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Electronic Supplementary Information

**Narrow bandgap difluorobenzochalcogenadiazole-based polymers
for high-performance organic thin-film transistors and polymer solar
cells**

Shengbin Shi,^{‡a} Qiaogan Liao,^{‡b} Hang Wang,^b and Guomin Xiao^{*a}

^aSchool of Chemistry and Chemical Engineering, Southeast University, Nanjing, Jiangsu 211189, China

^bDepartment of Materials Science and Engineering and The Shenzhen Key Laboratory for Printed Organic Electronics, Southern University of Science and Technology (SUSTech), Shenzhen, Guangdong 518055, China

[‡] These authors contributed equally to this work.

* Corresponding author

Email: xiaogm426@gmail.com

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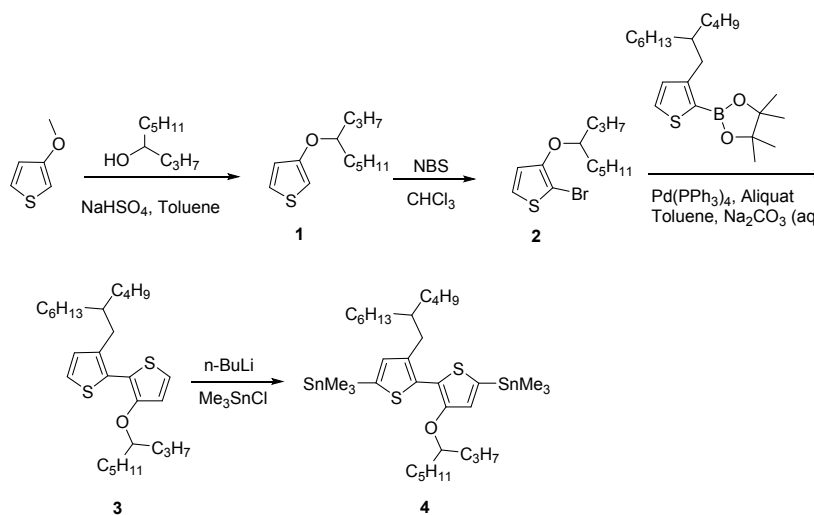
1. Materials and instruments

All reagent and chemicals were commercially available and used without further purification unless otherwise stated. THF and toluene were distilled from Na/benzophenone and used freshly. The compound 4,7-dibromo-5,6-difluorobenzo[*c*] [1,2,5]thiadiazole was purchased from Derthon Optoelectronic Materials Science Technology Co., Ltd (Shenzhen, China). Compound 4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]xadiazole was synthesized according to the literature.^{1,2} 3-(2-Butyl-1-octyl)-3'-(2-propylheptan-1-oloxo)-5,5'-bis-(trimethylstannyl)-2,2'-bithiophene (7) was synthesized according to literature.³ ¹H NMR and ¹³C NMR spectra were measured on Bruker Ascend 400 or 500 MHz spectrometers, respectively. Chemical shifts were referenced to residual protio-solvent signals. Polymers were prepared with a Biotage® Initiator⁺ microwave reactor. Elemental analyses (EAs) of monomers and polymers was performed on a Vario EL CUBE elemental analyzer. Polymer molecular weights were measured on Polymer Laboratories GPC-PL220 high temperature GPC/SEC system at 150 °C vs polystyrene standards using trichlorobenzene as the eluent. DSC curves were recorded on a differential scanning calorimetry (Mettler, STAR^e, heating rate = 10 °C min⁻¹, nitrogen purge). TGA curves were collected on a TA Instrument (Mettler, STAR^e). Optical absorption spectra of polymer solution and film at room temperature were collected on a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. Temperature dependent Optical absorption spectra of polymer solutions at various temperatures were collected on Perkin Elmer UV/VIS/NIR Spectrometer Lambda 950. Cyclic voltammetry measurements of polymers were carried out under argon atmosphere using a CHI760 evoltammetric analyzer with 0.1 M tetra-*n*-butylammoniumhexafluorophosphate in acetonitrile as supporting electrolyte. A platinum disk working electrode, a platinum wire counter electrode, and a silver wire reference electrode were employed, and Fc/Fc⁺ was used as internal reference for all measurements. The scanning rate was 50 mV s⁻¹. The external quantum efficiency (EQE) was measured by a QE-R3011 measurement system (Enli Technology, Inc.). The light intensity at each wavelength was calibrated with a standard single crystal Si photodiode. AFM measurements of polymer:PC₇₁BM blend films were performed by using a Dimension

Icon Scanning Probe Microscope (Asylum Research, MFP-3D-Stand Alone) in tapping mode. TEM specimens were prepared following identical conditions as the actual devices, but which were drop-cast onto 40 nm PEDOT:PSS covered substrate. After drying, substrates were transferred to deionized water and the floated films were transferred to TEM grids. TEM images were obtained on Tecnai Spirit (20 kV) TEM. X-ray energy was 10 keV and operated in top off mode. The scattering intensity was recorded on a 2D detector (Pilatus 2M) with a pixel size of 172 m (1475×1679 pixels). The samples were ~ 10 mm long in the direction of the beam path, and the detector was located at a distance of 300 mm from the sample center (distance calibrated by AgB reference). The incidence angle was chosen to be 0.16° (above critical angle) for the entire film structure measurement. Two dimensional grazing incidence X-ray diffraction (2D-GIXD) measurements were performed at the PLS-II 9A U-SAXS beam line of Pohang Accelerator Laboratory, Korea.

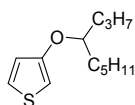
2. Monomer and polymer synthesis

2.1 Synthesis route



Synthesis route for monomer 4

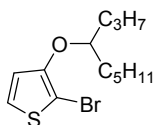
3-(4-nonanol)thiophene (1)⁴.



To a dry bottom flask was charged with 3-methoxythiophene (10.0 g, 87.6 mmol), 4-nonanol (16.0g, 110.9 mmol), and anhydrous sodium hydrogen sulfate (3.0 g, 25.0 mmol).

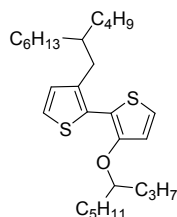
Toluene (200 mL) was then added, and the reaction mixture was purged with argon for 30 min, the mixture was heated to 130 °C and stirred for 19 h under argon protection. After cooling to room temperature, a saturate NaHCO₃ aqueous solution was added and the reaction mixture was extracted with ethyl acetate three times. The organic layer was dried over anhydrous MgSO₄, filtered, and concentrated for purification via silica gel column chromatography (eluent: petroleum ether) to afford the colorless oil (8.5 g, 42.6 %). ¹H NMR (500 MHz, CDCl₃) δ 7.15 (dd, *J* = 5.20, 3.15 Hz, 1H), 6.74 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.22 (dd, *J* = 2.85, 1.25 Hz, 1H), 4.09-4.05 (m, 1H), 1.68-1.58 (m, 4H), 1.48-1.28(m, 8H), 0.95-0.87 (m, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 157.49, 124.37, 120.42, 98.34, 80.64, 36.20, 33.97, 32.07, 25.24, 22.76, 18.83, 14.32, 14.19. MS (EI, m/z): calcd for C₁₃H₂₂OS: 226.14; found, 226.2.

2-bromo-3-(4-nonanol)thiophene (2)³.



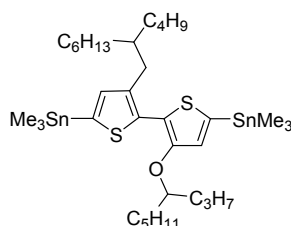
Compound 1 (7.6 g, 33.6 mmol) was dissolved in CHCl₃ (180 mL) and cooled down to 0–4°C using an ice bath. *N*-Bromobutanamide (3.88 g, 21.8 mmol) was added in the reaction mixture. The reaction mixture was stirred with shading light. After stirred for 1h, the reaction mixture was warmed to room temperature and stirred for 12 h, completion of the reaction was confirmed by GC-MS analysis. The addition of the *N*-Bromobutanamide can be repeated several times using 0.08 equivalent amounts if the reaction was not completed. Finally, the reaction mixture was added water and then extracted with CH₂Cl₂. The combined organic layer was dried over anhydrous MgSO₄, filtered, and concentrated for purification via silica gel column chromatography (eluent: petroleum ether) to afford the colorless oil (9.4 g, 91.7 %). ¹H NMR (500 MHz, CDCl₃) δ 7.17 (d, *J* = 5.9Hz, 1H), 6.69 (d, *J* = 5.9 Hz, 1H), 4.12–4.04 (m, 1H), 1.70–1.55 (m, 4H), 1.51–1.23 (m, 8H), 0.94–0.86 (m, 6H). ¹³C NMR (125 MHz, CDCl₃) δ 157.48, 124.36, 120.42, 98.35, 80.88, 34.00, 33.70, 31.95, 29.55, 27.76, 25.54, 22.95, 22.76, 14.22. MS (EI, m/z):calcd for C₁₃H₂₁BrOS: 304.05; found, 304.1.

3-(2-butyl-1-octyl)-3'-(4-nonanol)-2,2'-bithiophene (3)³.



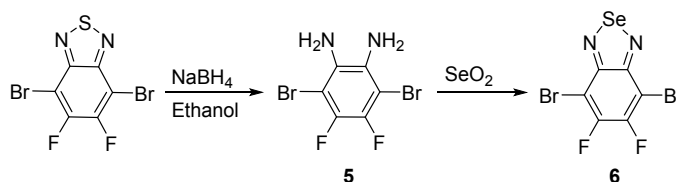
To a 150 mL three necked reaction flask was added 2-(3-(2-Butyl-1-octyl))-4,4,5,5-tetramethyl-1,3,2-dioxaborolane³ (1.46 g, 3.849 mmol), compound 2 (1.41 g, 4.62 mmol), and 65 mL anhydrous toluene. The resulting mixture was stirred and purged with argon before a series of 270 mg Pd(PPh₃)₄, 0.75 g Aliquat 336 in 5 mL toluene, and 6.0 mL 2 M aqueous Na₂CO₃ solution was added. Subsequently, the reaction mixture was heated at 105 °C for 15 h, cooled down to room temperature and diluted with CH₂Cl₂. After extraction with CH₂Cl₂, the combined organic phase was washed with water, dried over MgSO₄, and concentrated in vacuum. The crude product was purified by silica gel column chromatography (eluent: petroleum ether) to afford the colorless oil (534 mg, 30.1 %). ¹H NMR (500 MHz, CDCl₃) δ 7.21 (d, *J* = 5.1 Hz, 1H), 7.17 (d, *J* = 5.5 Hz, 1H), 6.87 (d, *J* = 5.2 Hz, 1H), 6.81 (d, *J* = 5.5 Hz, 1H), 4.10–4.04 (m, 1H), 2.61 (d, *J* = 7.1 Hz, 2H), 1.65–1.48 (m, 5H), 1.40–1.19 (m, 24H), 0.92–0.80 (m, 12H). ¹³C NMR (125 MHz, CDCl₃) δ 153.26, 140.17, 129.45, 128.63, 124.28, 123.22, 118.74, 114.41, 81.83, 38.82, 36.37, 34.13, 34.04, 33.62, 33.30, 32.08, 29.85, 28.86, 26.63, 25.07, 23.20, 22.84, 22.77, 18.66, 14.33, 14.29, 14.19. HRMS (ESI, *m/z*): calcd for C₂₉H₄₉OS₂ [M+H]⁺: 477.3219, Found: 477.3209.

3-(2-butyl-1-octyl)-3'-(4-nonanol)-5,5'-bis(trimethylstannyl)-2,2'-bithiophene (4)³.



