ELECTRONIC SUPPLEMENTARY INFORMATION

Effects of fluorination and thermal annealing on charge recombination processes in polymer bulk-heterojunction solar cells

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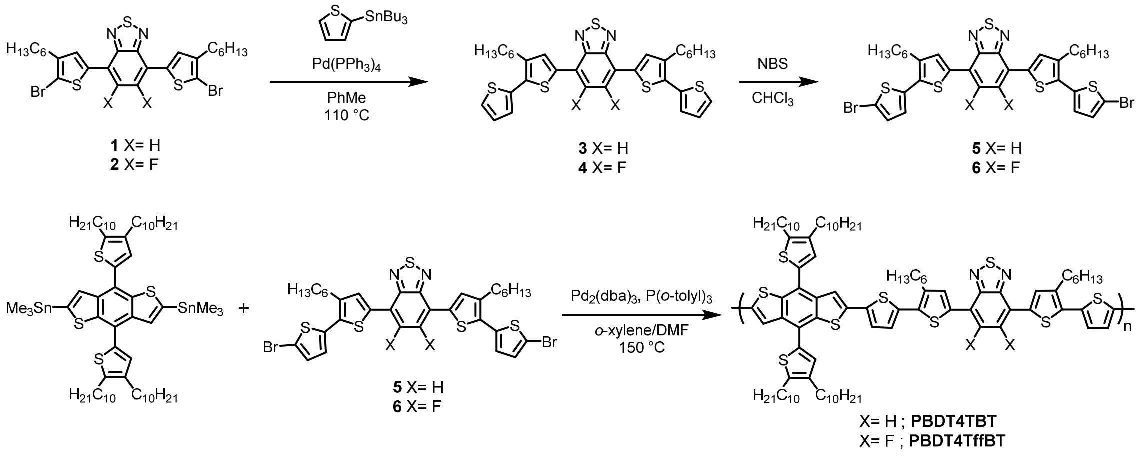
Synthetic procedures



Scheme S1 Synthesis route.

Compounds **1**[1] and **2**[2] were synthesized following previously reported experimental procedures. 2,6-Bis(trimethyltin)-4,8-di(2,3-didecylthiophen-5-yl)-benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) was purchased from SunaTech Inc.

4,7-bis(3-hexyl-[2,2'-bithiophen]-5-yl)benzo[*c*][1,2,5]thiadiazole, 3. A stirred solution of 4,7-bis(5-bromo-4-hexylthiophen-2-yl)benzo[*c*][1,2,5]thiadiazole, **1**, (0.25 g, 0.4 mmol), 2-(tributylstannyl)thiophene (0.51 mL, 1.3 mmol) and $Pd(PPh_3)_4$ (0.046 g, 10 mol %) in anhydrous toluene (20 mL) was degassed with argon at room temperature for 15 minutes. The resulting mixture was refluxed overnight. The crude reaction was allowed to cool to room temperature after which the organic layer was washed with water and brine, dried over anhydrous $MgSO_4$, filtered, and the solvent evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel eluting with dichloromethane:heptane (1:3) and precipitated in methanol to obtain **3** as a pure orange solid (0.24 g, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.83 (s, 2H), 7.35 (dd, *J* = 5.1, 1.1 Hz, 2H), 7.24 (dd, *J* = 3.6, 1.1 Hz, 2H), 7.11 (dd, *J* = 5.1, 3.6 Hz, 2H), 2.87-2.83 (m, 4H), 1.78-1.70 (m, 4H), 1.46-1.42 (m, 4H), 1.36-1.31 (m, 8H), 0.92-0.88 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 152.6, 140.5, 136.9, 136.0, 132.4, 130.6, 127.5, 126.07, 125.6, 125.5, 125.2, 31.7, 30.6, 29.5, 29.3, 22.7, 14.1. MALDI-TOFMS: [M^+] calcd: 632.16, found: 632.16.

5,6-difluoro-4,7-bis(3-hexyl-[2,2'-bithiophen]-5-yl)benzo[*c*][1,2,5]thiadiazole, 4. Compound **4** was synthesized according to the same procedure as described above (0.19 g, 98% yield) but using 4,7-bis(5-bromo-4-hexylthiophen-2-yl)-5,6-difluorobenzo[*c*][1,2,5]thiadiazole, **2**, (0.20 g, 0.3 mmol), 2-(tributylstannyl)thiophene (0.38 mL, 1.2 mmol) and $Pd(PPh_3)_4$ (0.035 g, 10 mol %) in anhydrous toluene (20 mL). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.13 (s, 2H), 7.38 (dd, *J* = 5.1, 1.1

Hz, 2H), 7.27 (dd, *J* = 3.6, 1.1 Hz, 2H), 7.12 (dd, *J* = 5.1, 3.6 Hz, 2H), 2.89-2.85 (m, 4H), 1.77-1.70 (m, 4H), 1.46-1.42 (m, 4H), 1.36-1.31 (m, 8H), 0.92-0.88 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 151.2, 148.9, 148.8, 148.8, 139.9, 135.6, 134.7, 134.6, 134.6, 134.0, 134.0, 129.4, 127.0, 126.4, 126.0, 111.2, 31.7, 30.6, 29.3, 29.3, 22.7, 14.1. ^{19}F NMR (376.3 MHz, $CDCl_3$, δ): -128.13. MALDI-TOFMS: [M^+] calcd: 668.13, found: 668.15.

4,7-bis(5'-bromo-3-hexyl-[2,2'-bithiophen]-5-yl)benzo[*c*][1,2,5]thiadiazole, 5. A solution of **3** (0.10 g, 0.16 mmol) was dissolved in $CHCl_3$ (5 mL) and cooled to 0 °C in the absence of light. NBS (0.062 g, 0.35 mmol) was added in small portions. After the addition was completed, the reaction mixture was stirred at room temperature until the disappearance of the starting material monitored by TLC (~7 hours). The reaction was quenched with water and the organic phase was washed with brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using dichloromethane:heptane (1:5) as eluent. Fractions containing the product were evaporated under reduced pressure and precipitated in methanol to afford **5** as a dark purple solid (0.11 g, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.96 (s, 2H), 7.82 (s, 2H), 7.06 (d, *J* = 3.8 Hz, 2H), 6.98 (d, *J* = 3.9 Hz, 2H), 2.82-2.78 (m, 4H), 1.74-1.68 (m, 4H), 1.45-1.40 (m, 4H), 1.36-1.31 (m, 8H), 0.92-0.89 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 152.5, 141.0, 137.5, 137.4, 131.4, 130.5, 130.3, 126.3, 125.5, 125.3, 112.2, 31.7, 30.6, 29.5, 29.3, 22.6, 14.1. MALDI-TOFMS: [M^+] calcd: 787.97, found: 788.00.

