Supporting Information

Temperature Modulated Optimization of High-Performance Polymer Solar Cells Based on Benzodithiophene-Difluorodialkylthienyl-benzothiadiazole Copolymers: Aggregation Effect

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Synthetic Procedures

1,2-Di(thiophen-3-yl)ethane-1,2-dione (1). The reaction was carried out by a modified literature procedure.[1] A solution of 3-lithiumthiophene, labelled as solution A, was prepared as follows: 100 mL of 2.5 molar *n*-BuLi (50 mmol) in hexanes was added *via* cannula to 50 mL of anhydrous THF (4.7 mL of 3-bromothiophene (8.2 g, 50 mmol) in THF), previously cooled to -78 °C. The mixture was stirred for 150 min while keeping at -78 °C. Meanwhile, a solution, labelled as solution B, was prepared as follows: In a 300 mL round-bottom flask (equipped with stir bar and a septum), containing 50 mL of anhydrous THF, was added LiBr (4.3 g, 50 mmol) and CuBr (7.2 g, 50 mmol). The CuBr and LiBr mixture was stirred until all the salts dissolved, then this mixture was cooled to -40 °C or lower temperature. Solution C: 1.9 mL of oxalyl chloride (2.9 g, 22.5 mmol) was dissolved in 50 mL of anhydrous THF in a 100 mL round bottom flask (previously equipped with a septum) and cooled to -40 °C or lower temperature. Solution A was added *via* cannula to Solution B, and the mixture was strongly stirred for 5 min.; then the Solution C was slowly added *via* cannula. The mixture was kept in the cold bath for 2 h, allowed to warm up to room temperature, and quenched with 20 mL of saturated NH_4Cl (aq). THF was removed by rotary evaporation. Then, 80 mL of ethyl acetate was added to the resulting mixture, which was then transferred to a separation funnel and washed with saturated NH_4Cl solution, water, and brine. The crude product was then loaded on silica gel chromatography and eluted by hexane:EA. A pale-yellow solid was isolated in 4.80 g, 43.2% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.40 (m, 2H), 7.70 – 7.69 (m, 2H), 8.36 – 8.35 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 126.9, 127.5, 137.4, 137.6, 185.8. HRMS (MALDI-TOF) m/z Calcd for $C_{10}H_6O_2S_2$ $[M]^+$ 221.9814, found 221.2656 $[M]^+$.

Benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-dione (2). 2.2 g of **1** was dissolved in 100 mL DCM. The mixture was vigorously stirred and then $FeCl_3$ (4.9 g, 40 mmol) was added in one portion. The mixture was continuously stirred for another 2 hours until no starting materials could be observed on TLC. Water was added to quench the reaction and the two-phase mixture was transferred into a separation funnel and washed with water and brine. Organic phase was collected as a dark purple solution and evaporated into dryness. The resulting solid was then mixed with silica gel and loaded on a short chromatography. hexane:DCM was used as eluent to wash out the product, which was recovered as dark-purple powder, affording 2.04 g, 92% yield of product. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (d, 2H, J = 5.2 Hz), 7.51 (d, 2H, J = 4.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.1, 127.8, 137.6, 137.8, 186.0. HRMS (MALDI-TOF) *m/z* Calcd for $C_{10}H_4O_2S_2$ $[M+1]^+$ 220.9725, found 220.9745 $[M+1]^+$.

Benzo[1,2-*b*:6,5-*b*']dithiophene-4,5-diyl diacetate (3). To a 500-mL round bottom flask equipped with a stir bar was added **2** (1.8 g, 8.3 mmol), zinc powder (5.4 g, 82.7 mmol) and 50 mL of dichloromethane.