To a 25 mL flask was added compound 3 (534 mg, 1.12 mmol) and 7.1 mL anhydrous THF, the resulting clear solution was cooled to -78 °C using dry ice/acetone bath. Then 1.12

mL n-BuLi solution in hexane (2.69 mmol, 2.4 M) was added dropwise. After stirring at -78 °C for 1 h and room temperature for 1 h, the reaction mixture was cooled to -78 °C again, 2.92 mL trimethyltin chloride (2.92 mmol, 1 M) was added in one portion, and cooling bath was removed. After being stirred at ambient temperature for 12 h, the reaction mixture was quenched with water carefully and then poured into cool water, extracted with diethyl ether twice. After removal of organic solvent, the monomer was obtained as a yellowish oil (736.9 mg, 82.0%). ¹H NMR (400 MHz, CDCl₃) δ 6.91 (s, 1H), 6.83 (s, 1H), 4.14–4.03 (m, 1H), 2.65 (d, *J* = 7.1 Hz, 2H), 1.68–1.45 (m, 5H), 1.43–1.15 (m, 24H), 0.90–0.82 (m, 12H), 0.46–0.25 (m, 18H). ¹³C NMR (125 MHz, CDCl₃) δ 154.38, 140.68, 137.88, 135.77, 135.23, 134.99, 126.28, 120.76, 81.72, 38.82, 36.39, 34.11, 33.81, 33.65, 33.35, 32.13, 32.10, 29.89, 28.87, 26.59, 25.05, 23.22, 22.85, 22.77, 18.69, 14.37, 14.34, 14.31, 14.23.



Synthesis route for monomer 6 (ffBSe)

1,2-diamino-3,6-dibromobenzene-4,5-fluorobenzene(5)⁵.

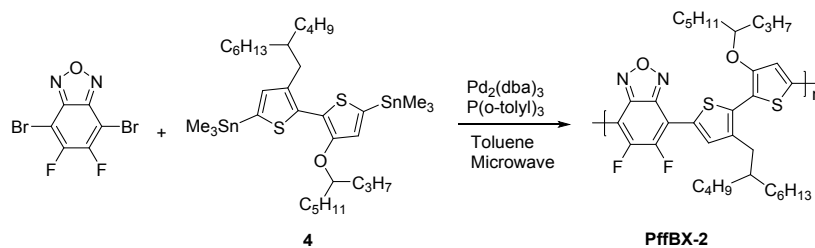
The sodium borohydride(10.32 g, 272.8 mmol) was dropped into a suspension of 4,7-dibromo-5,6-difluorobenzo[c][1,2,5]thiadiazole (5.0 g, 15.2mmol) in anhydrous ethanol(150mL) at 0 °C, then warm at room temperature for overnight. And then evaporated and purified by silica gel column chromatography (eluent: petroleum ether/ethyl acetate 2:1) to afford a brown solid (2.4 g, 52.5%). ¹H NMR (500 MHz, CDCl₃) δ 3.68 (s, 4H). ¹³C NMR (125 MHz, CDCl₃) δ 142.87 (d, *J* = 18.2 Hz), 140.95 (d, *J* = 18.2 Hz), 98.34 (dd, *J* = 12.6, 9.7 Hz). ¹⁹F NMR (376 MHz, CDCl₃) δ -139.06. HRMS (ESI, *m/z*): calcd for C₆H₅N₂Br₂F₂ [M+H]⁺: 302.8756, Found: 302.8762.

4,7-dibromo-5,6-fluorobenzo[c][1,2,5]selenadiazole (6).

Compound 1,2-diamino-3,6-dibromobenzene-4,5-fluorobenzene (154 mg, 0.51 mmol) was dissolved in ethanol (15 mL), then heated to reflux and stirred. Afterwards, a solution of SeO₂ (59.4 mg, 0.54 mmol) in 3.3 mL hot water was added dropwise. The resulting reaction mixture was refluxed for overnight to obtain a yellow precipitate in a pale brown solution. The reaction was cooled to room temperature, and extracted with ethyl acetate. The organic layer was evaporated in vacuo, the product was purified by silica gel column chromatography (eluent: petroleum ether/ dichloromethane 5: 1) to afford a pale yellow solid (160 mg, 83.2 %). ¹³C NMR (125 MHz, DMSO-*d*₆) δ 152.08, 149.94 (d, *J* = 22.68Hz) , 100.52 (dd, *J* = 15.12, 7.56Hz). ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ -121.65. HRMS (ESI, *m/z*): calcd for C₆H₂N₂Br₂F₂Se [M+H]⁺: 376.7624, Found: 376.7634.

The synthesis of polymers **PffBX-2**, **PffBX-3**, **PffBT-2**, **PffBT-3**, **PffBSe-2**, and **PffBSe-3**.

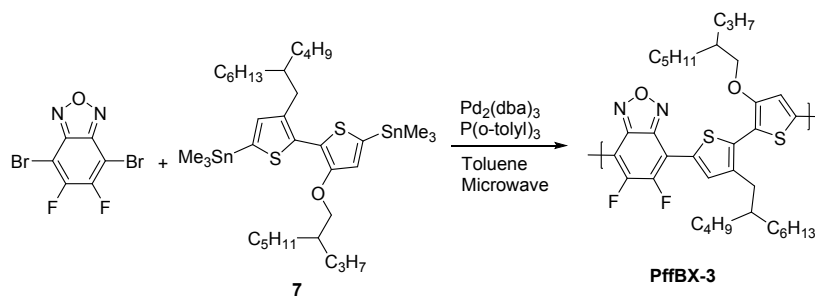
Polymer **PffBX-2**.



4,7-dibromo-5,6-difluoro-2,1,3-benzoxadiazole (88.6 mg, 0.282 mmol), compound 4 (230.9 mg, 0.288 mmol), tris(dibenzylideneacetone)dipalladium(0) (1.5 mol%), tri(*o*-tolyl)phosphine (12 mol%) and 4.8 mL anhydrous toluene were added in a 5 mL microwave vial. The microwave vial and its contents were subjected to 3 pump/purge cycles with argon. The microwave vial was sealed under argon flow and then stirred at 80 °C for 10 minutes, 100 °C for 10 minutes, and 140 °C for 4 h under microwave irradiation. Then, 2-(tributylstanny)thiophene (50 uL) was added and the reaction mixture was stirred under microwave irradiation at 140 °C for 20 min. Finally, 2-bromothiophene (100 uL) was added and the reaction mixture was stirred at 140 °C for another 20 min. After cooling to room temperature, the reaction mixture was dripped into 150 mL methanol containing 1 mL 12 N HCl under vigorous stirring. After stirring for 30 min, the polymer precipitate was transferred to a Soxhlet thimble. The crude product was subjected to sequential Soxhlet extraction with

methanol, acetone, hexane, dichloromethane, chloroform, chlorobenzene, and dichlorobenzene. The extracted compound in dichlorobenzene was concentrated to ~6 mL, and then dripped into 150 mL methanol under vigorous stirring. The polymer was collected by filtration and dried under reduced pressure to afford a deep colored solid with 65.5% yield. ^1H NMR (400 MHz, 80 °C, Toluene- d_8 , ppm) δ 8.47–8.25 (m, 2H), 4.72–4.45 (m, 1H), 3.40–3.10 (m, 2H), 1.70–1.35 (m, 29H), 1.10–0.46 (m, 12H). Elem. Anal.: Calcd. for $\text{C}_{35}\text{H}_{46}\text{F}_2\text{N}_2\text{O}_2\text{S}_2$ (%): C, 66.85; H, 7.37; N, 4.45; S, 10.20. Found (%): C, 66.54; H, 7.08; N, 4.15; S, 9.80. Molecular weight: $M_n = 10.8$ kDa, $M_w = 14.1$ kDa, PDI = 1.31.

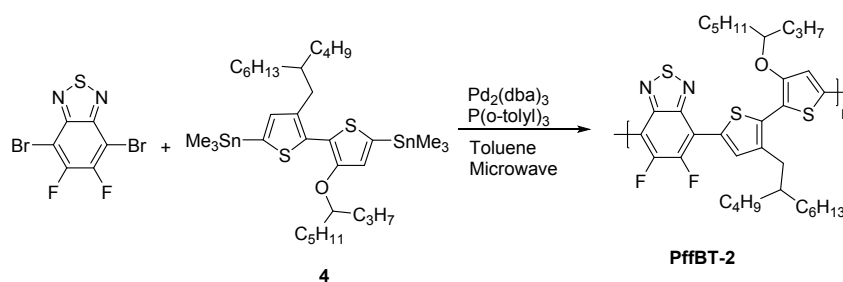
Polymer PffBX-3.



4,7-dibromo-5,6-difluoro-2,1,3-benzoxadiazole^{1, 2} (67.45 mg, 0.215 mmol), compound 7³ (177.2 mg, 0.217 mmol), tris(dibenzylideneacetone)dipalladium(0) (1.5 mol%), tri(o-tolyl)phosphine (12 mol%) and 4.8 mL anhydrous toluene were added in a 5 mL microwave vial. The microwave vial and its contents were subjected to 3 pump/purge cycles with argon. The microwave vial was sealed under argon flow and then stirred at 80 °C for 10 minutes, 100 °C for 10 minutes, and 140 °C for 4 h under microwave irradiation. Then, 2-(tributylstanny)thiophene (50 μL) was added and the reaction mixture was stirred under microwave irradiation at 140 °C for 20 min. Finally, 2-bromothiophene (100 μL) was added and the reaction mixture was stirred at 140 °C for another 20 min. After cooling to room temperature, the reaction mixture was dripped into 150 mL methanol containing 1 mL 12 N HCl under vigorous stirring. After stirring for 30 min, the polymer precipitate was transferred to a Soxhlet thimble. The crude product was subjected to sequential Soxhlet extraction with methanol, acetone, hexane, dichloromethane, chloroform, chlorobenzene, and dichlorobenzene. The extracted compound in dichlorobenzene was concentrated to ~6 mL,

and then dripped into 150 mL methanol under vigorous stirring. The polymer was collected by filtration and dried under reduced pressure to afford a deep colored solid with 31.3% yield. $^1\text{H NMR}$ (400 MHz, 80 °C, $\text{C}_2\text{D}_2\text{Cl}_4$) δ 8.20–8.07 (m, 2H), 4.26–4.19 (m, 2H), 3.08–2.87 (m, 2H), 1.89–1.57 (m, 2H), 1.68–1.06 (m, 28H), 1.09–0.81 (m, 12H). Elem. Anal.: Calcd. for $\text{C}_{36}\text{H}_{48}\text{F}_2\text{N}_2\text{O}_2\text{S}_2$ (%):C, 67.26; H, 7.53; N,4.36; S, 9.97. Found (%): C, 67.31; H, 7.76; N, 4.25; S, 9.85. Molecular weight: $M_n=15.6$ kDa, $M_w = 23.4$ kDa, PDI=1.50.

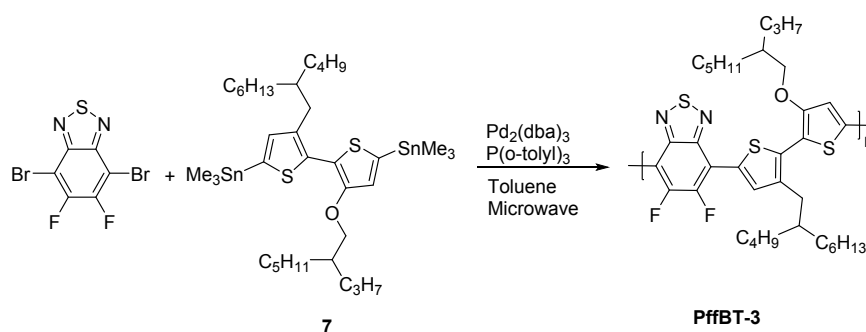
Polymer PffBT-2.