4,7-bis(5'-bromo-3-hexyl-[2,2'-bithiophen]-5-yl)-5,6-difluorobenzo[*c*][1,2,5]thiadiazole, 6. Compound **6** was synthesized according to the same procedure as described above (0.11 g, 92% yield) but using **4**, (0.10 g, 0.15 mmol) and NBS (0.059 g, 0.33 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.11 (s, 2H), 7.07 (d, *J* = 3.9 Hz, 2H), 7.01 (d, *J* = 3.9 Hz, 2H), 2.83-2.79 (m, 4H), 1.75-1.68 (m, 4H), 1.41-1.45 (m, 4H), 1.35-1.31 (m, 8H), 0.92-0.88 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 151.4, 151.2, 148.8, 148.6, 140.4, 137.2, 134.1, 134.0, 133.8, 130.5, 129.9, 126.7, 112.8, 111.4, 111.3, 31.8, 30.8, 29.5, 29.4, 22.8, 14.3. ^{19}F NMR (376.3 MHz, $CDCl_3$, δ): -127.87. MALDI-TOFMS: [M^+] calcd: 823.95, found: 823.99.

General polymerization procedure: BDT (0.081 mmol) and the corresponding dibromo monomer, **5** or **6**, (1 equivalent) were placed under argon atmosphere in a Schlenk tube. The mixture was dissolved in anhydrous *o*-xylene (1.8 mL) and anhydrous dimethylformamide (0.2 mL) and degassed with argon at room temperature for 15 minutes. Subsequently, $Pd_2(dba)_3$ (2 mol %) and $P(o\text{-tolyl})_3$ (16 mol %) were added in one portion and the reaction mixture was further degassed for 15 more minutes. Then, the flask was sealed and the crude was stirred at 115 °C overnight under argon atmosphere. 2-(tributylstannyl)thiophene and 2-bromothiophene were sequentially added and the mixture was stirred for 2 hours after each addition. The crude was diluted with *o*-dichlorobenzene and then water and sodium diethyldithiocarbamate trihydrate were added and the mixture was refluxed for 2 more hours. Afterwards, the mixture was cooled to room temperature and slowly poured into methanol.

The resulting precipitate was filtered into a Soxhlet thimble. The dark solid was subject to sequential Soxhlet extractions under argon atmosphere to remove impurities and oligomeric fractions with acetone, dichloromethane and chloroform until the extraction solvent became colorless. The chloroform fraction of **PBDT4TBT** was evaporated under reduced pressure. In the case of **PBDT4TffBT**, the residue in the thimble was boiled with *o*-dichlorobenzene, filtered while hot and the solvent was evaporated under reduced pressure. The corresponding solids were precipitated in methanol, filtered and dried under vacuum.

Poly{(4,8-di(2,3-didecylthiophen-5-yl)-benzo[1,2-*b*:4,5-*b′*]dithiophen-2,6-diyl)-*alt*-((4,7-di(3-hexyl-(2,2'-bithiophen-5-yl)benzo[*c*][1,2,5]thiadiazole)-5,5’-diyl)}, PBDT4TBT. $CHCl_3$ fraction (91 mg, 98% yield). GPC (*o*-DCB, 140 °C): M_n = 40.1 kg mol^{-1}, M_w = 111.7 kg mol^{-1}, PDI= 2.79.

Poly{(4,8-di(2,3-didecylthiophen-5-yl)-benzo[1,2-*b*:4,5-*b′*]dithiophen-2,6-diyl)-*alt*-((4,7-di(3-hexyl-(2,2'-bithiophen-5-yl)-5,6-difluorobenzo[*c*][1,2,5]thiadiazole)-5,5’-diyl)}, PBDT4TffBT. *o*-DCB fraction (65 mg, 51% yield). GPC (*o*-DCB, 140 °C): M_n = 24.2 kg mol^{-1}, M_w = 48.6 kg mol^{-1}, PDI= 2.01.

