

Supporting Information

The Effect of Fluorine Substitution on the Molecular Interactions and Performance in Polymer Solar Cells

In-Bok Kim^a, Soo-Young Jang^{b,c}, Yeong-A Kim^c, Rira Kang^d, In-Sik Kim^e, Do-Kyeong Ko^e, Dong-Yu Kim^{a,c*}

^aResearch Institute for Solar and Sustainable Energies (RISE), Gwangju Institute of Science and Technology (GIST), 123 Cheomdangwagi-ro, Buk-gu, Gwangju, 61002, Republic of Korea

^bDepartment of Chemistry and Centre for Plastic Electronics, Imperial College London, Exhibition Rd, London, SW7 2AZ, UK.

^cHeeger Center for Advanced Materials (HCAM), School of Material Science and Engineering (SMSE), Gwangju Institute of Science and Technology (GIST), 123 Cheomdangwagi-ro, Buk-gu, Gwangju, 61002, Republic of Korea.

^dRadiation Research Division for Industry and Environment, Korea Atomic Energy Research Institute (KAERI), 29 Geungu-gil, Jeongeup-si, Jeollabuk-do, 56212, Republic of Korea

^eSchool of Physics and Chemistry, Gwangju Institute of Science and Technology (GIST), 123 Cheomdangwagi-ro, Buk-gu, Gwangju, 61002, Republic of Korea

Corresponding author: Dong-Yu Kim

*E-mail: kimdy@gist.ac.kr

Synthesis of Monomers

The monomers were prepared by modifying the previously reported literatures.^{1,2,3}

4,7-Bis(4-dodecylthiophen-2-yl)-2,1,3-benzothiadiazole (2-1). 2-Tributylstannyl-4-octyldodecylthiophene (4.3 g, 8.4 mmol), 4,7-dibromo-[2,1,3]benzothiadiazole (1-1, 0.816 g, 2.8 mmol), Pd₂(dba)₃ (25 mg), and P(o-tolyl)₃ (17 mg) were dissolved in 25 mL of anhydrous toluene. The solution was degassed and refluxed 2 days. After cooling to room temperature, the mixture was extracted three times with CH₂Cl₂. The combined CH₂Cl₂ extraction was dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using hexane as eluent. The desired product was obtained as a yellow solid (1.56 g). ¹H NMR (400 MHz, CDCl₃) δ 7.94 (s, 2H), 7.83 (s, 2H), 7.0 (s, 2H), 2.57 (d, 4 H), 1.75 (s, 2H), 1.5-1.15 (br, 60 H), 0.86 (m, 12 H). Elemental Anal. Calcd. For (C₅₄H₈₈N₂S₃): C, 75.29; H, 10.30; N, 3.25; S, 11.16. Found: C, 75.30; H, 10.38; N, 3.21; S, 11.09.

4,7-Bis(4-dodecylthiophen-2-yl)-5-Fluoro-2,1,3-benzothiadiazole (2-2). The compound (2-2) was synthesized by following similar procedure of compound (2-1). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (d, 2 H), 7.73 (d, 1 H), 7.08 (d, 2 H), 2.63 (t, 4 H), 1.68 (s, 2 H), 1.4-1.1 (br, 60 H), 0.86 (m, 12 H). Elemental Anal. Calcd. For (C₅₄H₈₇FN₂S₃): C, 73.75; H, 9.97; F, 2.16; N, 3.19; S, 10.94. Found: C, 73.56; H, 9.95; N, 3.25; S, 10.88.

4,7-Bis(4-dodecylthiophen-2-yl)-5,6-difluoro-2,1,3-benzothiadiazole (2-3). The compound (2-3) was synthesized by following similar procedure of compound (2-1). ¹H NMR (400 MHz, CDCl₃) δ 8.09 (s, 2 H), 7.17 (s, 2 H), 2.64 (t, 4 H), 1.68 (s, 2 H), 1.38-1.11 (br, 60 H), 0.86 (m, 12 H). Elemental Anal. Calcd. For (C₅₄H₈₆F₂N₂S₃): C, 72.27; H, 9.66; F, 4.23; N, 3.12; S, 10.72. Found: C, 72.96; H, 10.21; N, 2.41; S, 10.35.