4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (73.1 mg, 0.222 mmol), compound 4 (181.3 mg, 0.226 mmol), tris(dibenzylideneacetone)dipalladium(0) (1.5 mol%), tri(*o*-tolyl)phosphine (12 mol%) and 4.2 mL anhydrous toluene were added in a 5 mL microwave vial. The microwave vial and its contents were subjected to 3 pump/purge cycles with argon. The microwave vial was sealed under argon flow and then stirred at 80 °C for 10 minutes, 100 °C for 10 minutes, and 140 °C for 4 h under microwave irradiation. Then, 2-(tributylstannyl)thiophene (50 μL) was added and the reaction mixture was stirred under microwave irradiation at 140 °C for 20 min. Finally, 2-bromothiophene (100 μL) was added and the reaction mixture was stirred at 140 °C for another 20 min. After cooling to room temperature, the reaction mixture was dripped into 150 mL methanol containing 1 mL 12 N HCl under vigorous stirring. After stirring for 30 min, the polymer precipitate was transferred to a Soxhlet thimble. The crude product was subjected to sequential Soxhlet extraction with methanol, acetone, hexane, dichloromethane, chloroform, chlorobenzene, and dichlorobenzene. The extracted compound in dichlorobenzene was concentrated to ~ 6 mL, and then dripped into 150 mL methanol under vigorous stirring. The polymer was collected by filtration and dried under reduced pressure to afford a deep colored solid with 60.9% yield.

^1H NMR (400 MHz, 80 °C, Toluene- d_8 , ppm) δ 8.44–8.36 (m, 2H), 4.54 (s, 1H), 3.22–3.19 (m, 2H), 2.03–1.18 (m, 29H), 1.17–0.74 (m, 12H). Elem. Anal.: Calcd. for $\text{C}_{35}\text{H}_{46}\text{F}_2\text{N}_2\text{OS}_3$ (%): C, 65.18; H, 7.19; N, 4.34; S, 14.91. Found (%): C, 65.48; H, 7.12; N, 4.35; S, 14.64. Molecular weight: $M_n = 23.3$ kDa, $M_w = 34.0$ kDa, PDI = 1.46.

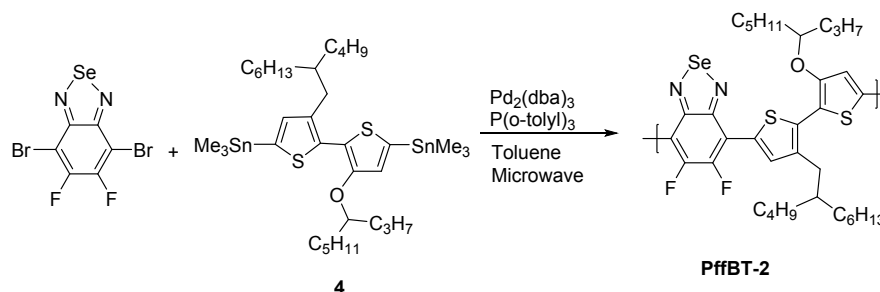
Polymer PffBT-3³.



4,7-dibromo-5,6-difluorobenzo[*c*][1,2,5]thiadiazole (69.9 mg, 0.212 mmol), compound 7³ (176.4 mg, 0.216 mmol), tris(dibenzylideneacetone)-dipalladium(0) (1.5 mol%), tri(*o*-tolyl)phosphine (12 mol%) and 4 mL anhydrous toluene were added in a 5 mL microwave vial. The microwave vial and its contents were subjected to 3 pump/purge cycles with argon. The microwave vial was sealed under argon flow and then stirred at 80 °C for 10 minutes, 100 °C for 10 minutes, and 140 °C for 4.5 h under microwave irradiation. Then, 2-(tributylstanny)thiophene (50 μL) was added and the reaction mixture was stirred under microwave irradiation at 140 °C for 20 min. Finally, 2-bromothiophene (100 μL) was added and the reaction mixture was stirred at 140 °C for another 20 min. After cooling to room temperature, the reaction mixture was dripped into 150 mL methanol containing 1 mL 12 N HCl under vigorous stirring. After stirring for 30 min, the polymer precipitate was transferred to a Soxhlet thimble. The crude product was subjected to sequential Soxhlet extraction with methanol, acetone, hexane, dichloromethane, chloroform, chlorobenzene, and dichlorobenzene. The extracted compound in dichlorobenzene was concentrated to ~ 6 mL, and then dripped into 150 mL methanol under vigorous stirring. The polymer was collected by filtration and dried under reduced pressure to afford a deep colored solid with 52.4% yield. The ^1H NMR is same to the literature.³ Molecular weight: $M_n = 35.5$ kDa, $M_w = 58.0$ kDa,

PDI = 1.63.

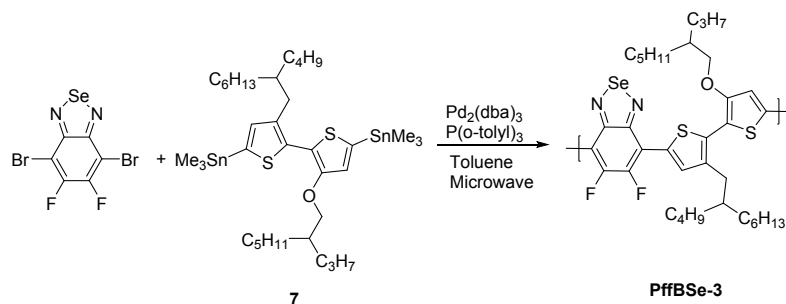
Polymer PffBSe-2.



4,7-dibromo-5,6-fluorobenzo[c][1,2,5] selenadiazole (113.1 mg, 0.300 mmol), compound 4 (245.6 mg, 0.306 mmol), tris(dibenzylideneacetone)dipalladium(0) (1.5 mol%), tri(*o*-tolyl)phosphine (12 mol%) and 5 mL anhydrous toluene were added in a 5 mL microwave vial. The microwave vial and its contents were subjected to 3 pump/purge cycles with argon. The microwave vial was sealed under argon flow and then stirred at 80 °C for 10 minutes, 100 °C for 10 minutes, and 140 °C for 4.5 h under microwave irradiation. Then, 2-(tributylstanny)thiophene (50 uL) was added and the reaction mixture was stirred under microwave irradiation at 140 °C for 20 min. Finally, 2-bromothiophene (100 uL) was added and the reaction mixture was stirred at 140 °C for another 20 min. After cooling to room temperature, the reaction mixture was dripped into 150 mL methanol containing 1 mL 12 N HCl under vigorous stirring. After stirring for 30 min, the polymer precipitate was transferred to a Soxhlet thimble. The crude product was subjected to sequential Soxhlet extraction with methanol, acetone, hexane, dichloromethane, and chloroform. The extracted compound in chloroform was concentrated to ~6 mL, and then dripped into 150 mL methanol under vigorous stirring. The polymer was collected by filtration and dried under reduced pressure to afford a deep colored solid with 66.0 % yield. ¹H NMR (400 MHz, 80 °C, C₂D₂Cl₄) δ 8.30–8.04 (m, 2H), 4.59–4.37(s, 1H), 3.10–2.81 (m, 2H), 2.05–1.82 (m, 1H), 1.70–1.21 (m, 28H), 1.20–0.74 (m, 12H). Elem. Anal.: Calcd. for C₃₅H₄₆F₂N₂OS₂Se (%): C, 60.76; H, 6.70; N, 4.05; S, 9.27. Found (%): C, 60.53; H, 6.61; N, 3.95; S, 9.14. Molecular weight: M_n = 16.0

kDa, $M_w = 27.6$ kDa, PDI = 1.73.

Polymer PffBSe-3.



4,7-dibromo-5,6-fluorobenzo[*c*][1,2,5] selenadiazole (54.0 mg, 0.143 mmol), compound 7 (118.2 mg, 0.145 mmol), tris(dibenzylideneacetone)dipalladium(0) (1.5mol%), tri(*o*-tolyl)phosphine (12 mol%) and 2.3 mL anhydrous toluene were added in a 5 mL microwave vial. The microwave vial and its contents were subjected to 3 pump/purge cycles with argon. The microwave vial was sealed under argon flow and then stirred at 80 °C for 10 minutes, 100 °C for 10 minutes, and 140 °C for 4.5 h under microwave irradiation. Then, 2-(tributylstanny)thiophene (50 uL) was added and the reaction mixture was stirred under microwave irradiation at 140 °C for 20 min. Finally, 2-bromothiophene (100 uL) was added and the reaction mixture was stirred at 140 °C for another 20 min. After cooling to room temperature, the reaction mixture was dripped into 150 mL methanol containing 1 mL 12 N HCl under vigorous stirring. After stirring for 30 min, the polymer precipitate was transferred to a Soxhlet thimble. The crude product was subjected to sequential Soxhlet extraction with methanol, acetone, hexane, dichloromethane and chloroform. The extracted compound in chloroform was concentrated to ~5 mL, and then dripped into 150 mL methanol under vigorous stirring. The polymer was collected by filtration and dried under reduced pressure to afford a deep colored solid with 70.8 % yield. ^1H NMR (400 MHz, 80 °C, Toluene-*d*₈, ppm) δ 8.37–8.30 (m, 2H), 4.22 (s, 2H), 3.20 (s, 2H), 1.97–1.95 (m, 2H), 1.80–1.38 (m, 28H), 1.05–0.91 (m, 12H). Elem. Anal.: Calcd. for C₃₆H₄₈F₂N₂OS₂Se (%): C, 61.26; H, 6.85; N, 3.97; S, 9.08. Found (%): C, 60.64; H, 6.61; N, 3.84; S, 8.86. Molecular weight: $M_n = 17.2$ kDa, $M_w = 26.8$ kDa, PDI = 1.56.

3. NMR Spectra of Monomers and Polymers.

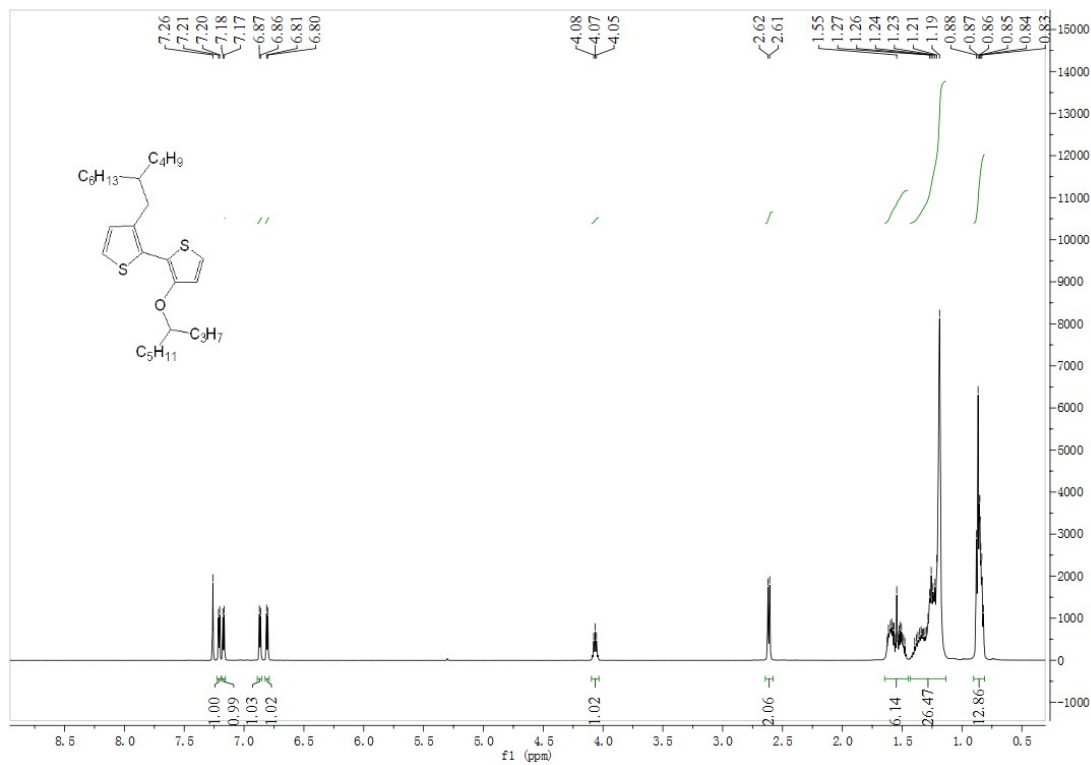


Fig. S1 ^1H NMR spectrum of compound 3 (r.t., in CDCl_3).