Acetic anhydride (7.8 mL, 82.7 mmol) and triethylamine (17.3 mL, 12.4 mmol) were added quickly. The mixture was stirred overnight at room temperature. The solution was filtered through celite, and then extracted successively with water, 1 M HCl solution, water, $NaHCO_3$ saturated and water. The organic phase was dried over anhydrous magnesium sulfate and the solution was concentrated under vacuum affording 2.19 g (86.6%) of a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 6H), 7.29 (d, J = 5.2 Hz, 2H), 7.44 (d, 2H, J = 5.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.77, 121.42, 126.16, 132.02, 132.27, 134.54, 168.44. HRMS (MALDI-TOF) *m/z* Calcd for $C_{14}H_{10}O_4S_2$ $[M]^+$ 306.0015, found 306.0121 $[M]^+$.

4,5-*Bis*(ethylhexyl)benzo[1,2-*b*:6,5-*b*']dithiophene (4). To a 10-mL round bottom flask equipped with a stir bar was added $BDT(OAc)_2$ (463 mg, 1.37 mmol), cesium carbonate (2.4 g, 6.8 mmol), 2-ethylhexyl bromide (1.2 mL, 6.8 mmol) and 50 mL of acetonitrile. The mixture was refluxed for 3 days. After cooling to room temperature, acetonitrile was evaporated and the resulting paste was dilute in dichloromethane and extracted successively with a solution of 1 M HCl, brine (× 2 times) and dried with anhydrous magnesium sulphate. The solution was concentrated and purified by column chromatography using hexane as the eluent affording 0.53 g (87%) of product as colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88-0.92 (m, 6H), 1.24-1.40 (m, 16H), 1.49-1.57 (m, 4H), 1.80-1.88 (m, 4H), 4.16-4.20 (m, 4H), 7.34 (d, J = 5.2 Hz, 2H), 7.50 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.7, 26.2, 29.3, 29.5, 30.4, 31.8, 74.4, 122.0, 124.1, 129.1, 134.3, 143.4. HRMS (MALDI-TOF) *m/z* Calcd for $C_{14}H_{10}O_4S_2$ $[M]^+$ 446.2308, found 446.2321 $[M]^+$.

(4,5-*Bis*((2-ethylhexyl)oxy)benzo[1,2-*b*:6,5-*b*']dithiophene-2,7-diyl)-*bis*(tributylstannane) (5). To a 100 mL two-neck round bottom flask was added **4** (357 mg, 0.8 mmol) and dry THF (10 mL). After deoxygenated with nitrogen three times, the solution was cooled to -78 °C and 1.6 M of *n*-BuLi (1.3 mL, 2.0 mmol) was added dropwise. The resulting white suspension was stirred at -78 °C for 1 h and *tri*-*n*-butyltin chloride (651 mg, 2.0 mmol) was added in one portion. Upon complete addition, the mixture was stirred at -78 °C for 10 min, and then warmed to room temperature and stirred for 3 h. The reaction mixture was poured into ethyl acetate (100 mL), washed with H_2O (2 × 30 mL), brine (2 × 30 mL), and dried over anhydrous Na_2SO_4. After solvent removal, the residue was added 5 mL of triethylamine and stirred at room temperature for 2 h. After evaporating triethylamine, the residue was purified by silica gel column chromatography using hexane as the eluent affording the desired product as colourless liquid (772 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89-0.93 (m, 24H), 0.96-1.00 (m, 6H), 1.09-1.18 (m, 12H), 1.33-1.37 (m, 22H), 1.58-1.63 (m, 18H), 1.77-1.83 (m, 2H), 4.05-4.07 (m, 4H), 7.53 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.9, 11.2, 14.2, 15.6, 23.2, 23.8, 27.8, 29.2, 29.3, 30.6, 40.5, 77.20, 129.8, 133.6, 134.8, 137.3, 142.8. HRMS (MALDI-TOF) *m/z* Calcd for $C_{50}H_{90}O_2S_2Sn_2$ 1024.4430, found 1024.4478 $[M+H]^+$.