4,7-Bis(5-bromo-4-dodecylthiophen-2-yl)-2,1,3-benzothiadiazole (3-1). NBS (0.65 g, 3.64 mmol) was added in small portions to a solution of compound (2-1) (1.56 g, 1.82 mmol) in 60

mL of CHCl_3 . The reaction mixture was stirred in the dark at room temperature overnight. The mixture was poured into water and extracted three times with CHCl_3 . The combined CHCl_3 was dried over MgSO_4 . Solvent was removed under reduced pressure and the residue was purified by chromatography using hexane/chloroform as an eluent. The desired product was obtained as a red solid (1.6 g). MALDI TOF: 1057.0. ^1H NMR (400 MHz, CDCl_3) δ 7.73 (s, 2 H), 2.57 (d, 4 H), 1.75 (s, 2H), 1.5-1.15 (br, 60 H), 0.86 (m, 12 H). Elemental Anal. Calcd. For ($\text{C}_{54}\text{H}_{86}\text{Br}_2\text{N}_2\text{S}_3$): C, 63.63; H, 8.50; Br, 15.68; N, 2.75; S, 9.44. Found: C, 63.85; H, 8.42; N, 2.81; S, 9.69.

4,7-Bis(5-bromo-4-dodecylthiophen-2-yl)-5-fluoro-2,1,3-benzothiadiazole (3-2). The compound (3-2) was synthesized by following similar procedure of compound (3-1). MALDI TOF: 1036.5. ^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, 2 H), 7.58 (d, 1 H), 2.55 (t, 4 H), 1.73 (s, 2 H), 1.4-1.1 (br, 60 H), 0.86 (m, 12 H) Elemental Anal. Calcd. For ($\text{C}_{54}\text{H}_{85}\text{Br}_2\text{FN}_2\text{S}_3$): C, 62.53; H, 8.26; Br, 15.41; F, 1.83; N, 2.70; S, 9.27. Found: C, 62.85; H, 8.28; N, 2.73; S, 9.36.

4,7-Bis(5-bromo-4-dodecylthiophen-2-yl)-5,6-difluoro-2,1,3-benzothiadiazole (3-3). The compound (3-2) was synthesized by following similar procedure of compound (3-1). MALDI TOF: 1018.4. ^1H NMR (400 MHz, CDCl_3) δ 7.93 (s, 2 H), 2.58 (t, 4 H), 1.74 (s, 2 H), 1.41-1.11 (br, 60 H), 0.85 (m, 12 H). Elemental Anal. Calcd. For ($\text{C}_{54}\text{H}_{84}\text{Br}_2\text{F}_2\text{N}_2\text{S}_3$): C, 61.46; H, 8.02; Br, 15.14; F, 3.60; N, 2.65; S, 9.11. Found: C, 61.66; H, 7.99; N, 2.66; S, 9.16.

2,6-Bis(tri-methylstannyl)-dithieno[3,2-b:2',3'-d]thiophene (5). 100 ml two neck round bottom flask was prepared with 2,6-dibromodithieno[3,2-b:2',3'-d]thiophene (4) (1.0 g, 2.8 mmol) and purged with nitrogen. Distilled THF (40 ml) was added to the flask and cooled to $-80\text{ }^\circ\text{C}$. After 1 hour, a solution of n-BuLi in hexane (4.2 ml, 6.72 mol, 1.6 M) was added dropwise. The white solid was precipitated and stirred at $-80\text{ }^\circ\text{C}$ for 1 hour and at room temperature for 1 hour. The mixture was cooled again to $-40\text{ }^\circ\text{C}$ and trimethyltin chloride (8.4 ml, 1 M in THF) was added in one portion. The mixture was stirred at $-40\text{ }^\circ\text{C}$ for 1 hour, then let it warm to room

temperature. After the mixture was warmed to room temperature, the mixture was quenched with the water and stirred for 30 min and removing THF. The mixture was washed with water (2×100 ml), extracted with hexane (2×100 ml), and dried over MgSO_4 . After removing solvent, to the residue was recrystallized using acetonitrile. GC/MS: m/z (M^+) = 522, ^1H NMR (400 MHz, CDCl_3) δ 7.28 (s, 2H), 0.38 (t, 18 H), Elemental Anal. Calcd. For ($\text{C}_{14}\text{H}_{20}\text{S}_3\text{Sn}_2$): C, 32.22; H, 3.86; S, 18.43. Found: C, 32.38; H, 3.88; S, 18.36.