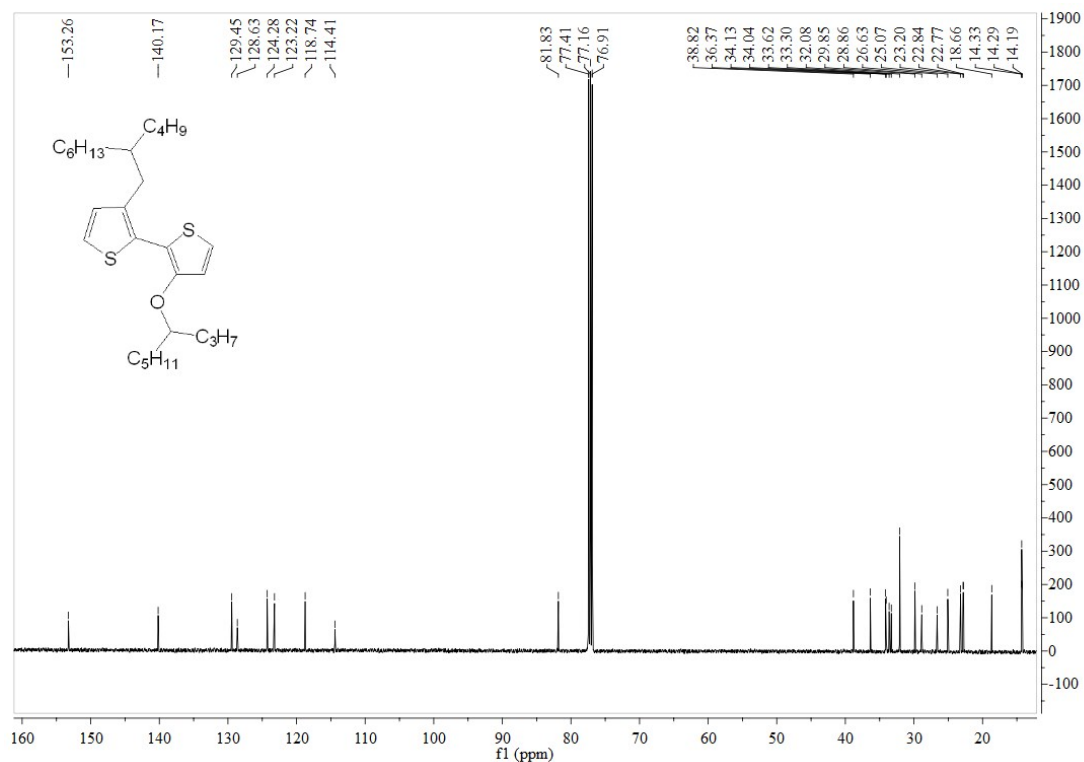


Fig. S2 ^{13}C NMR spectrum of compound 3 (r.t., in CDCl_3).

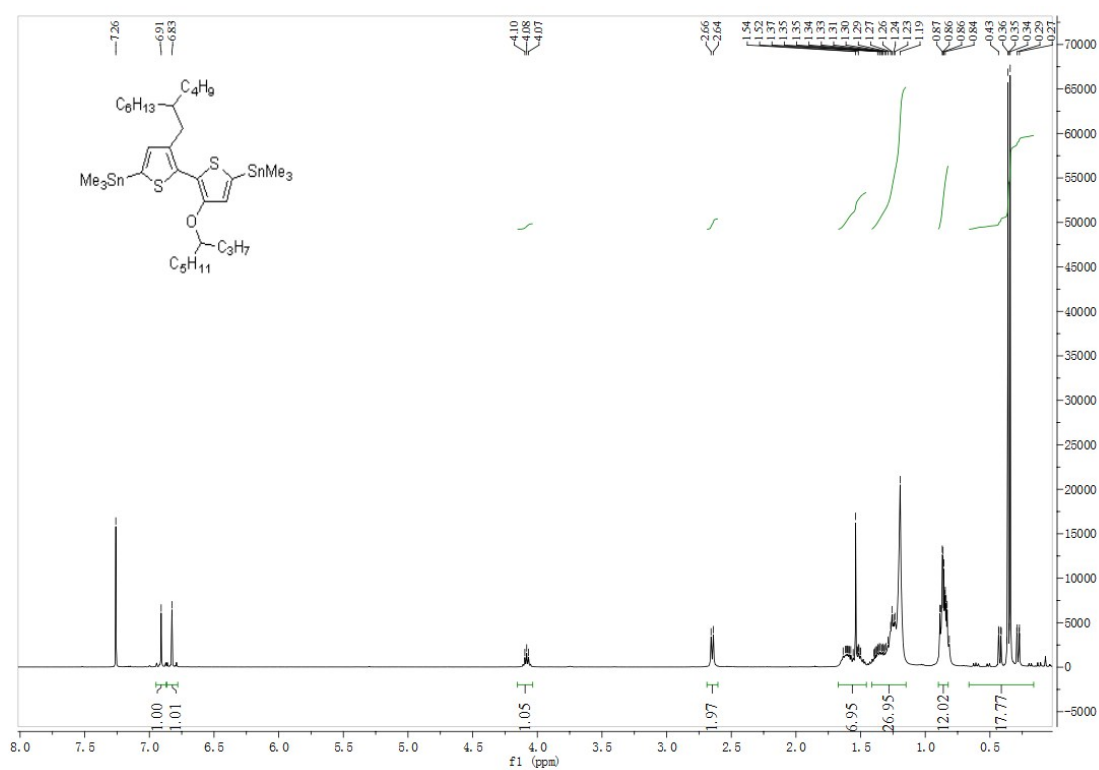


Fig. S3 ^1H NMR spectrum of monomer 4 (r.t., in CDCl_3).

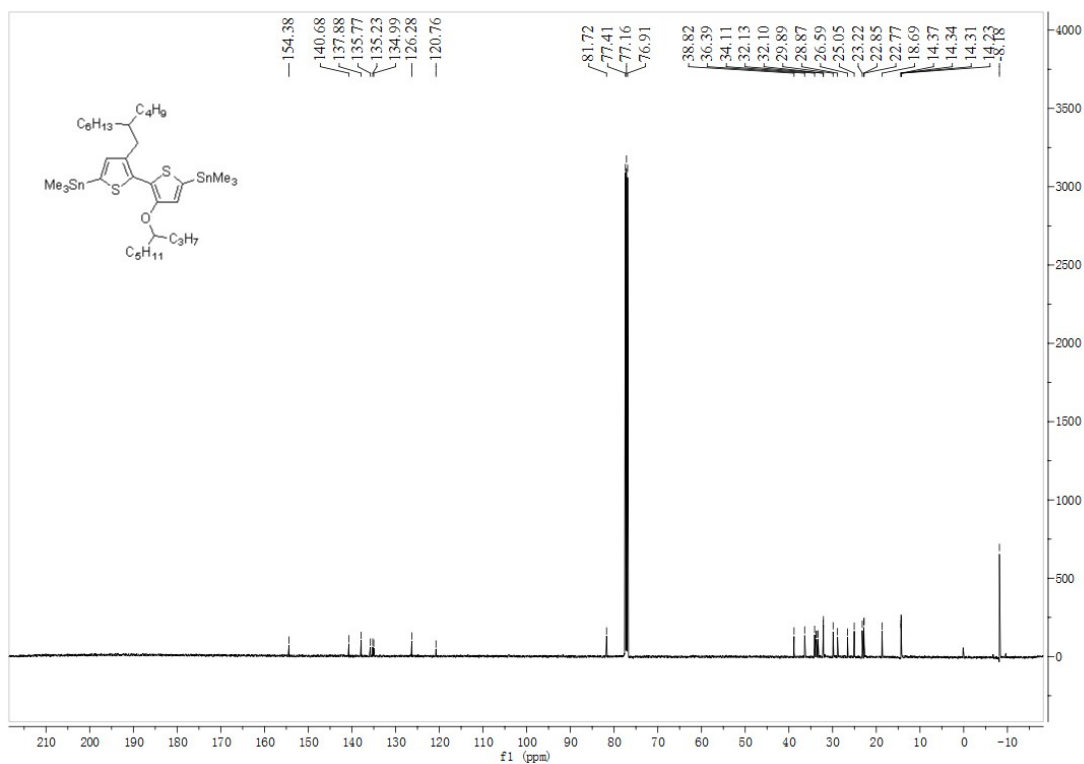


Fig. S4 ¹³C NMR spectrum of monomer 4 (r.t., in CDCl₃).

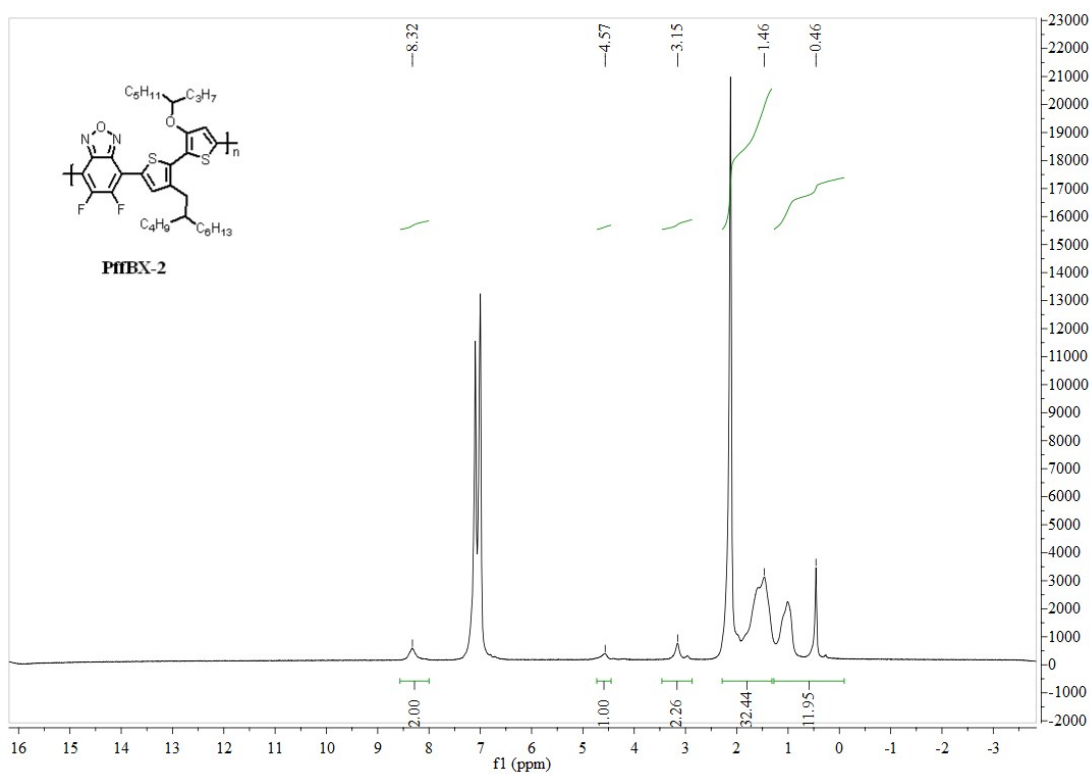


Fig. S5 ¹H NMR spectrum of polymer PffBX-2 (80 °C in Toluene-*d*₈).

