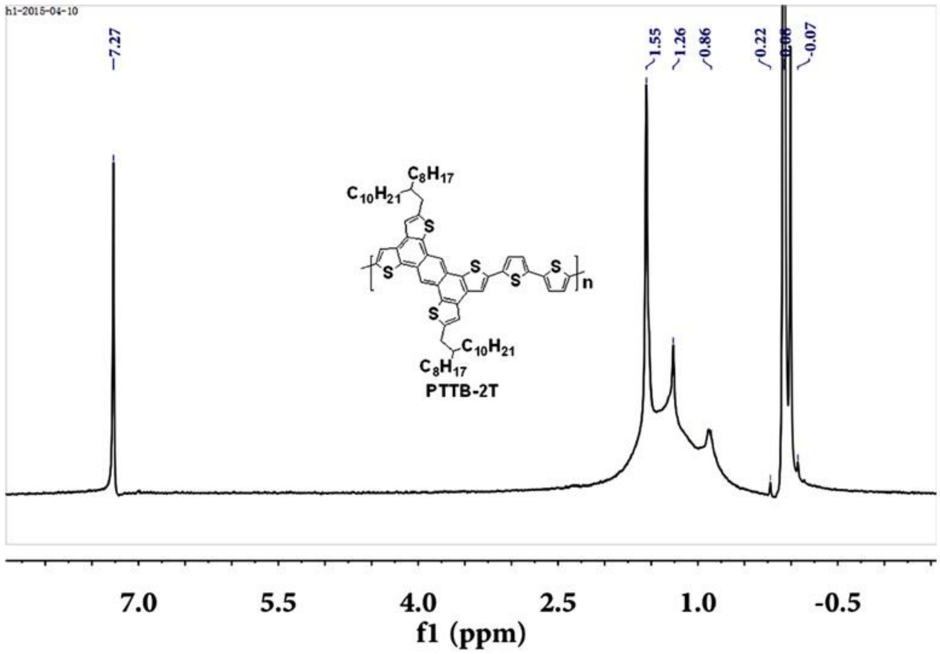

Fig. S1 ^{1}H NMR spectrum of polymer PTTB-2T in $CDCl_3$.

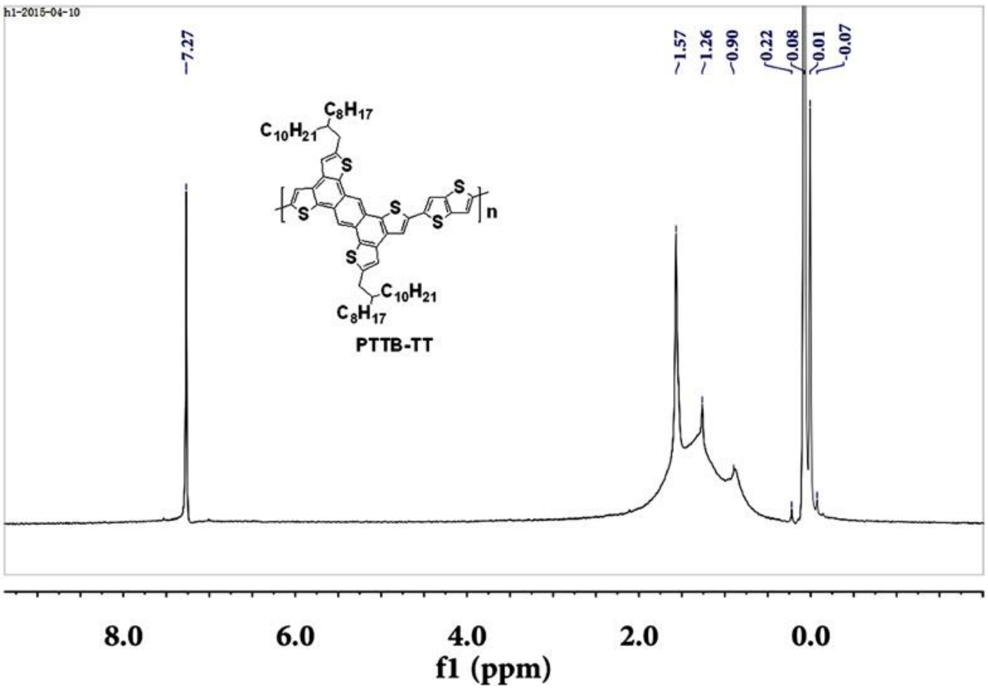

Fig. S2 ^{1}H NMR spectrum of polymer PTTB-TT in $CDCl_3$.