Reference

1. J. Frey, S. Proemmel, M. A. Armitage, A. B. Homes, *Org. Synth.*, 2006, **11**, 843-849.
2. T.-H. Kwon, V. Armel, A. Nattestad, D. R. MacFarlane, U. Bach, S. J. Lind, K. C. Gordon, W. Tang, D. J. Jones, A. B. Homes, *J. Org. Chem.*, 2011, **76**, 4088-4093.
3. Y. Zhang, S.-C. Chien, K.-S. Chen, H.-L. Yip, Y. Sun, J. A. Davies, F.-C. Chenb, A. K.-Y. Jen, *Chem. Commun.*, 2011, **47**, 11026-11028.

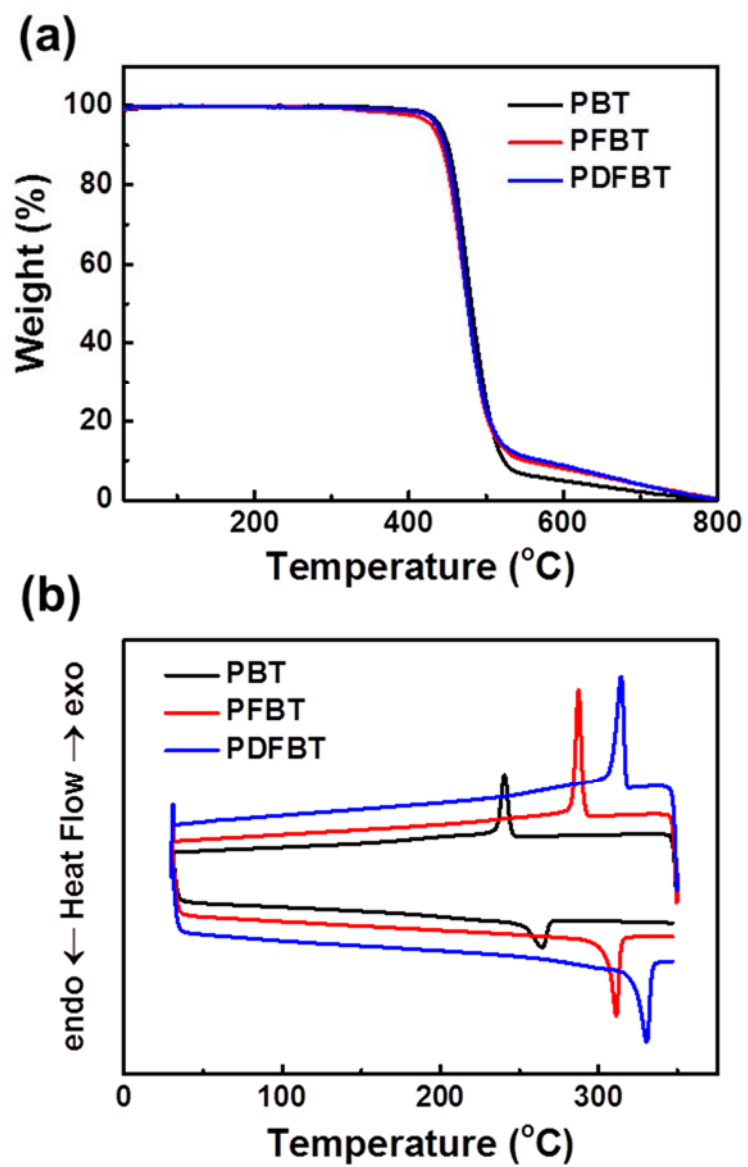


Figure S1. (a) Thermogravimetric analysis (TGA) and (b) differential scanning calorimetry (DSC) thermograms of PBT, PFBT and PDFBT.