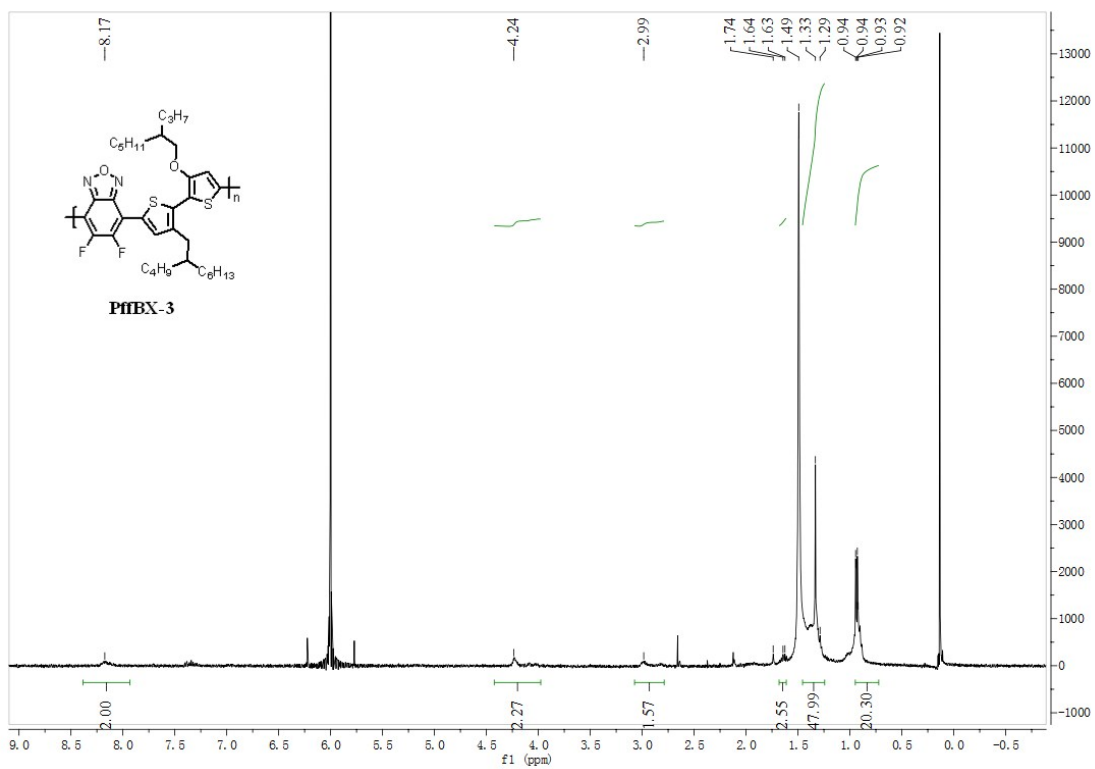


Fig. S6 ^1H NMR spectrum of polymer PffBX-3 (80 °C in $\text{C}_2\text{D}_2\text{Cl}_4$).

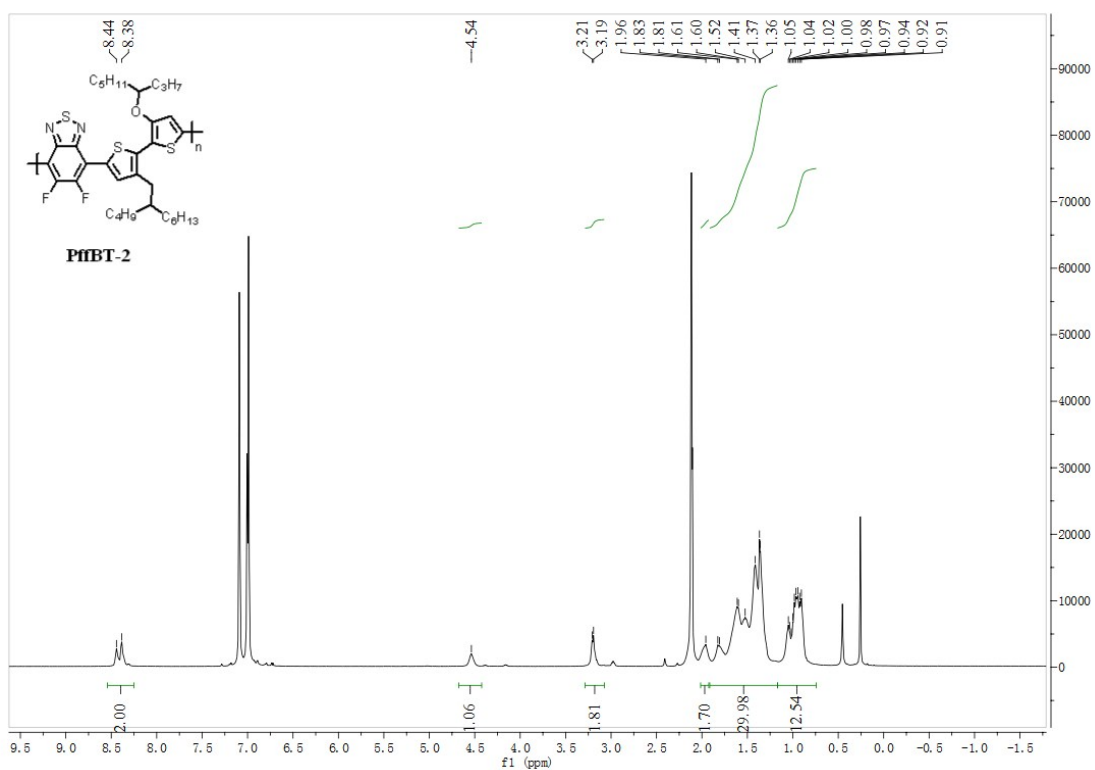


Fig. S7 ^1H NMR spectrum of polymer PffBT-2 (80 °C in Toluene- d_3).

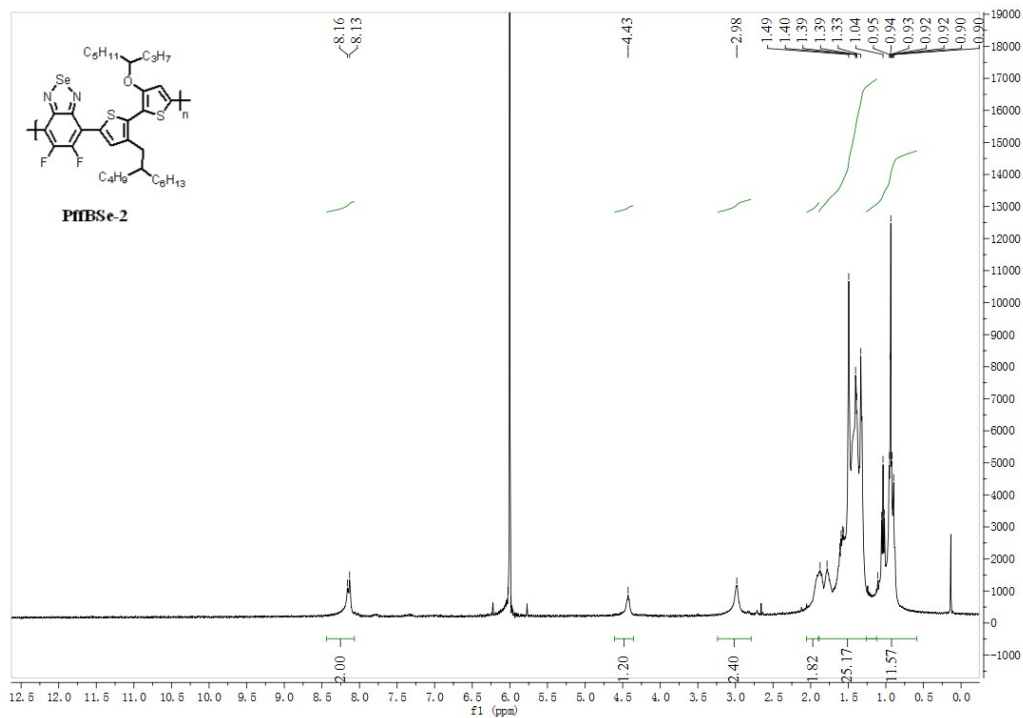


Fig. S8 ^1H NMR spectrum of polymer PffBSe-2 (80 °C in $\text{C}_2\text{D}_2\text{Cl}_4$).

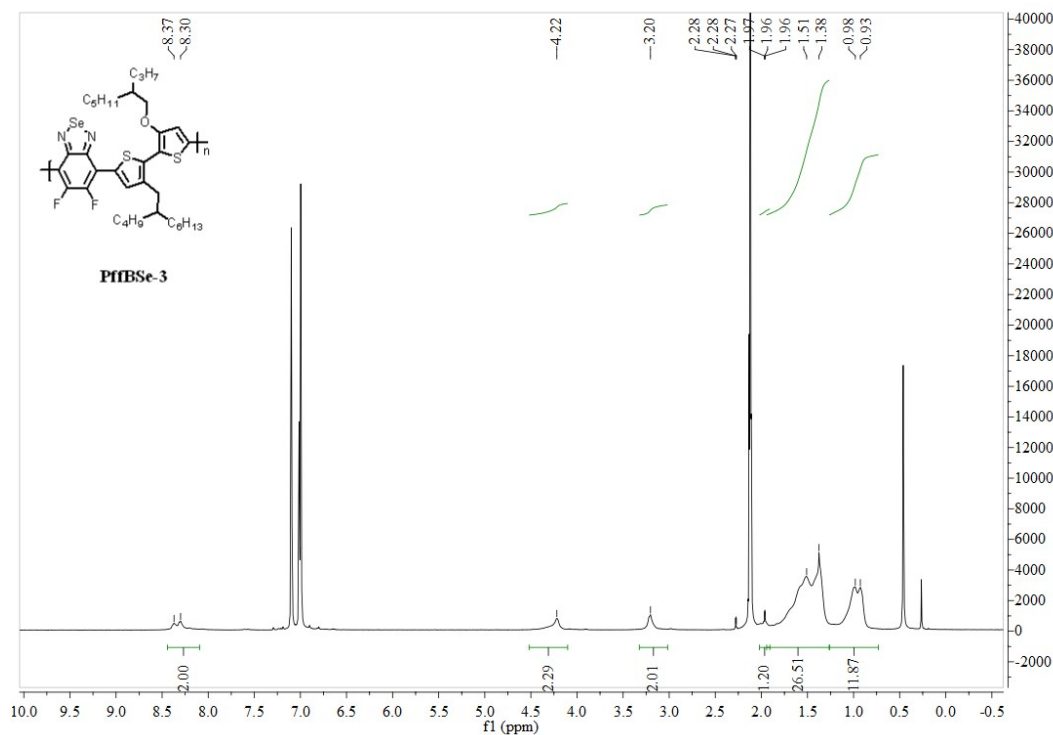


Fig. S9 ^1H NMR spectrum of polymer PffBSe-3 (80 °C in Toluene- d_8).