NMR spectra

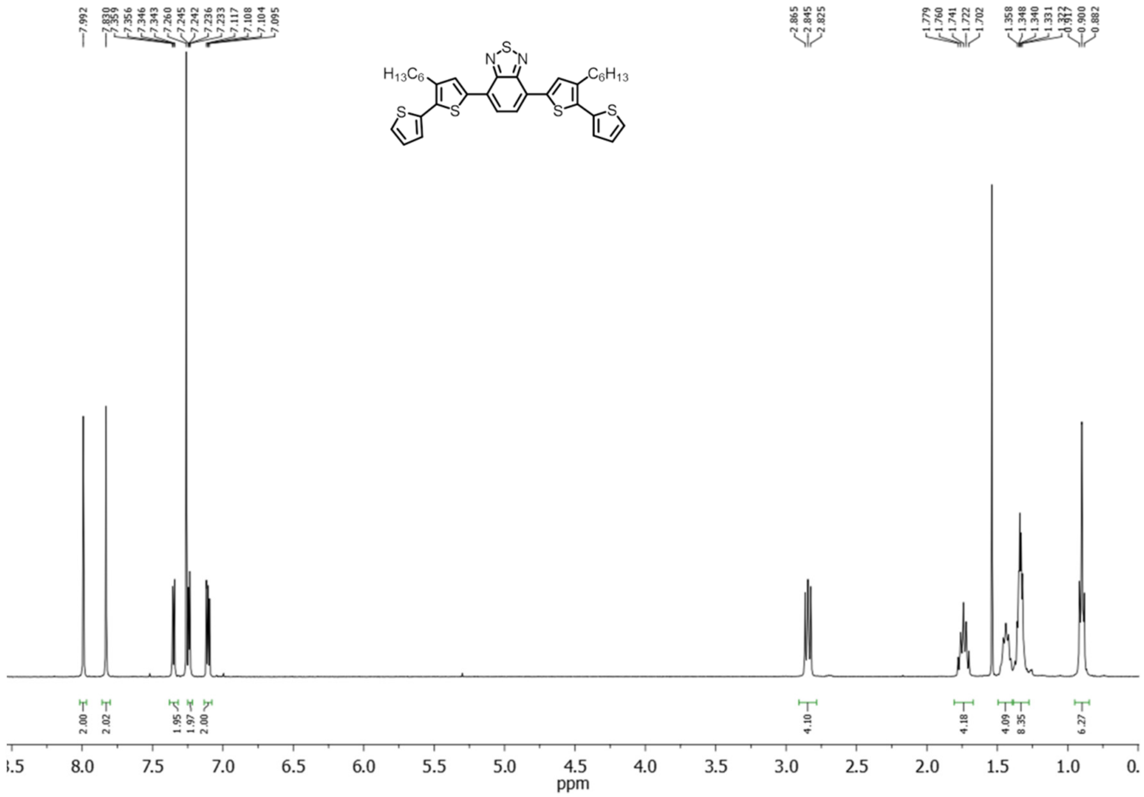


Fig. S1 ^{1}H NMR spectrum of compound **3**.

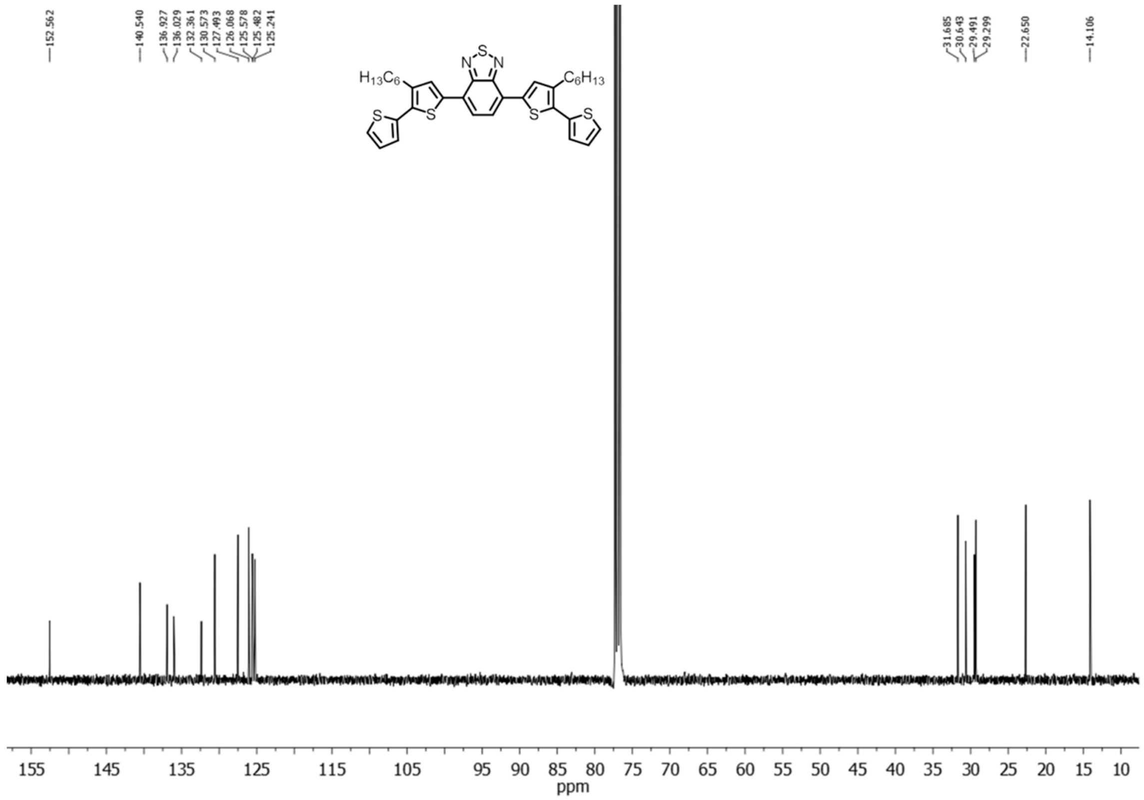


Fig. S2 ^{13}C NMR spectrum of compound **3**.