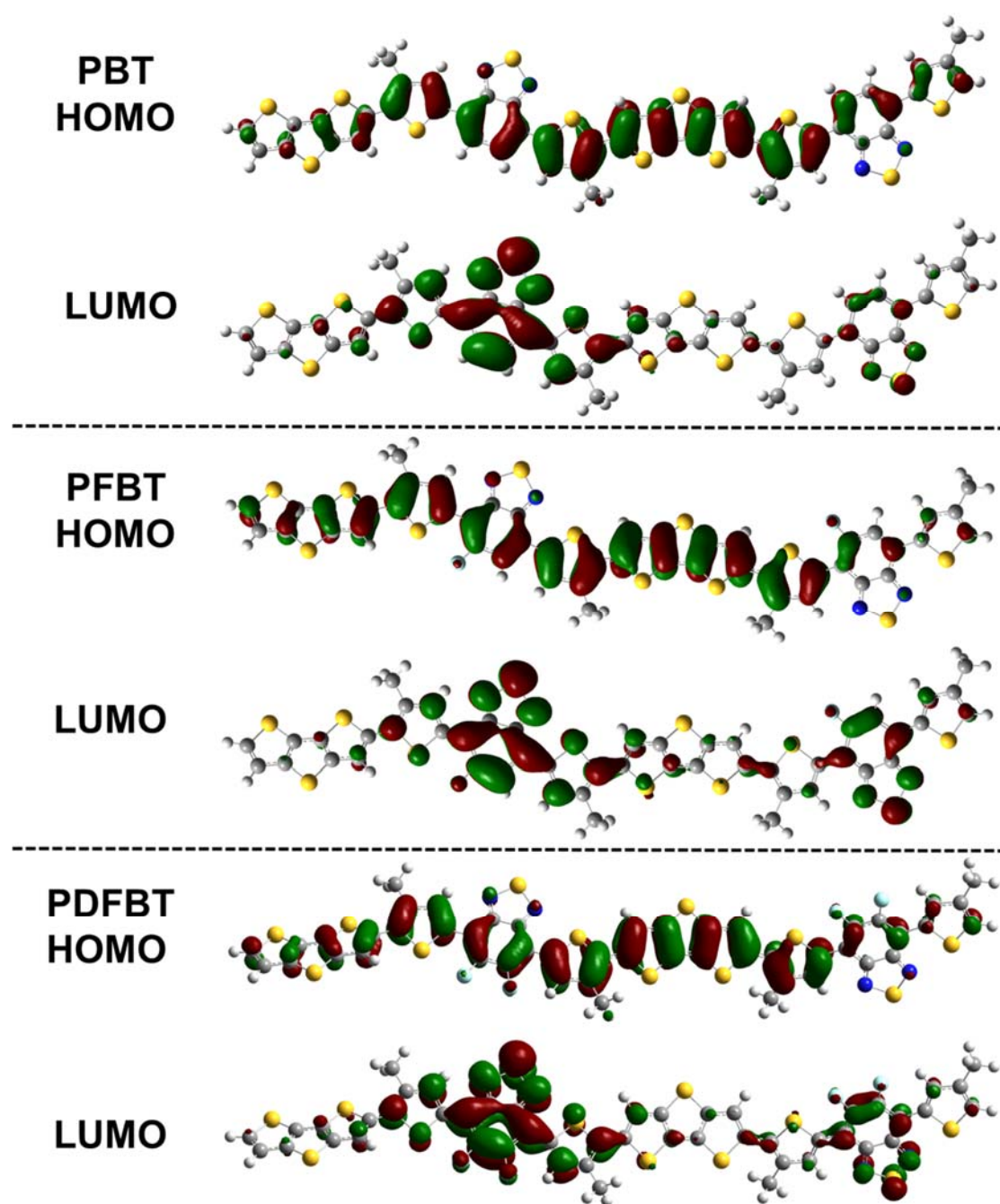


Figure S2. Electronic structure of polymers simulated by Density Functional Theory (DFT).

Table S1. Torsion angles and energy level of dimers for PBT, PFBT and PDFBT calculated by DFT.

Polymer	θ_1 (Deg)	θ_2 (Deg)	Bond length (pm)	Δ Length (pm) ^a	HOMO (eV)	LUMO (eV)
PBT	32	6.4	145.87	-	-5.04	-2.99
PFBT	31	0.6	145.71	-0.16	-5.07	-3.06
PDFBT	30	1.6	145.68	-0.19	-5.15	-3.10

^a Δ Length was calculated by the difference between the bond length of PBT and that of others.

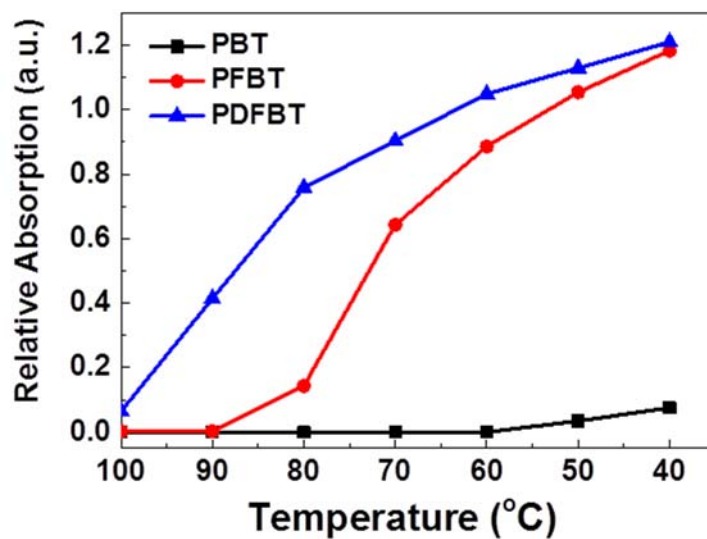


Figure S3. Relative absorption at various solution temperatures of PBT, PFBT and PDFBT. Relative absorption means the relative intensity of the absorption peak at 700 nm with a maximum peak at 150 °C.