4. Structure and optical properties of monomers and polymers in solutions

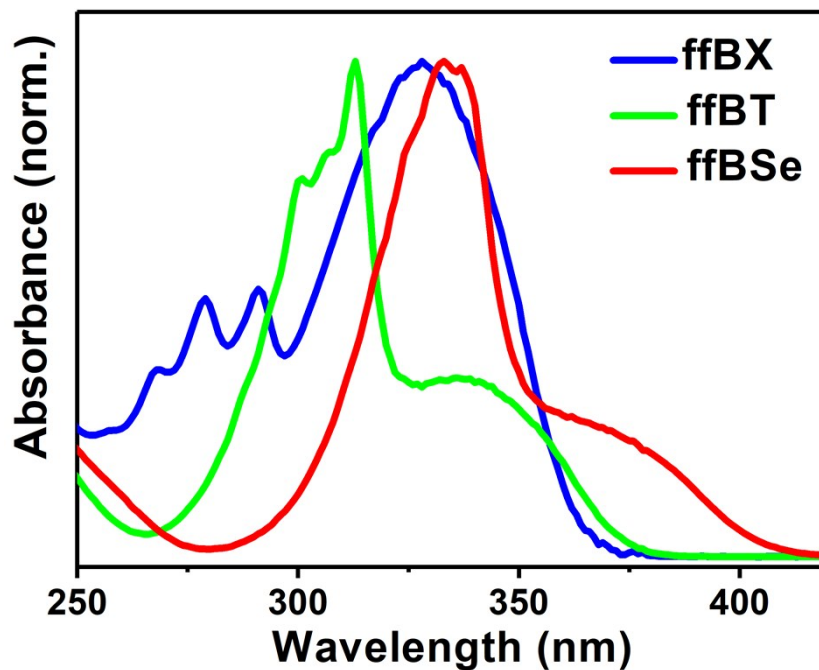


Fig. S10 Optical absorption spectra of the monomers (ffBX, ffBT and ffBSe) in solution (1×10^{-5} M in dichloromethane).

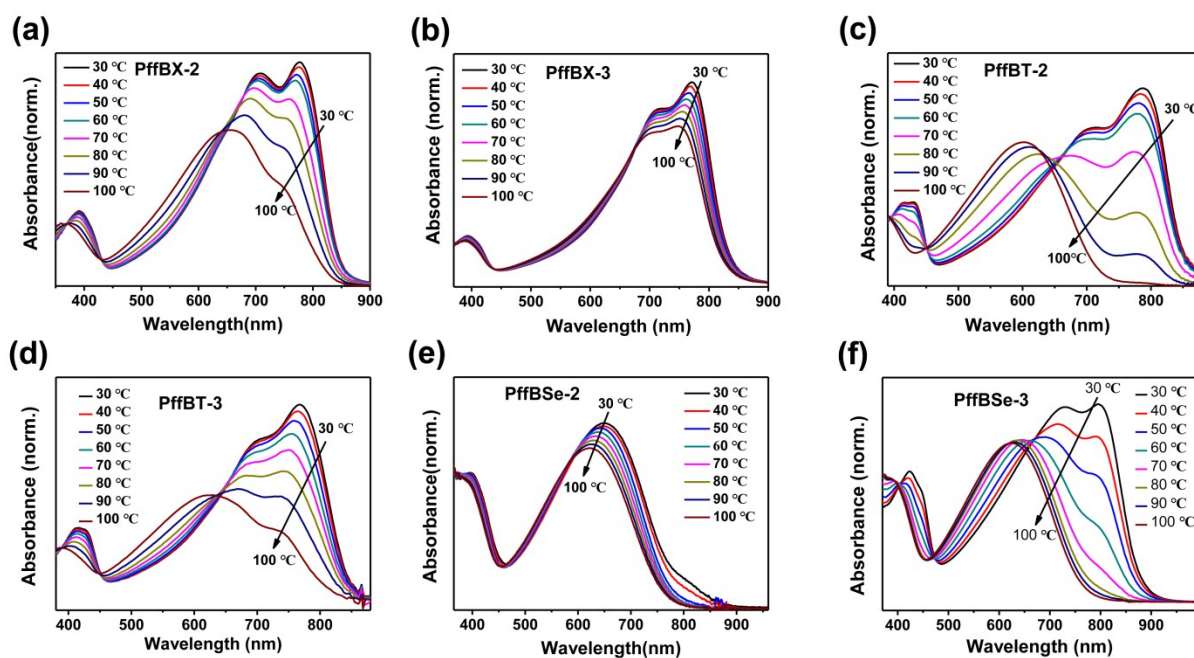


Fig. S11 Optical absorption spectra of PffBZ-base polymers in solution (1×10^{-5} M in *o*-dichlorobenzene) at various temperatures as indicated.

5. Thermal properties of PffBZ-base polymers

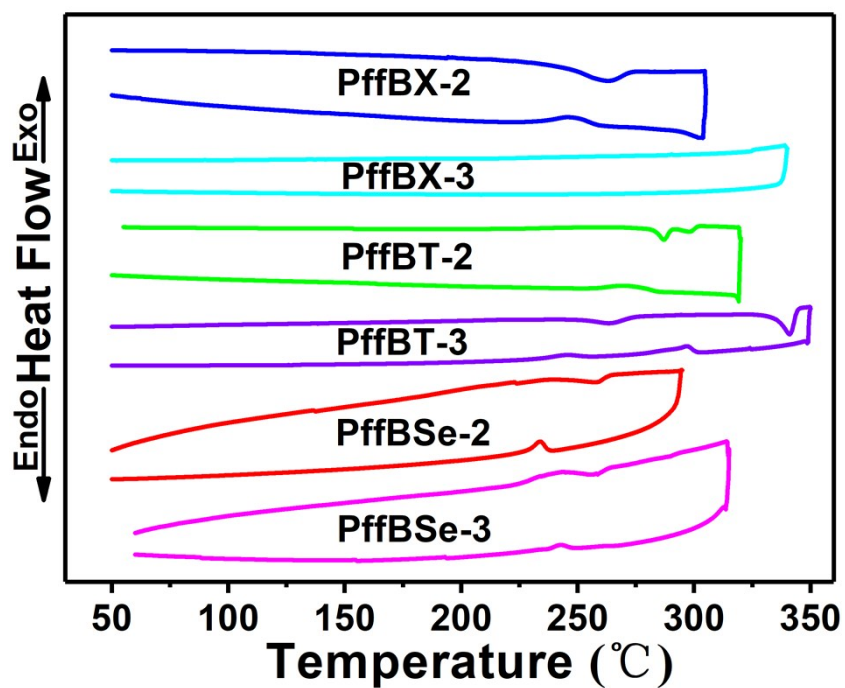


Fig. S12 DSC thermograms of the PffBZ-based polymers at a temperature ramp of $10\text{ }^{\circ}\text{C min}^{-1}$ under N_2 . The bottom line is from the cooling run, and the top line is from the heating run.

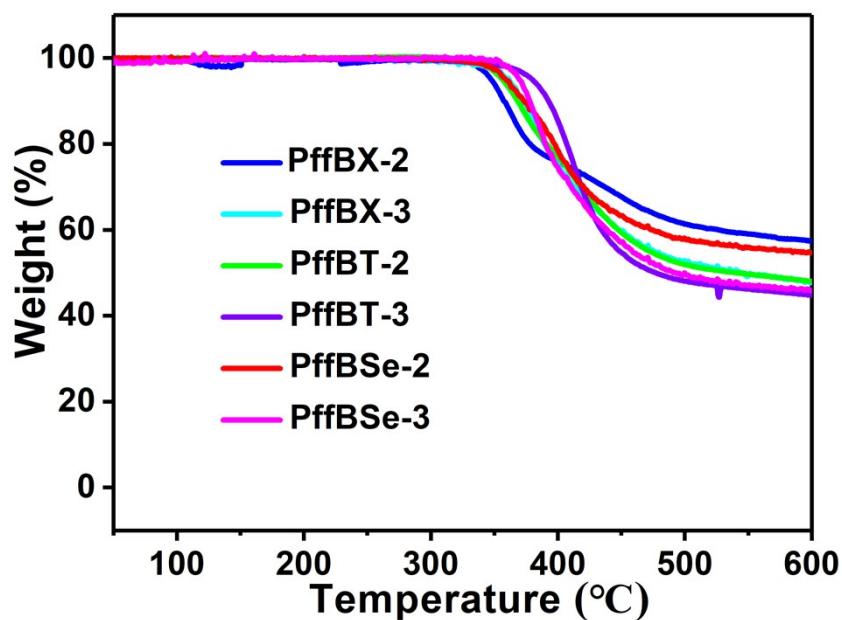
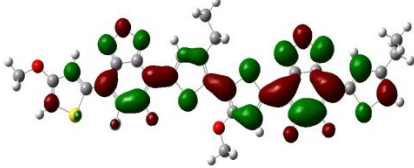
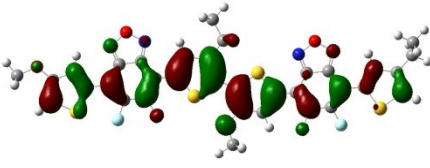
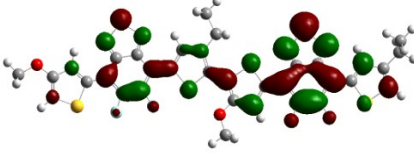
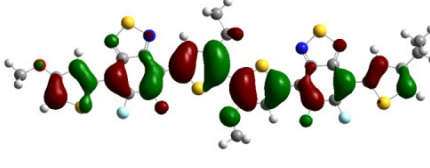
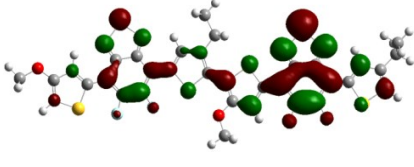
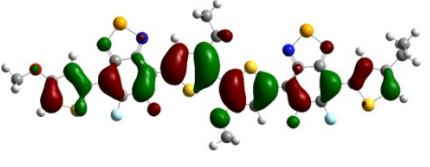


Fig. S13 Thermal gravimetric analysis of the PffBZ-based polymers.

6. DFT calculation

Table S1. Chemical structures and optimized geometries for the dyads of repeat PffBZ-based

polymer units. Calculations were carried out at the DFT//B3LYP/6-31G (d, p) level; alkyl substituents are truncated to simplify the calculation.

Trimers	LUMO	HOMO
PffBX-3	 -3.00eV	 -4.99eV
PffBT-3	 2.87eV	 -4.80eV
PffBSe-3	 2.91eV	 4.74eV

7. Organic thin-film fabrication and characterization

7.1 Organic thin-film transistor fabrication and characterization: Source–drain electrodes (3 nm Cr and 30 nm Au) were patterned on borosilicate glass by photolithography process. The patterned glass substrates were cleaned by sonication in acetone and isopropanol for 10 min each, followed by UV-ozone treatment for 30 min. The cleaned substrates were transferred into N₂-filled glove box (O₂, H₂O concentration <0.1 ppm) to deposit the semiconductor layer on top. The polymer active layers were spin-coated from 5 mg mL⁻¹ *o*-DCB solutions, and then they were thermally annealed at various temperatures for 10 min.

Dielectric layers were spin-coated from diluted CYTOP solutions (CTL-809M:CT-SOLV180 = 2:1 (v:v), Asahi Glass Co., Ltd.), then they were annealed at 250 °C for 10 min. Finally, 50 nm Al was evaporated on top as the gate electrode. The OTFT devices (L = 10, 20, 50, or 100 μm ; W = 5 mm) were characterized with Keithley 4200 semiconductor characterization system. All device fabrication and characterization were carried out in N₂-filled glove box.