3-(2-Ethylhexyl)thiophene (6). To magnesium turnings (7.7 g, 320 mmol) in diethyl ether (100 mL) was added 2-ethylhexyl bromide dropwise (28.5 mL, 160 mmol). After complete addition, the mixture was refluxed for 3 h and then transferred to a solution of 3-bromothiophene (13.0 g, 80 mmol) and Ni(dppp)Cl_2 (150 mg) at 0 ºC. The solution mixture was refluxed overnight under N_2. The reaction mixture was poured into ice water and extracted with diethyl ether. The combined organic extract was washed with brine, water and then dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography using petroleum ether as eluent affording the desired product as colourless liquid (15.8 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85-0.89 (m, 6H), 1.25-1.30 (m, 8H), 1.52-1.59 (m, H), 2.56 (d, *J* = 6.8 Hz, 2H), 6.89-6.91 (m, 2H), 7.22-7.24 (dd, *J* = 2.8 Hz, 4.8 Hz, H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.8, 14.1, 23.0, 25.6, 28.9, 32.5, 40.4, 120.6, 124.8, 128.8, 141.9.

Synthesis of **7** to **9** followed the same procedure of **6** with high yield.

3-Dodecylthiophene (7): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.20 (m, 1H), 6.97-6.89 (m, 2H), 2.67-2.58 (m, 2H), 1.61 (dd, *J* = 14.9, 7.4 Hz, 2H), 1.29 (d, *J* = 18.0 Hz, 18H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.54, 128.56, 125.29, 120.01, 32.23, 30.87, 30.58, 30.08, 23.00, 14.44.

3-Tetradecylthiophene (8): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.19 (m, 1H), 6.95 – 6.90 (m, 2H), 2.64 – 2.57 (m, 2H), 1.63 – 1.57 (m, 2H), 1.26 (s, 22H), 0.88 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.56, 128.57, 125.30, 120.02, 32.23, 30.86, 30.58, 30.14, 22.99, 14.42.

3-Hexadecylthiophene (9): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.20 (m, 1H), 6.97-6.88 (m, 2H), 2.66-2.57 (m, 2H), 1.61 (dt, *J* = 14.9, 7.4 Hz, 2H), 1.25 (s, 26H), 0.87 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.55, 128.56, 125.29, 120.01, 32.23, 30.87, 30.58, 30.11, 23.01, 14.44.

***Tri*-butyl(4-decyl)thiophen-2-yl)stannane (10)**. To a solution of **6** (3.0 g, 15.3 mmol) in anhydrous 100 mL THF was dropwise added 2.4 M *n*-BuLi in hexane (7 mL, 16.8 mmol) at -78 ºC under N_2 protection. After deprotonation by *n*-BuLi, tributyltin chloride (5.2 mL, 18.3 mmol) was added in one portion, and the mixture was stirred at room temperature overnight. The resulting mixture was poured into water, extracted with EA.

The combined organic phase was washed with water, brine, and dried over anhydrous Na_2SO_4. Solvent was evaporated to dryness and the crude product was collected as colourless oil (7.1 g, 95%), which was used in next step without further purification.

Other alkyl substituted stannane (**11** to **13**) were synthesised following the same procedure as for **10**, which were used directly in the next step without further purification.

5,6-Difluoro-4,7-bis(4-decylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (14): To a round bottom flask was added 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (1 g, 3.21 mmol), 3-8 (5.88 g, 12.12 mmol), $Pd(PPh_3)_4$ (100 mg), and toluene (100 mL). The reaction mixture was heated to 140 ^oC under N_2 protection overnight. Aqueous HCl solution was added to quench excessive stannane, and the resulting mixture was extracted with $CHCl_3$. The combined organic phase was washed with water, brine and dried over anhydrous Na_2SO_4. The crude product was dissolved in hot acetone and cooled to room temperature to afford the title compound as an orange powder (1.19 g, 70%) and it was used directly in next step without further purification. ^1H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, 2H), 7.20 (d, 2H), 2.71 (t, 4H), 1.70-1.68 (m, 4H), 1.39-1.27 (m, 28H), 0.88 (t, 6H).