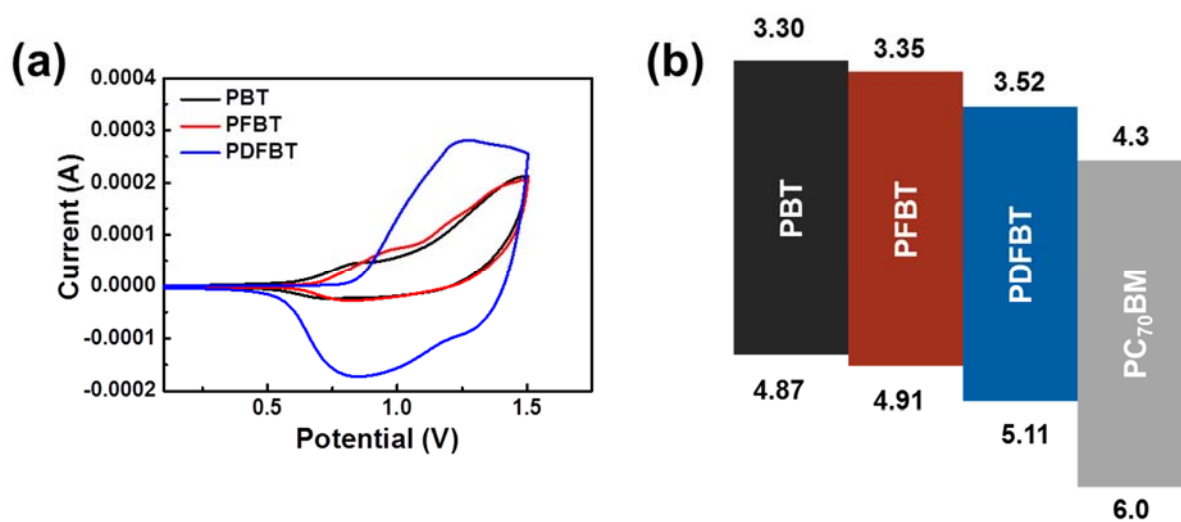


Figure S4. (a) Cyclic voltammogram of PBT, PFBT and PDFBT in Bu₄NClO₄/acetonitrile at a scan rate of 50 mVs⁻¹ and (b) energy band diagram.