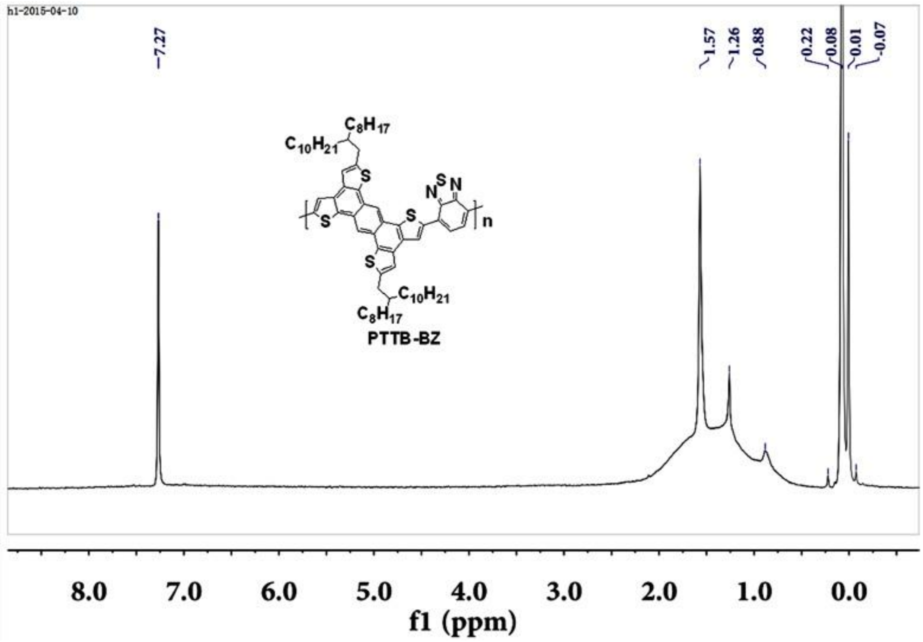

Fig. S3 ^{1}H NMR spectrum of polymer PTTB-BZ in $CDCl_3$.

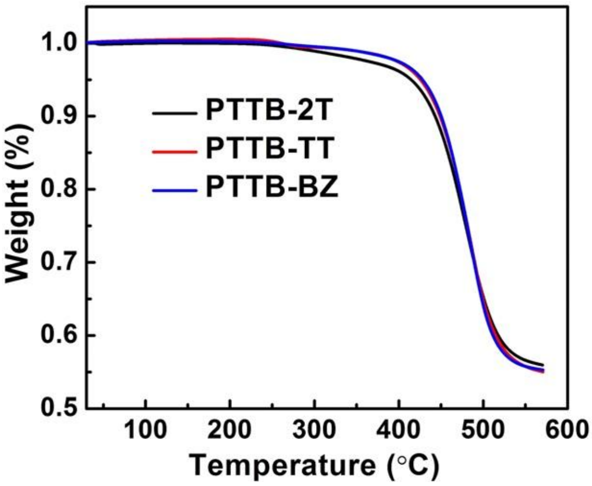

Fig. S4 TGA traces of the various TTB-based polymers.