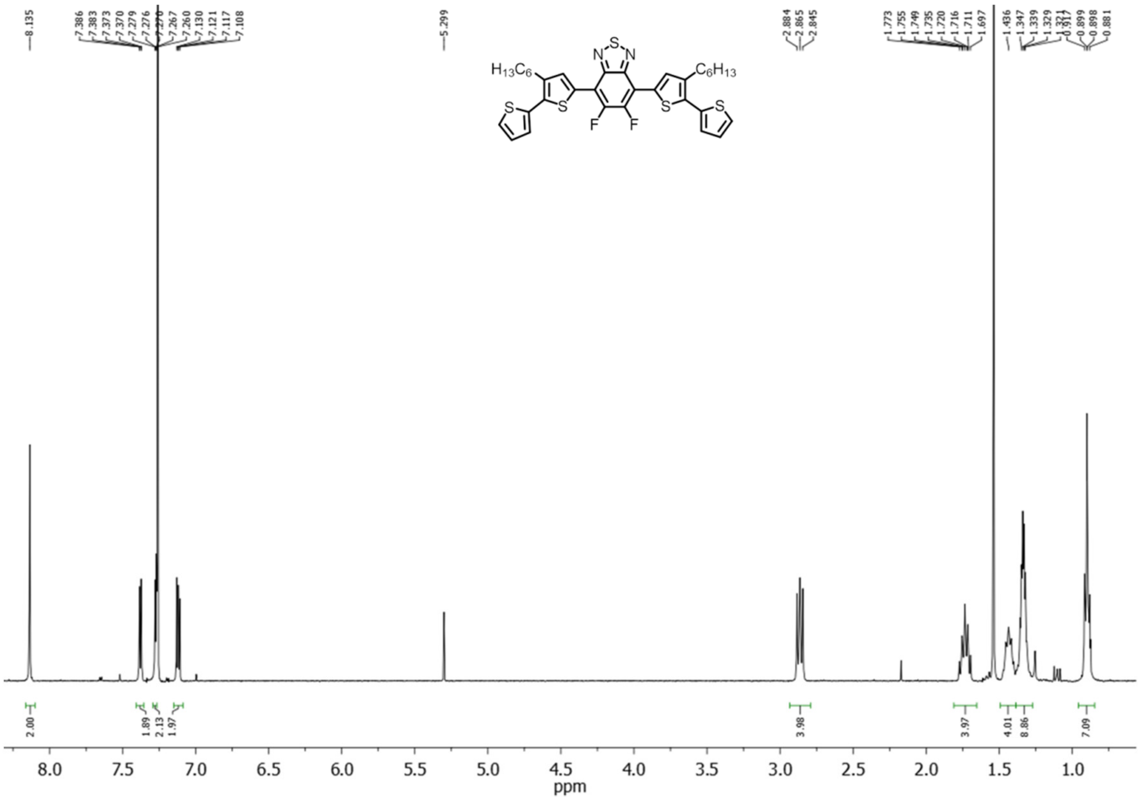


Fig. S3 ^{1}H NMR spectrum of compound **4**.

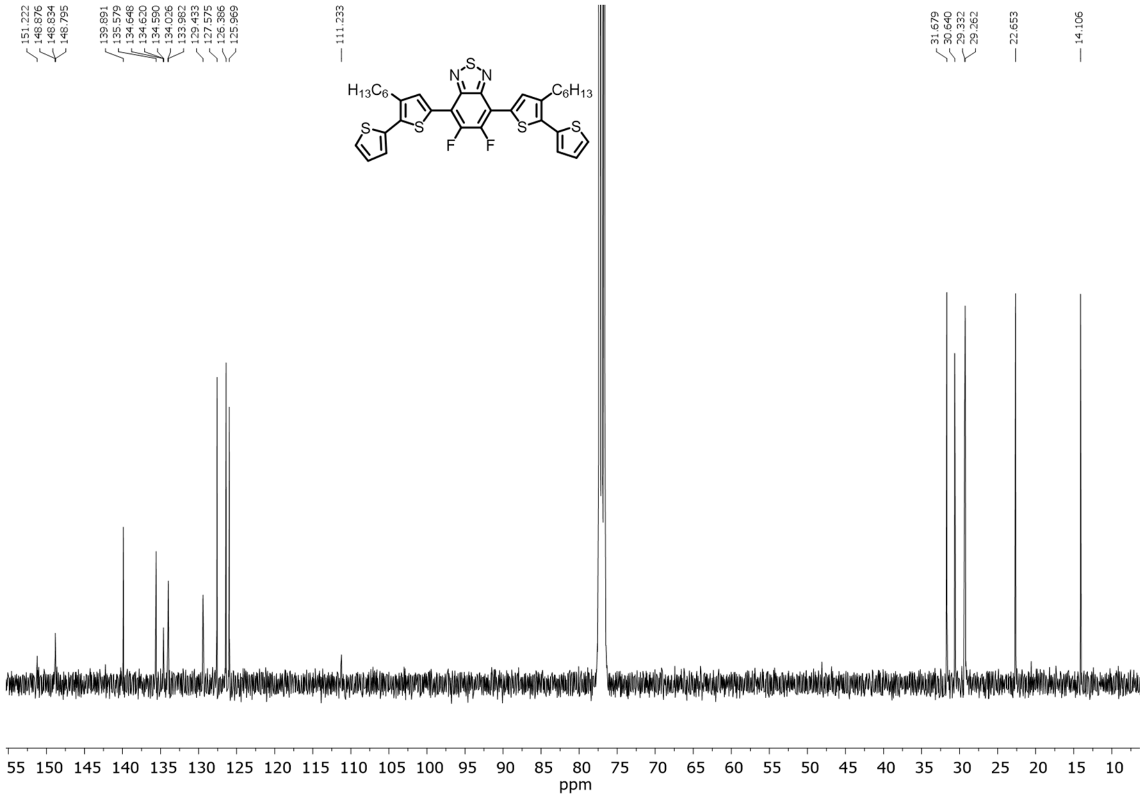


Fig. S4 ^{13}C NMR spectrum of compound **4**.