7.2 Off-center spin-coat to fabrication the OTFT devices. The source and drain electrodes (3 nm Cr and 30 nm Au) were patterned on borosilicate glass by standard photolithography process. The patterned glass substrates were cleaned by sonication in acetone and isopropanol for 10 min each, followed by UV-ozone treatment for 30 min. The cleaned substrates were transferred into N₂-filled glove box (O₂, H₂O concentration <0.1 ppm) to deposit the semiconductor layer on top. For the off-center spin-coating process, the substrates were fixed onto glass slide and place at a distance of ~3 cm from the center of spin-coater. The semiconductor layer was spin-coated from hot solution (mixed solvent, chlorobenzene: *o*-dichlorobenzene=3:1, volume ratio, 5 mg mL⁻¹), then annealed at 200 °C for 30 min followed by quench cooling down process. The dielectric layer was spin-coated from diluted CYTOP solutions (CTL-809M:CT-SOLV180 = 2:1 volume ratio, Asahi Glass Co., Ltd.), then annealed at 90 °C for 30 min, the thickness of the CYTOP layer is about 400 nm. Finally, 50 nm Aluminum was thermally evaporated on top through a shadow mask under high vacuum (< 10⁻⁶ Torr) as a gate electrode to finish device fabrication. The field-effect transistor devices were measured in N₂-filled glove box with Keithley S4200 SCS semiconductor characterization system.

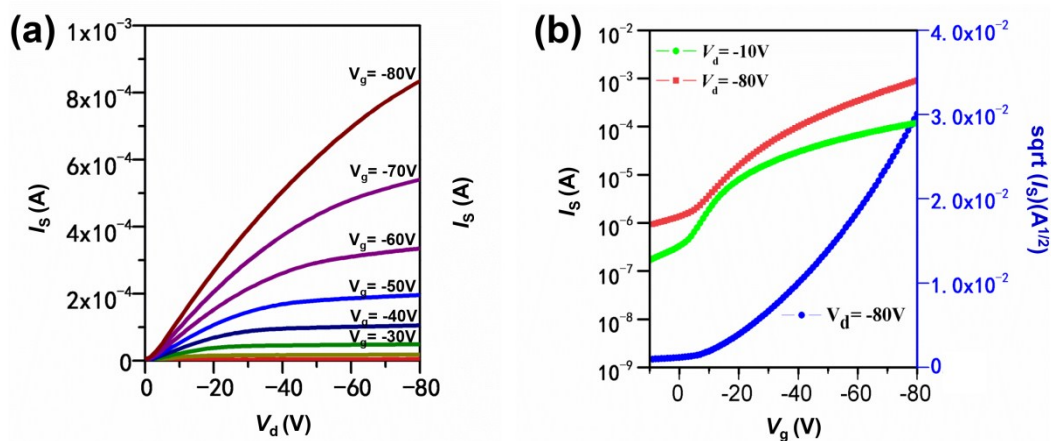


Fig. S14 (a) Output and (b) transfer characteristics of PffBT-3 TGBC device with off-center spin-coated semiconductor layer, with the flow parallel to the source to drain direction. The channel length and channel width is 50 μm and 5 mm respectively. The gate voltage scanning range in output plot is 0 to -80 V with -10 V interval.

8. Experimental section of fabrication polymer solar cells.

Polymer solar cell fabrication and characterization: Pre-patterned ITO-coated glass with a sheet resistance of $< 10 \Omega \text{ sq}^{-1}$ was used as the substrate, which was cleaned by sequential sonication in water containing detergent, deionized water, acetone and isopropanol followed by UV/ozone (BZS250GF-TC, HWOTECH, Shenzhen) treatment for 15 min. ZnO precursor was prepared according to the published procedure.⁶ The precursor solution was spin-coated (3000 rpm for 20 s) onto the pre-patterned ITO-coated glass. The films were annealed at 200 $^{\circ}\text{C}$ for 30 min in air, and then transferred into a N_2 -filled glovebox. The ZnO film thickness is ~ 30 nm. A PFN (0.2 mg/ml) in methanol solution was spin-coated onto the ZnO layer. Polymer (12 mg/ml):PC₇₁BM blend (varied w/w ratios) solutions were prepared in *o*-DCB with 3 vol% 1,8-octanedithiol (ODT). To completely dissolve the polymer, the blend solutions should be stirred on a hot plate at 120 $^{\circ}\text{C}$ overnight. Before spin-coating, both blend

solutions and ITO substrates were preheated at 110 °C, and then the active layers were spin-coated onto the ZnO/PFN interfacial layer. To optimize the active layer thickness, the spin rate and the concentration of the blend were systematically varied. Finally, MoO_x (~10 nm) and Ag (~100 nm) were thermally evaporated using a shadow mask under vacuum (pressure ca. 10⁻⁴ Pa). The effective area for the devices is 0.045 cm². For device characterization, all current-voltage (I-V) characteristics of the devices was measured under simulated AM1.5G irradiation (100 mW/cm²) using a Xe lamp-based SS-F5-3A Solar Simulator (Enli Technology, Inc.). A Xe lamp equipped with an AM1.5G filter was used as the white light source. The light intensity was controlled with an NREL-calibrated Si solar cell with a KG-5 filter. The external quantum efficiency (EQE) was measured by a QE-R3011 measurement system (Enli Technology, Inc.).

SCLC mobility measurements: Hole and electron mobility were measured using the space charge limited current (SCLC) method. Device structures of ITO/PEDOT:PSS/Polymer:PC₇₁BM/MoO₃/Ag and ITO/ZnO/Polymer:PC₇₁BM/Ca/Al were used for hole-only devices and electron-only devices, respectively. The SCLC mobilities were calculated by MOTT-Gurney equation:

$$J = \frac{9}{8} \epsilon_0 \epsilon_r \mu \frac{V^2}{d^3}$$

Where J is the current density, ϵ_r is the relative dielectric constant of active layer material usually 2-4 for organic semiconductors, herein we use a relative dielectric constant of 3.9 for polymer and 3.0 for PC₇₁BM, ϵ_0 is the permittivity of empty space, μ is the mobility of hole or electron and d is the thickness of the active layer, V is the internal voltage in the device, and $V = V_{\text{app}} - V_{\text{bi}}$, where V_{app} is the voltage applied to the device, and V_{bi} is the built-in

voltage resulting from the relative work function difference between the two electrodes (in the hole-only and the electron-only devices, the V_{bi} values can be neglected).

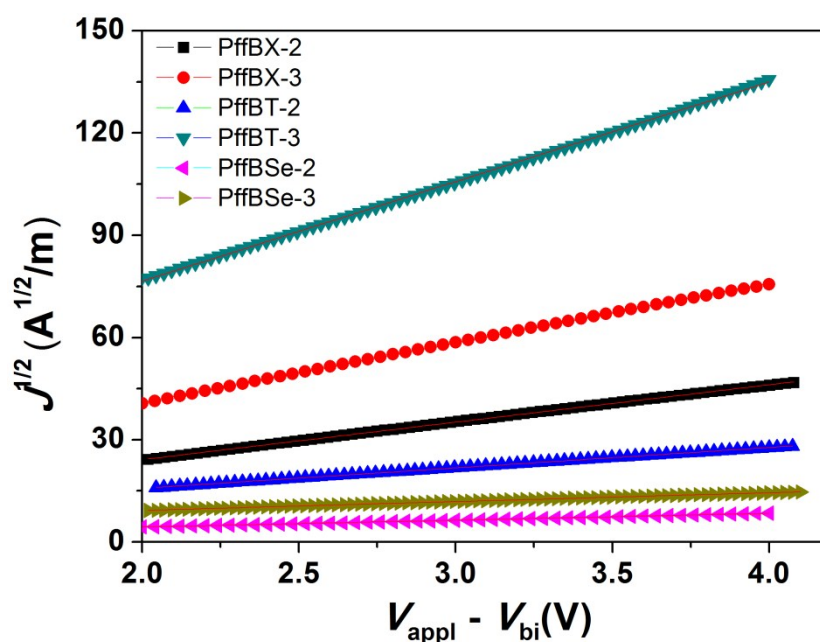


Fig. S15 Hole mobility of six PffBZ-based polymer blend films.

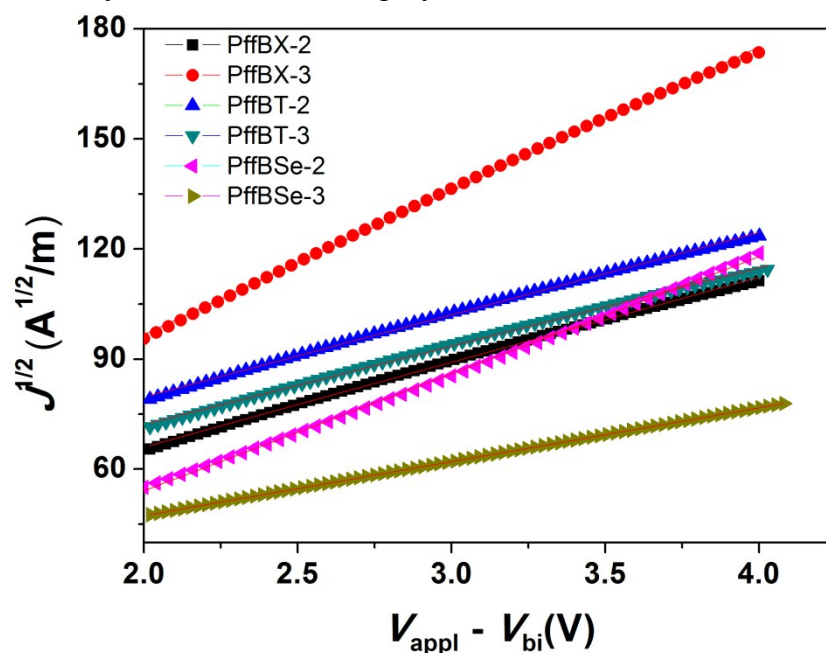


Fig. S16 Electron mobility of six PffBZ-based polymer blend films.

Table S2. Device performance parameters of inverted PSCs with architecture of ITO/ZnO/polymer:PC₇₁BM/MoO₃/Ag device parameters with various polymer:PC₇₁BM ratios.

Polymer	Polymer:PC ₇₁ BM	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE _{max} (PCE _{ave}) [%]
PffBX-2	1:1	0.75	12.63	55.6	5.36(5.27)
	1:1.5	0.74	13.03	57.1	5.47(5.42)
	1:2.0	0.74	12.83	56.7	5.33(5.26)
PffBT-2	1:1	0.64	18.08	53.4	6.13(6.05)
	1:1.5	0.65	20.01	57.2	7.42(7.28)
	1:2.0	0.62	18.90	46.6	5.49(5.25)
PffBSe-3	1:1.0	0.58	8.03	40.3	1.89(1.82)
	1:1.5	0.57	11.70	43.7	2.89(2.86)
	1:2.0	0.54	3.48	45.9	0.86(0.85)

Table S3. Device performance parameters of inverted cells with architecture of ITO/ZnO/polymer:PC₇₁BM/MoO₃/Ag having varied active layer thickness. 3% (volume) of ODT is used as the processing additive.

Polymer	Blend thickness [nm]	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE _{max} (PCE _{ave}) [%]
PffBX-2	164	0.74	9.19	61.7	4.19(4.10)
	129	0.74	13.03	57.1	5.47(5.42)
	117	0.73	13.70	53.5	5.37(5.27)
PffBT-2	148	0.64	19.72	50.0	6.30(6.25)
	181	0.65	20.01	57.2	7.42(7.28)
	204	0.65	18.31	48.5	5.80(5.64)
	242	0.64	19.82	40.6	5.16(5.02)
PffBSe-3	64	0.49	13.30	40.5	2.63(2.51)
	95	0.54	12.99	44.2	3.13(3.10)
	117	0.55	13.57	49.3	3.65(3.41)
	153	0.54	13.76	44.8	3.12(3.02)

Table S4. Device performance parameters of inverted cells with architecture of ITO/ZnO/polymer:PC₇₁BM/MoO₃/Ag device parameters with 3vol% ODT and without ODT.