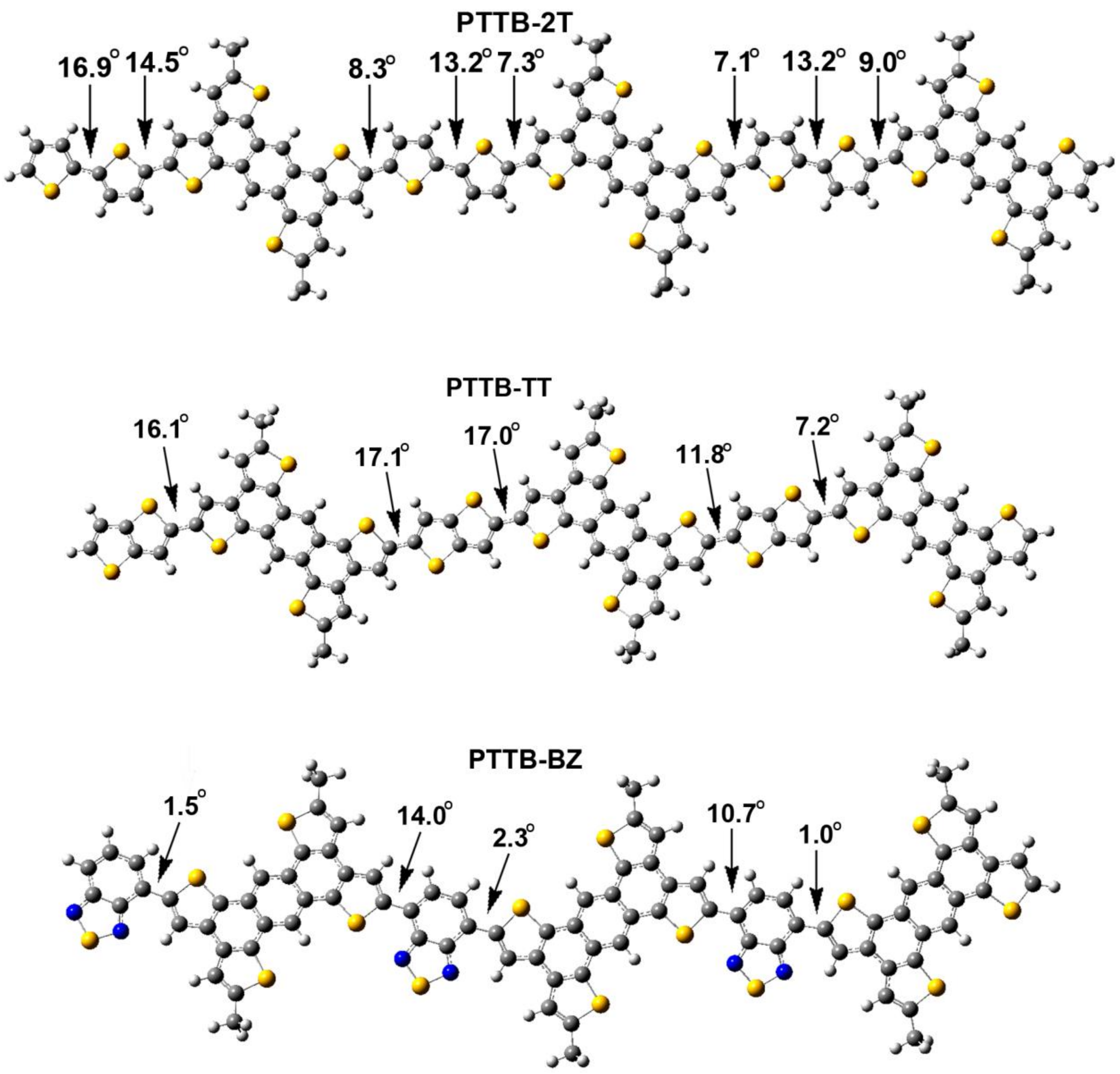

Fig. S5 Calculated molecular structures calculated by B3LYP/6-31G* of the polymer repeat units.