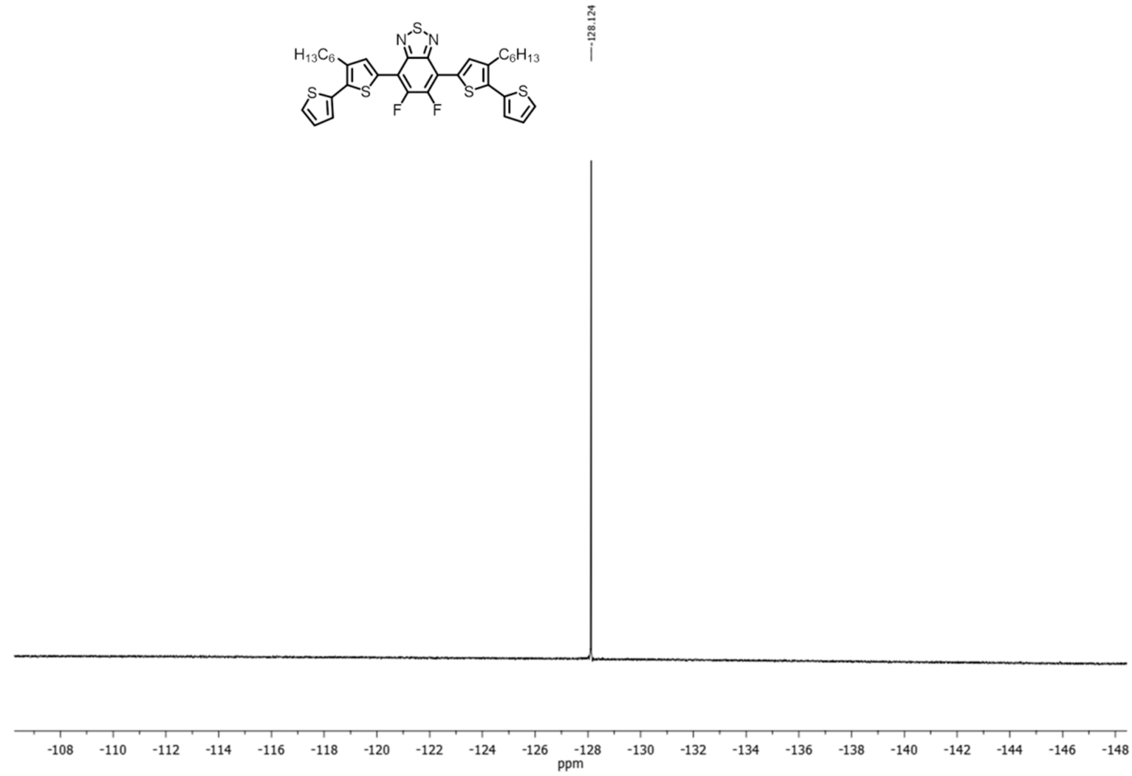


Fig. S5 ^{19}F NMR spectrum of compound **4**.

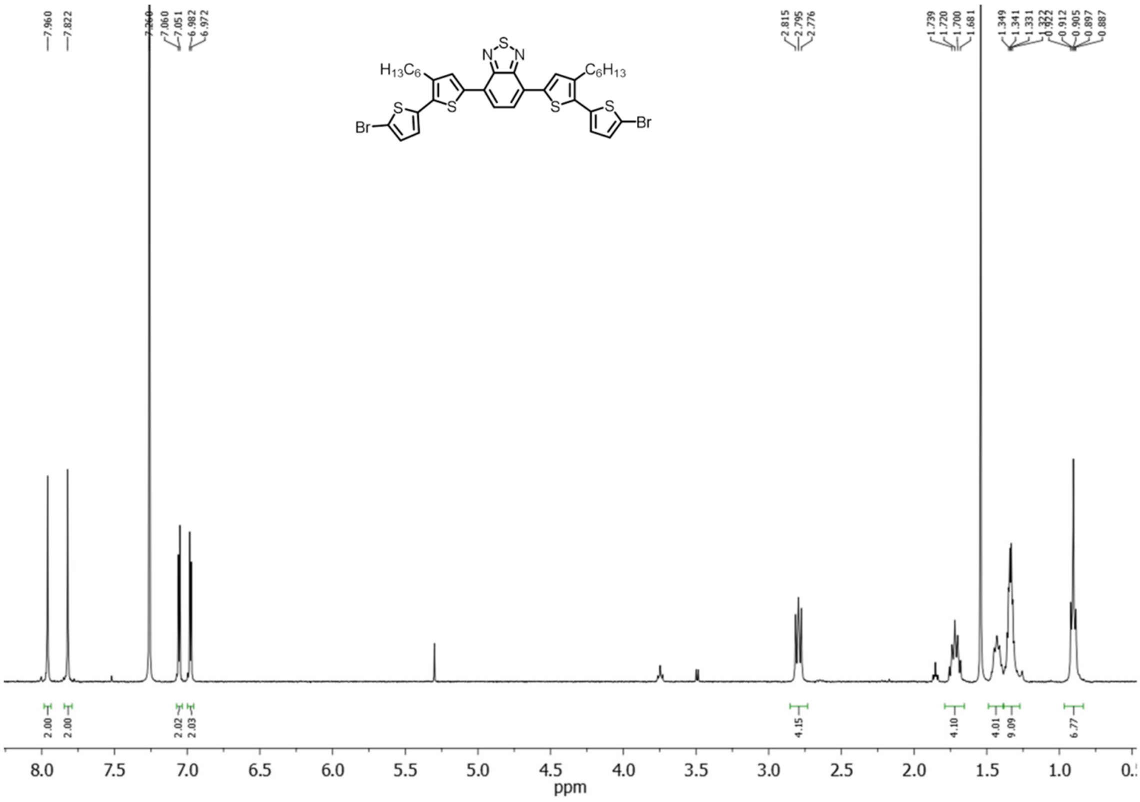


Fig. S6 ^{1}H NMR spectrum of compound **5**.