15 to **17** were synthesised following the same procedure as synthesis **14**.[2]

4,7-*Bis*(5-bromo-4-decylthiophen-2-yl)-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (18): To a solution of **14** (1.2 g, 2.1 mmol) in $CHCl_3$/AcOH (100 mL, blend ratio 1:1) was added NBS (831 mg, 4.7 mmol) at room temperature. The reaction was stirred overnight and quenched with water. The organic phase was extracted with $CHCl_3$, washed with water, brine and dried over anhydrous Na_2SO_4. Solvent was evaporated to dryness affording orange solid. The orange crude product was washed with cold acetone and recrystallized from hexane, affording the tittle compound as orange powder (1.37 g, 90%). 1H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 2H), 2.66 (t, 4H), 1.68-1.65 (m, 4H), 1.36-1.27 (m, 28H), 0.88 (t, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.84, 148.73, 142.63, 131.77, 131.22, 114.45, 111.04, 31.91, 29.76, 29.63, 29.60, 29.55, 29.43, 29.35, 29.26, 22.70, 14.13. HRMS (MALDI-TOF) *m/z* for Calcd $C_{34}H_{44}Br_2F_2N_2S_3$ $[M]^+$ 774.0977, found 774.0941 $[M]^+$.

Compounds **19** to **21** were synthesised following the same procedure as for **14**, which were carefully purified by recrystallization from hexane and was prepared for Stille polycondensation.

4,7-*Bis*(5-bromo-4-dodecylthiophen-2-yl)-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (19): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 2H), 2.68 – 2.60 (m, 4H), 1.65 (dd, *J* = 14.7, 7.2 Hz, 4H), 1.29 (d, *J* = 28.7 Hz, 37H), 0.87 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.04, 148.40, 142.62, 131.72, 131.23, 114.48, 111.49, 31.93, 29.75, 29.69, 29.67, 29.66, 29.60, 29.55, 29.49, 29.43, 29.37, 29.26, 22.70, 14.13. HRMS (MALDI-TOF) *m/z* for Calcd $C_{38}H_{52}Br_2F_2N_2S_3$ $[M]^+$ 830.1604, found 830.1622 $[M]^+$.

4,7-*Bis*(5-bromo-4-tetradecylthiophen-2-yl)-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (20): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 2H), 2.66 (t, *J* = 7.6 Hz, 4H), 1.88 – 1.65 (m, 4H), 1.31 (d, *J* = 43.2 Hz, 44H), 0.87 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.02, 148.20, 142.51, 131.69, 131.22, 114.45, 111.05, 31.96, 29.79, 29.72, 29.69, 29.62, 29.58, 29.45, 29.40, 29.26, 22.73, 14.17. HRMS (MALDI-TOF) *m/z* for Calcd $C_{42}H_{60}Br_2F_2N_2S_3$ $[M]^+$ 886.2231, found 886.2245 $[M]^+$.

4,7-*Bis*(5-bromo-4-hexadecylthiophen-2-yl)-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (21): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 2H), 2.68 – 2.61 (m, 4H), 1.70 – 1.64 (m, 4H), 1.36 (s, 42H), 0.87 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.01, 148.14, 142.34, 131.27, 131.11, 114.42, 111.03, 31.96, 29.74, 29.70, 29.62, 29.51, 29.45, 29.40, 29.26, 22.73, 14.17. HRMS (MALDI-TOF) *m/z* for Calcd $C_{46}H_{68}Br_2F_2N_2S_3$ $[M]^+$ 942.2857, found 942.2815 $[M]^+$.

PffBB-10: (4,5-*Bis*(2-ethylhexyloxy)benzo[2,1-b:3,4-b']dithiophene-2,7-diyl)*bis*(*tri*-butyl-stannane) **(5)** (102.5 mg, 0.1 mmol), 4,7-*bis*(5-bromo-4-decylthiophen-2-yl)-5,6-difluorobenzo[*c*][1,2,5]thiadiazole **(18)** (77.4 mg, 0.1 mmol) and 30 mL of fresh distilled chlorobenzene were weighted in a round bottom flask. After 5 cycles of deoxygenation and refilling with N_2 gas, 10 mg of $Pd(PPh_3)_4$ was added. The flask was then undergone deoxygenation-refilling with N_2 again, and heated up to 140 ^{o}C for three days. After cooling to room temperature, the mixture was poured into cold methanol. Precipitate was collected and transferred for the Soxhlet extraction with a sequential washing with solvent of methanol, hexane and DCM, respectively. High molecular weight polymers were extracted by chloroform and dissolved in minimum volume of chlorobenzene. After precipitated in cold methanol, the polymer was collected by filtration and dried in vacuum for 12 hours, affording the product as a deep dark green solid (35 mg, 24%).