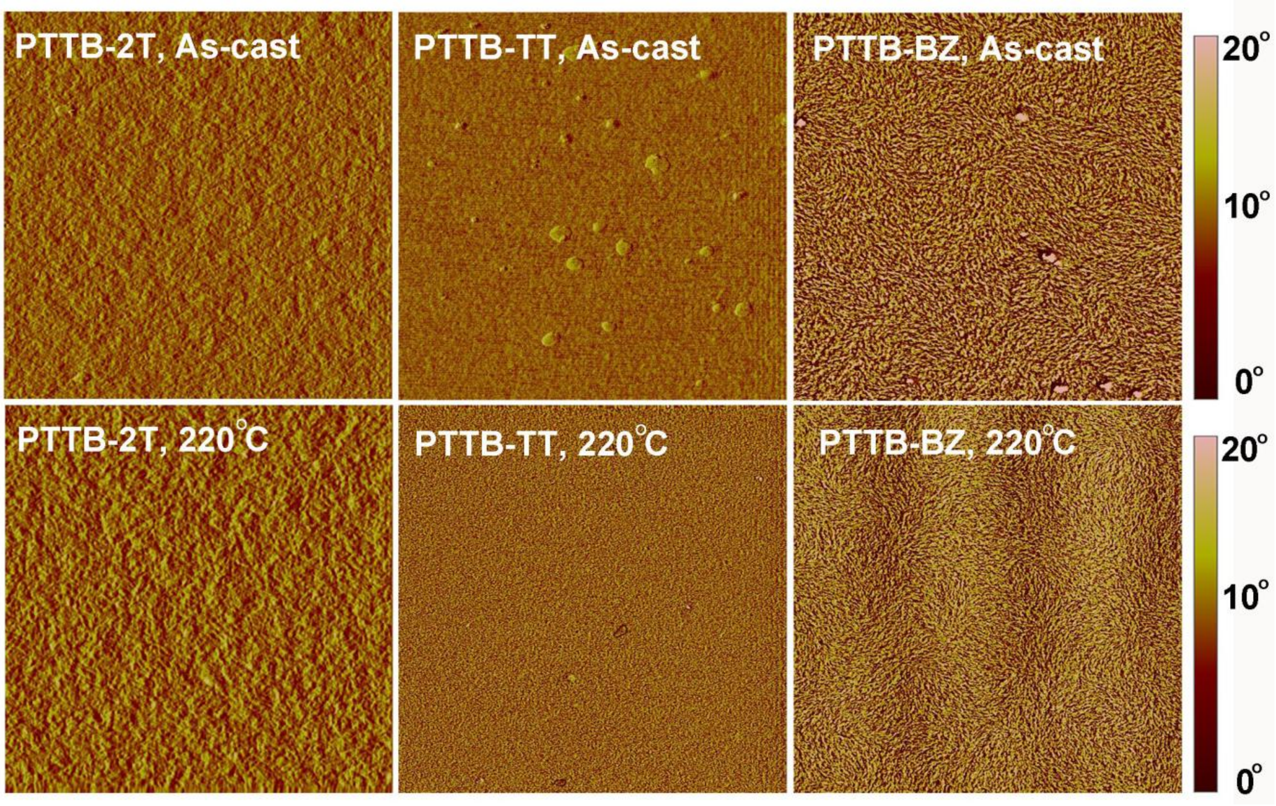

Fig. S6 AFM phase images (5 × 5 μm) of as-cast (top row) and annealed (bottom row) TTB-based polymer thin films.

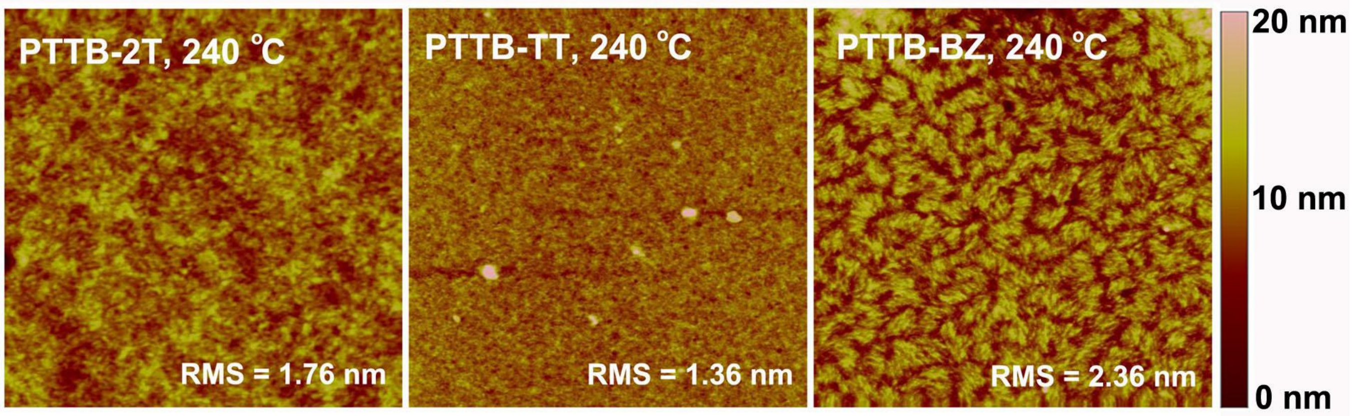

Fig. S7 AFM topography images (5 × 5 μm) of the TTB-based polymer thin films annealed at 240 °C.