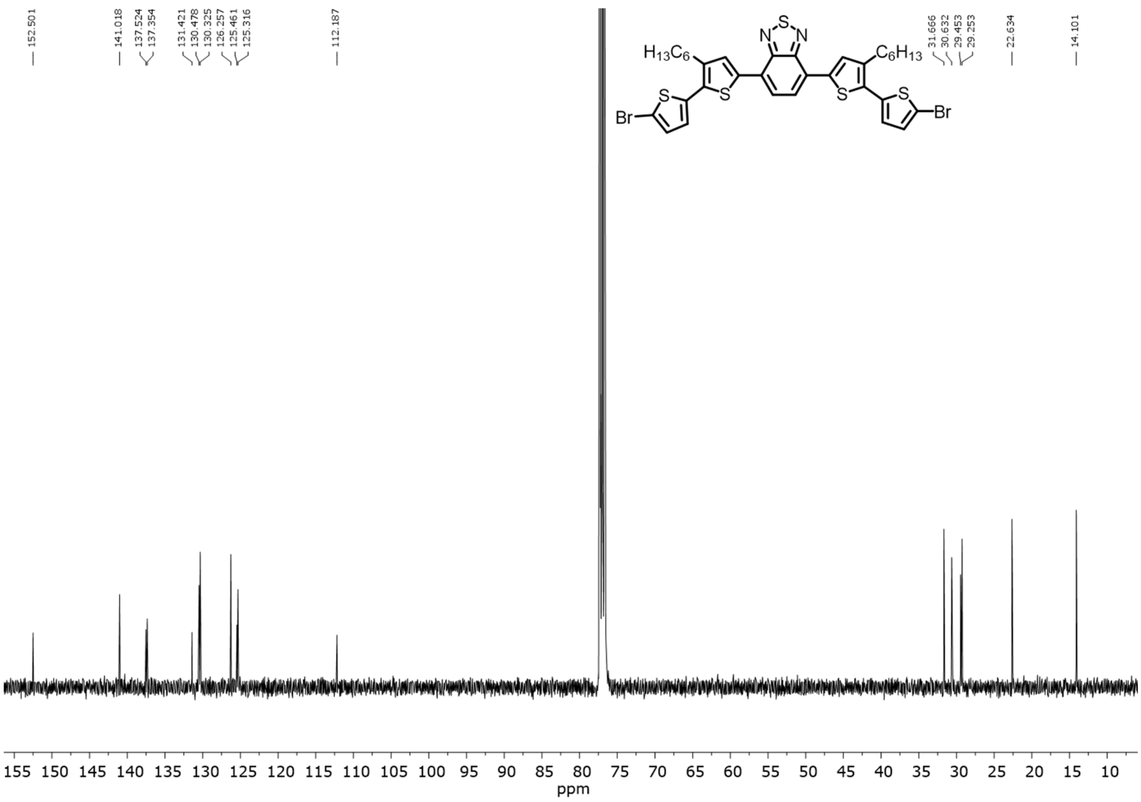


Fig. S7 ^{13}C NMR spectrum of compound **5**.

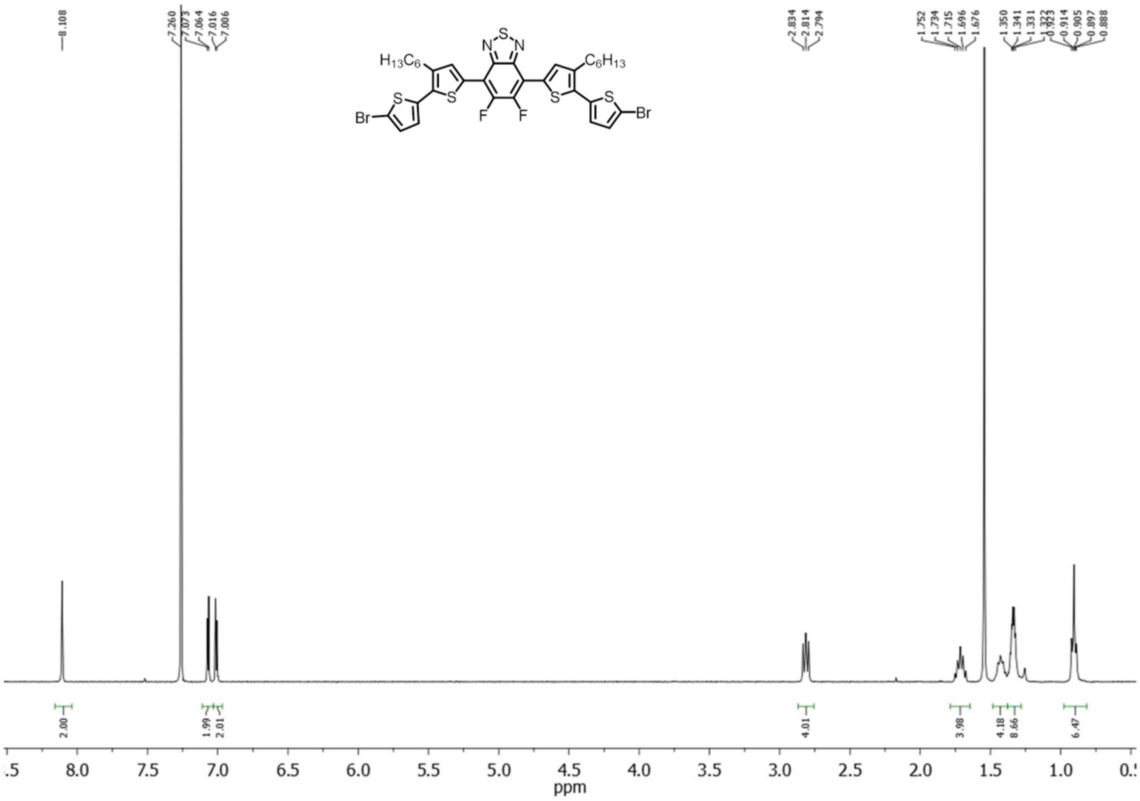


Fig. S8 ^{1}H NMR spectrum of compound **6**.