Synthesis of **PfBB-12**, **PffBB-14** and **PffBB-16**: This polymer was synthesised following the same procedure as for **PffBB-10**, desired product was purified by Soxhlet extraction and collected as a black solid (~30%).

Thermal and Electrochemical Properties of PffBB-n Polymers

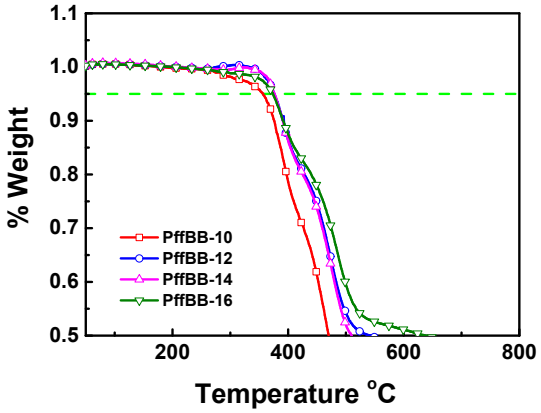

Figure S1. TGA traces of **PffBB-n**

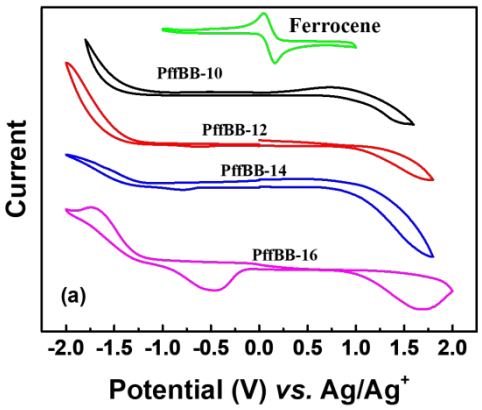

Figure S2. CV traces of **PffBB-n**

Optical Properties of PffBB-n Polymers (Solvent and Temperature Effects)