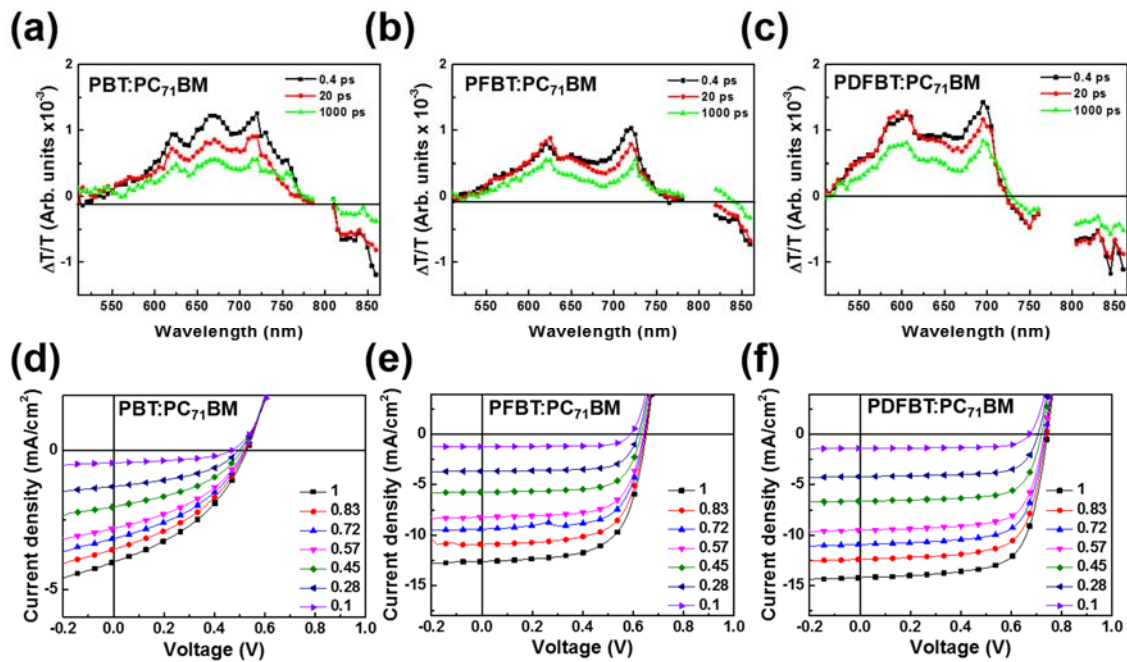


Figure S5. TA spectra of (a) PBT:PC₇₁BM, (b) PFBT:PC₇₁BM and (c) PDFBT:PC₇₁BM films measured at several time delays. J-V characteristics of (d) PBT:PC₇₁BM, (e) PFBT:PC₇₁BM and (f) PDFBT:PC₇₁BM solar cells under various incident light intensities.

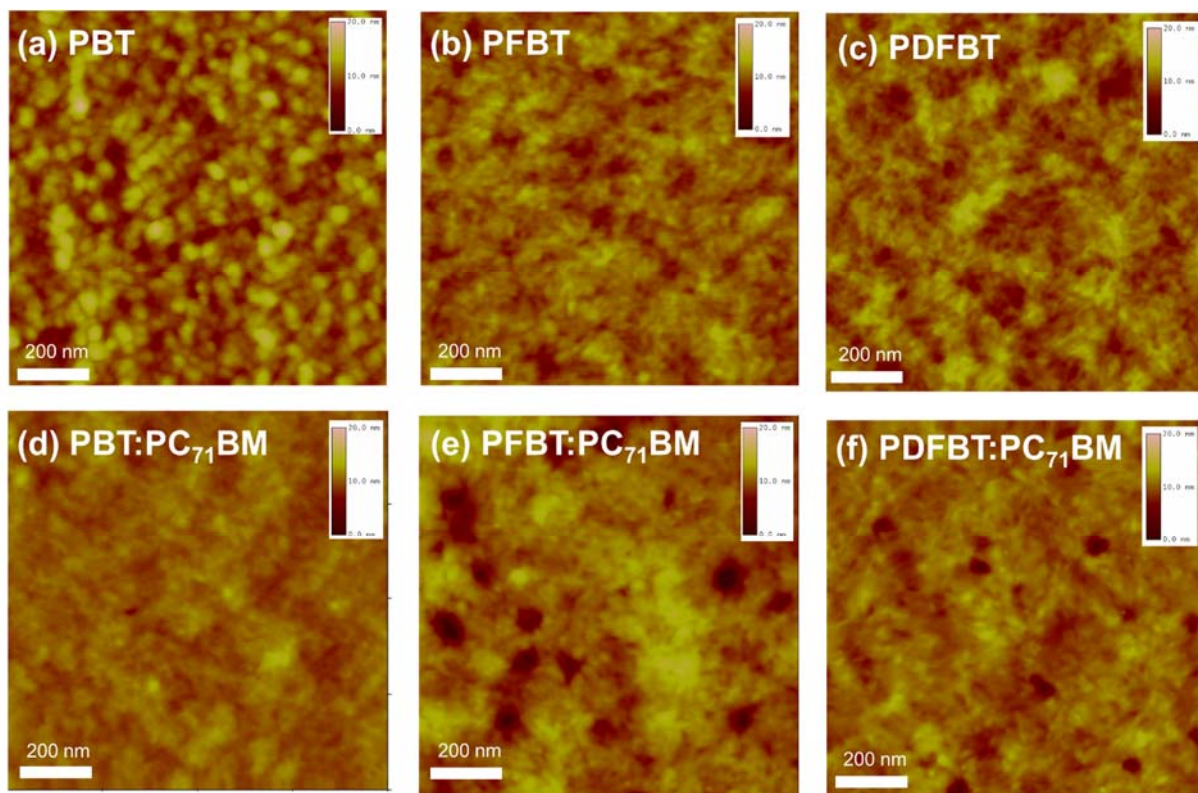


Figure S6. Height images of atomic force microscopy (AFM) for (a) PBT, (b) PFBT, (c) PDFBT, (d) PBT:PC₇₁BM, (e) PFBT:PC₇₁BM and (f) PDFBT:PC₇₁BM, respectively.