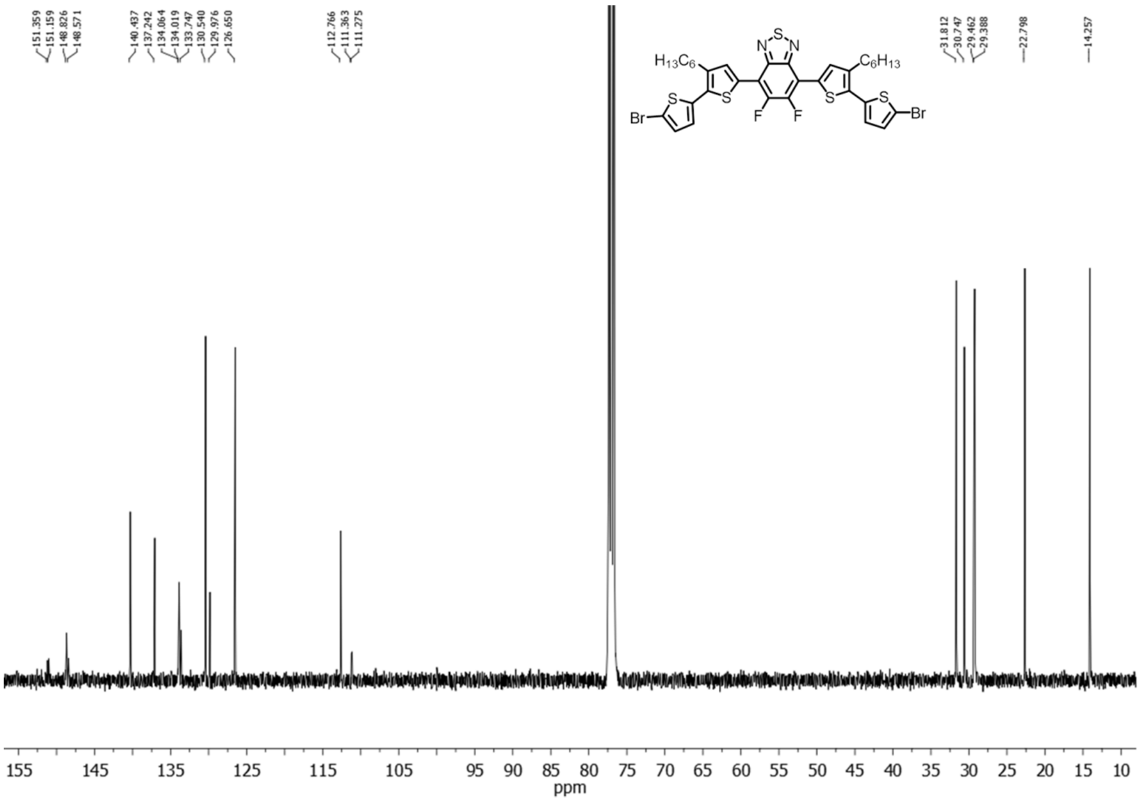


Fig. S9 ^{13}C NMR spectrum of compound **6**.

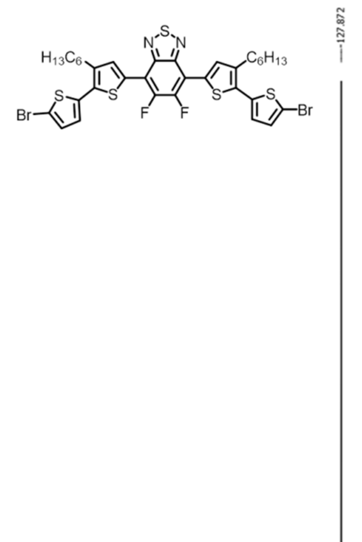


Fig. S10 ^{19}F NMR spectrum of compound **6**.

Thermal characterization

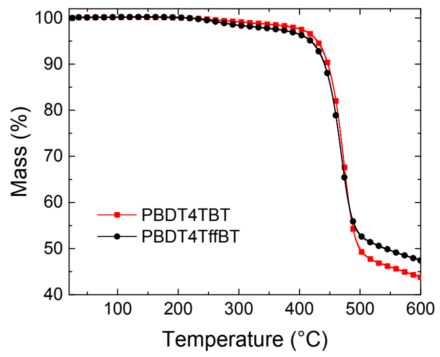


Fig. S11 Thermogravimetric curves. The temperatures corresponding to 5% weight loss are 429 °C for **PBDT4TBT** and 418 °C for **PBDT4TffBT**.

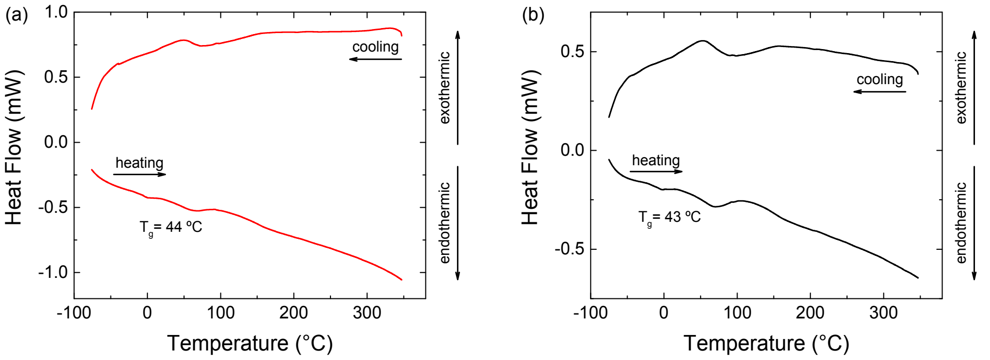


Fig. S12 Differential scanning calorimetry thermograms corresponding to the second heating-cooling cycle for (a) **PBDT4TBT** and (b) **PBDT4TffBT**.

Dark *J-V* characteristics

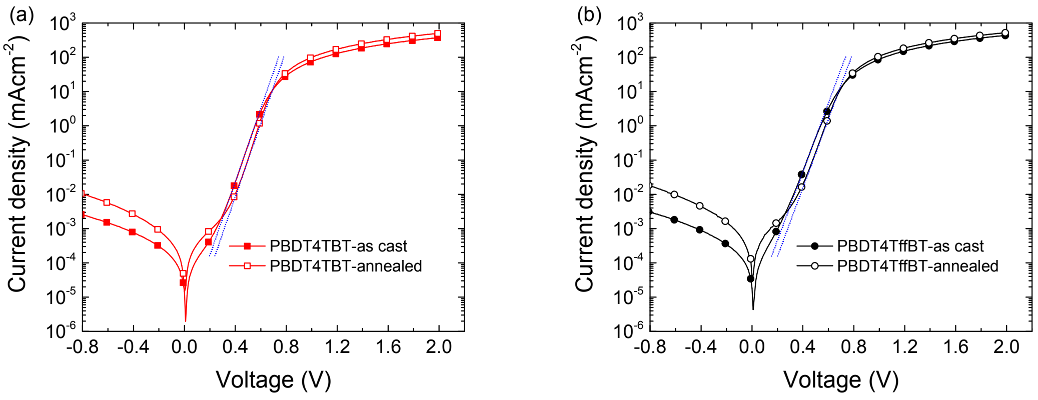


Fig. S13 Dark *J-V* characteristics in semi-logarithmic scale before and after thermal annealing for (a) **PBDT4TBT** and (b) **PBDT4TffBT**. Dashed lines indicate the exponential region.