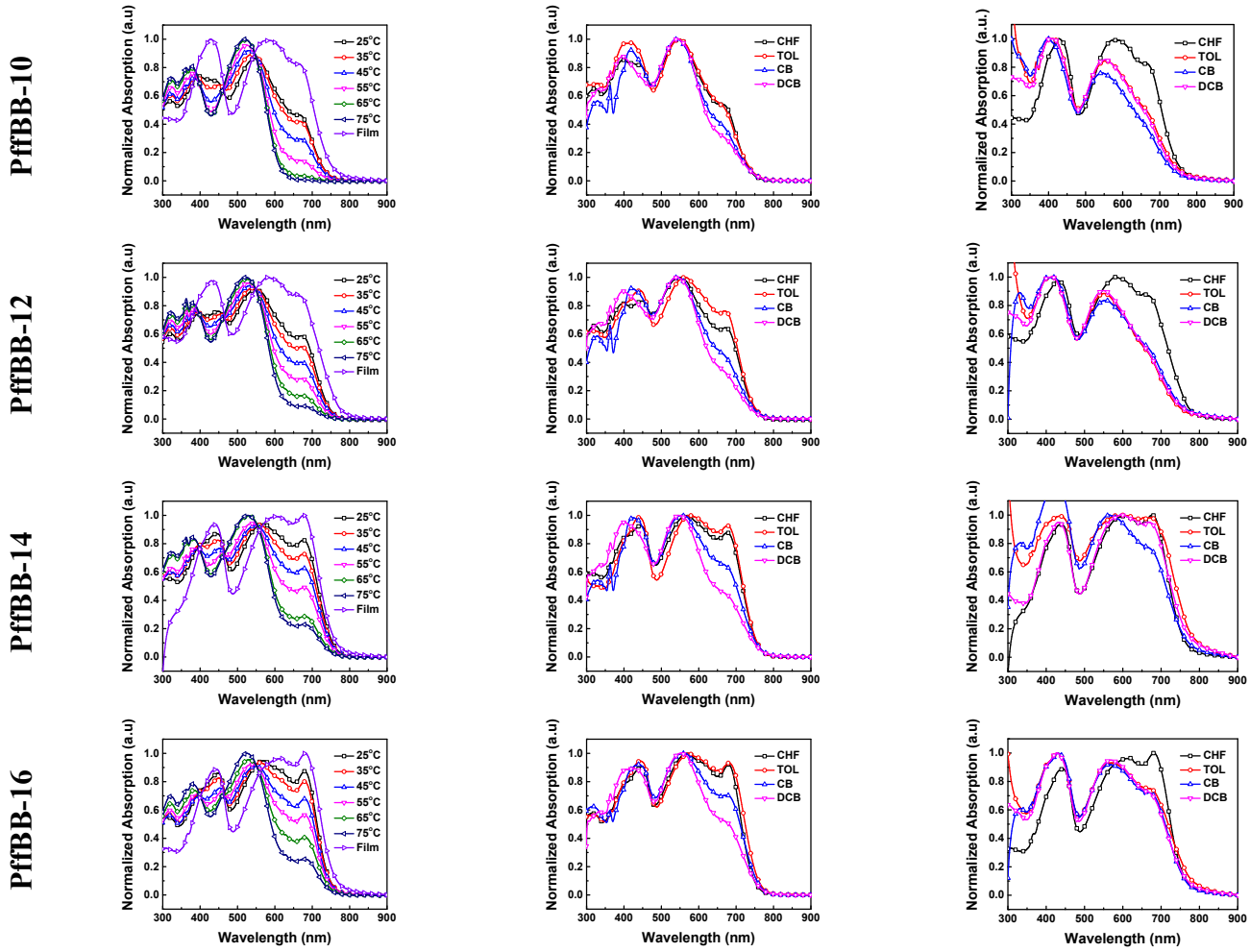

Figure S3. (a) Temperature dependent aggregation of **PffBB-n** polymers in chloroform measured under sealed conditions, (b) Solvent dependent aggregation in different solvents and (c) Film absorption coated from different solvents.

Optical Properties of PffBB-n:$PC_{71}BM$ Blend Active Layers

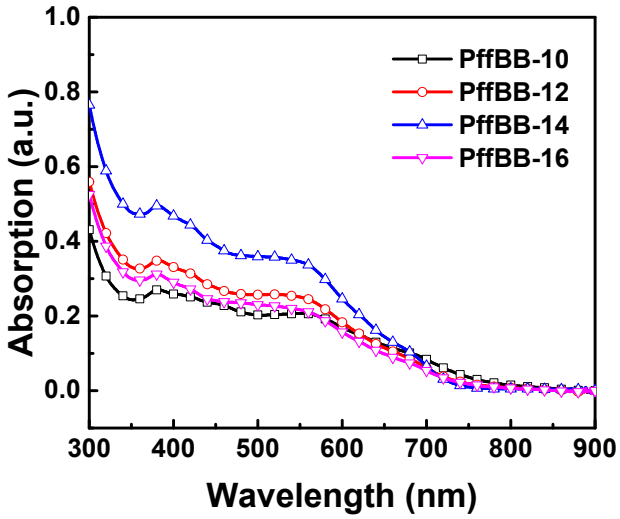

Figure S4. Absorption spectra of **PffBB-n:$PC_{71}BM$** blend active layers fabricated at 80 °C.

Reference

[1] F. A. Arroyave, C. A. Richard, J. R. Reynolds, *Organic letters* **2012**, *14*(24), 6138-6141.

[2] Y. Wang, X. Xin, Y. Lu, T. Xiao, X. Xu, N. Zhao, X. Hu, B. S. Ong, S. C. Ng, *Macromolecules* **2013**, *46*(24), 9587-9592.