2D-GIWAXS

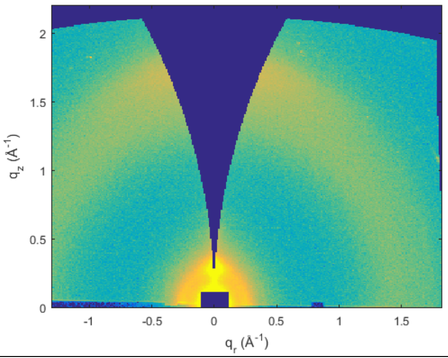
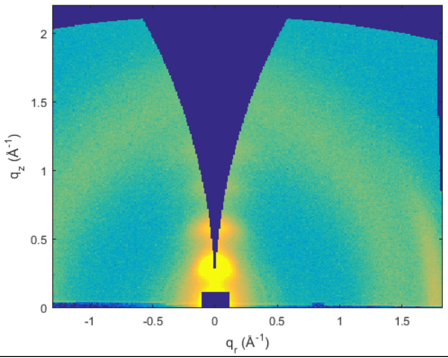
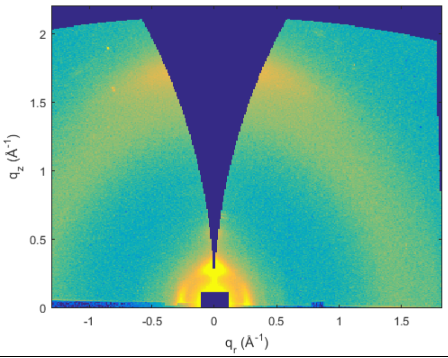
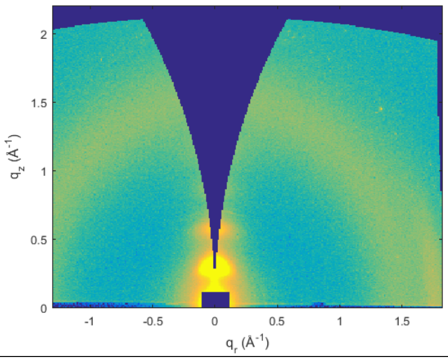
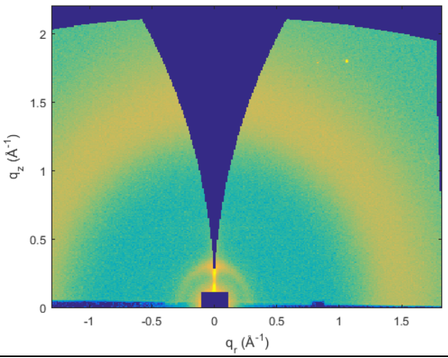
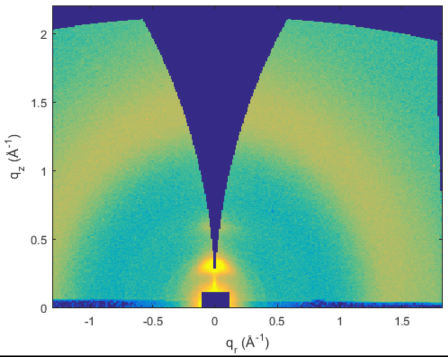
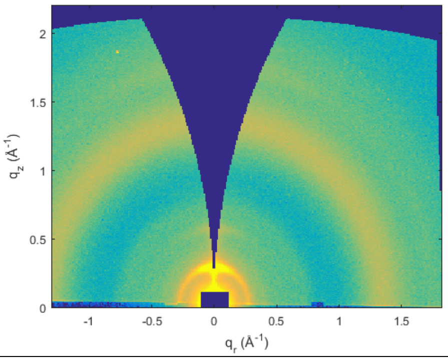
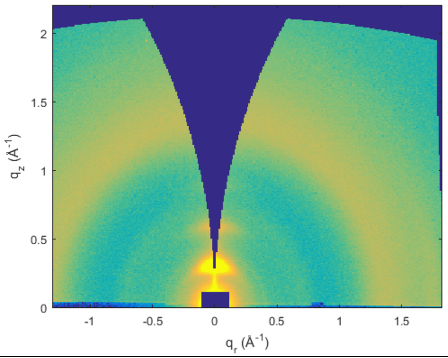
PBDT4TBT	**PBDT4TffBT**
Pristine as cast 	Pristine as cast 
Pristine annealed 	Pristine annealed 
Blend with [70]PCBM as cast 	Blend with [70]PCBM as cast 
Blend with [70]PCBM annealed 	Blend with [70]PCBM annealed 

Fig. S14 2D-GIWAXS the pristine **PBDT4TBT** and **PBDT4TffBT** polymers and their blends with [70]PCBM before and after thermal annealing.

Dark ideality factors

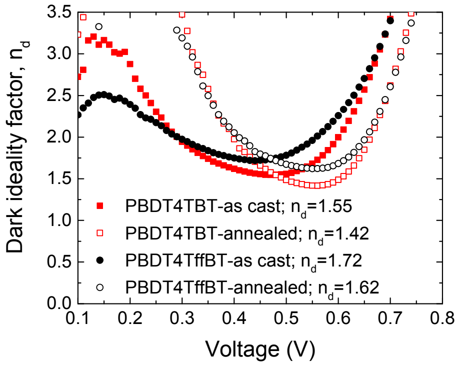


Fig. S15 Dark ideality factors calculated from the dark *J-V* curves.

Electroluminescence spectra

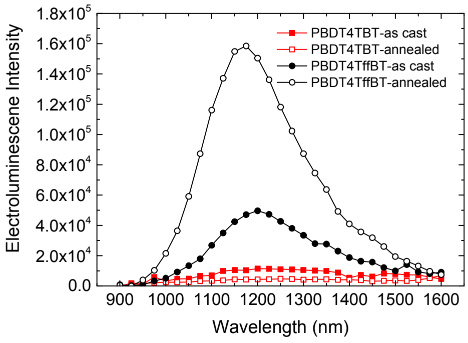


Fig. S16 EL spectra recorded for **PBDT4TBT**-[70]PCBM and **PBDT4TffBT**-[70]PCBM photovoltaic devices before and after thermal annealing. Note that absolute intensities of these data cannot be compared because they were measured at the same voltage bias and because the characteristics of the experimental setup cause the EL intensity to be sensitively dependent on the pixel position relative to the aperture of the detector of the spectrophotometer.

References

1 S. P. Mishra, A. K. Palai, R. Srivastava, M. N. Kamalasanan and M. Patri, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 6514-6525.

2 N. Wang, Z. Chen, W. Wei and Z. Jiang, *J. Am. Chem. Soc.*, 2013, **135**, 17060-17068.