Polymer	additive	V_{oc} [V]	J_{sc} [mA/cm ²]	FF [%]	PCE _{max} (PCE _{ave}) [%]
PffBX-2	w/o	0.74	8.96	56.5	3.76(3.56)
	3vol% ODT	0.74	13.03	57.1	5.47(5.42)
PffBX-3	w/o	0.75	6.06	41.4	1.89

	3vol% ODT	0.75	6.65	48.9	2.44(2.23)
PffBT-2	w/o	0.63	19.06	55.8	6.67(6.61)
	3vol% ODT	0.65	20.01	57.2	7.42(7.28)
PffBT-3	w/o	0.63	16.82	48	5.08(4.99)
	3vol% ODT	0.67	21.46	70.9	10.12(9.81)
PffBSe-2	w/o	0.52	5.20	30.2	0.81
	3vol% ODT	0.53	13.30	33.3	2.32(2.11)
PffBSe-3	w/o	-	-	-	-
	3vol% ODT	0.55	13.57	49.3	3.65(3.41)

9. Polymer film morphology and microstructure

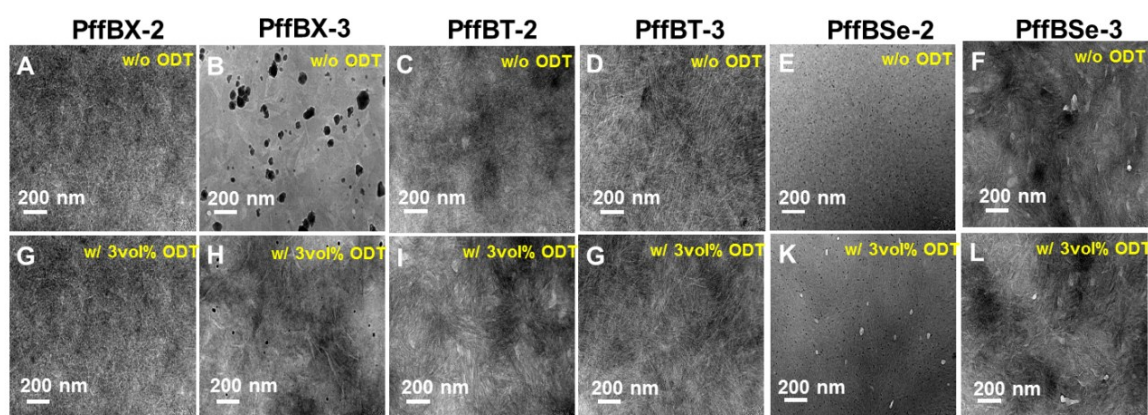


Fig. S17 TEM images of the active containing PffBX-2:PC₇₁BM (A, G), PffBX-3:PC₇₁BM (B, H), PffBT-2:PC₇₁BM (C, I), PffBT-3:PC₇₁BM (D, G) PffBSe-2PC₇₁BM (E, K), and PffBSe-3:PC₇₁BM (F, L) blend films prepared without processing additive ODT and with processing additive ODT.

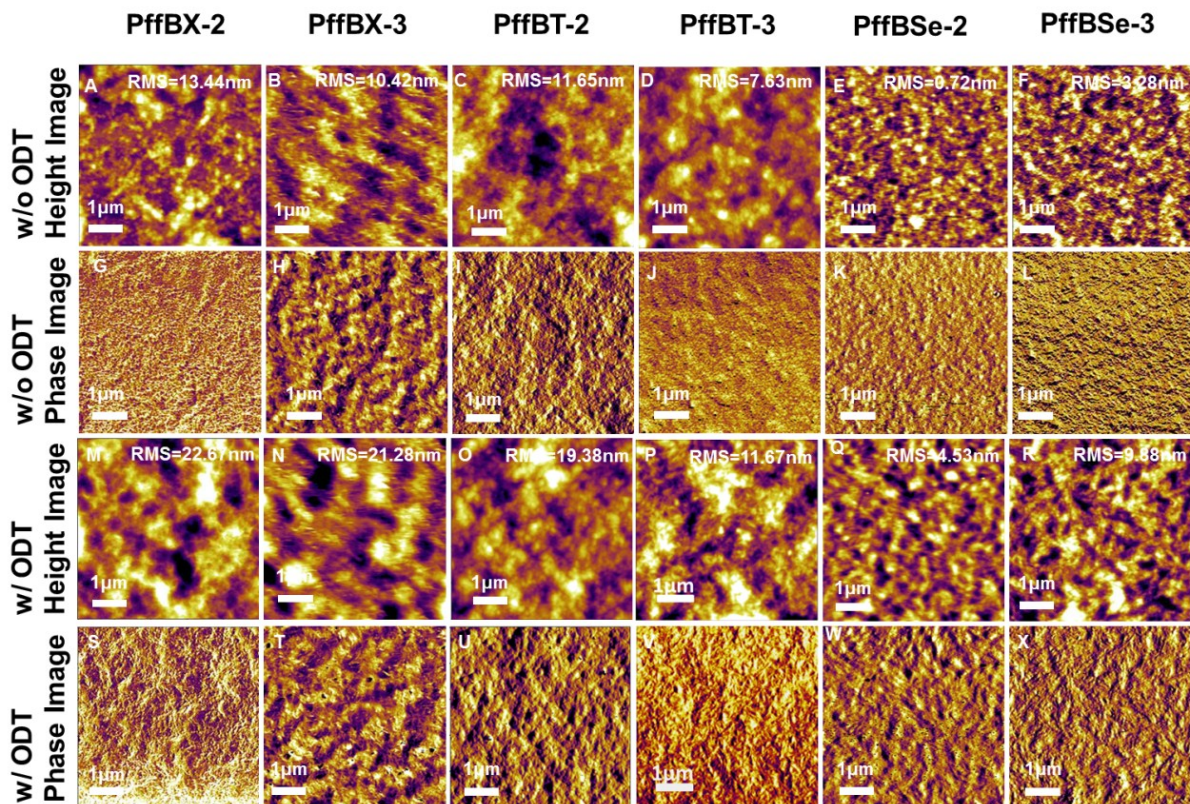


Fig. S18 Tapping-mode AFM height and phase image of polymer:PC₇₁BM blend films of PffBX-2 (A, G, M, S), PffBX-3 (B, H, N, T), PffBT-2 (C, I, O, U), PffBT-3 (D, J, P, V), PffBTSe-2 (E, K, Q, W) and PffBSe-3 (F, L, R, X) processed without (1st and 2nd row) and with (3rd and 4th rows) additive ODT. The image size is 5 μm \times 5 μm .

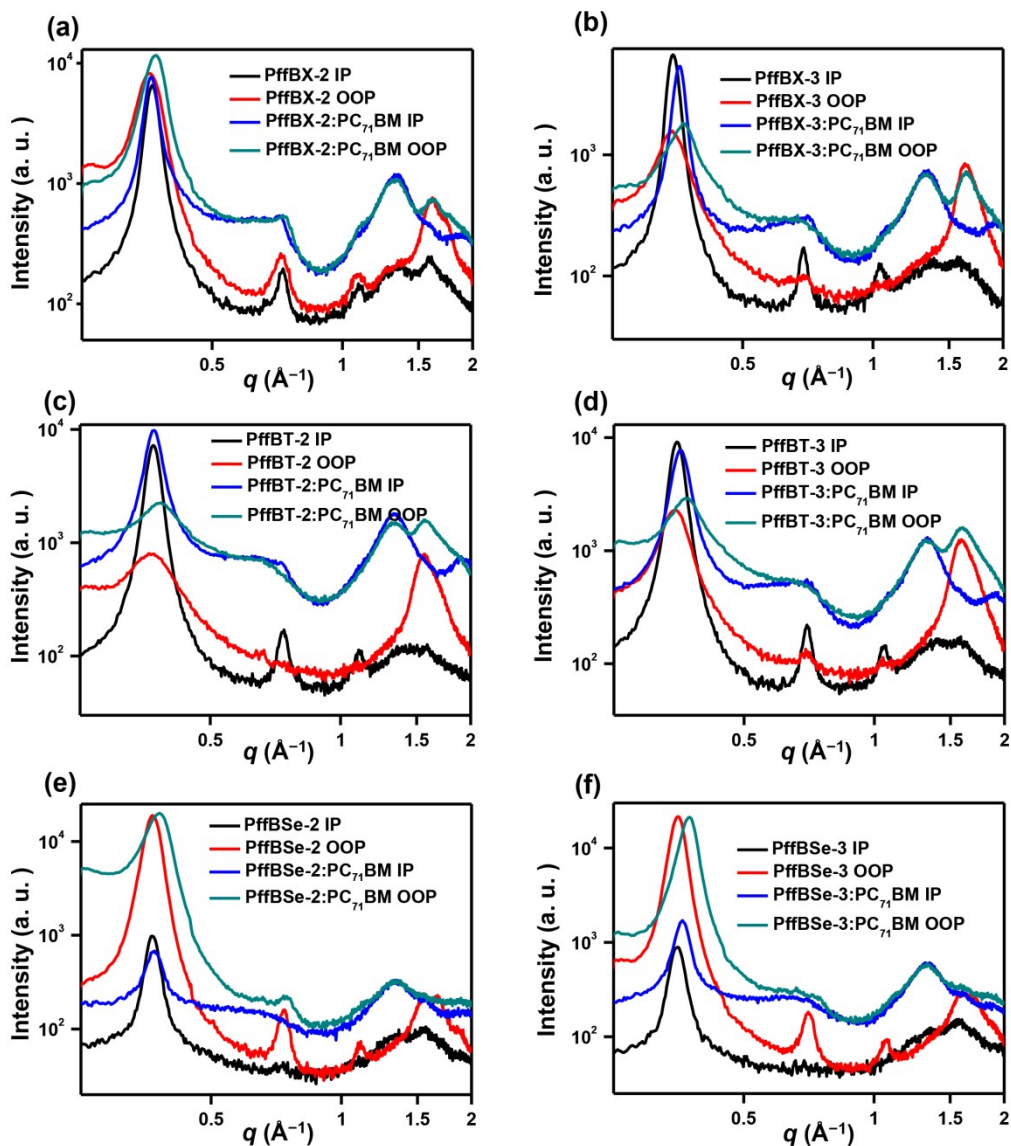


Fig. S19 In-plane (IP) and out-of-plane (OOP) line-cut profiles of 2D-GIXD measurements.

Table S5. Summary of the lamellar distances, the π - π stacking distances, and CCLs of thermal annealed pure films and blend films.

Polymer	Crystallographic parameters		Pure film	BHJ film
PffBX-2	q_{xy} profile (100)	q [\AA^{-1}]	0.36	0.36
		d -spacing [\AA]	17.5	17.5
		CCL [\AA]	209.5	216.8
	q_z profile (100)	q [\AA^{-1}]	0.36	0.37
		d -spacing [\AA]	17.5	17.0
		CCL [\AA]	113.6	125.7
q_z profile	q [\AA^{-1}]	1.62	1.62	

	(010)	d -spacing [Å]	3.90	3.90
PffBX-3	q_{xy} profile (100)	q [Å ⁻¹]	0.34	0.36
		d -spacing [Å]	18.5	17.5
		CCL [Å]	245.7	239.7
	q_z profile (100)	q [Å ⁻¹]	0.34	0.36
		d -spacing [Å]	18.5	17.5
		CCL [Å]	90.2	91.7
	q_z profile (010)	q [Å ⁻¹]	1.63	1.64
		d -spacing [Å]	3.90	3.80
	PffBT-2	q_{xy} profile (100)	q [Å ⁻¹]	0.37
d -spacing [Å]			17.0	17.0
CCL [Å]			198.5	173.0
q_z profile (100)		q [Å ⁻¹]	0.37	0.38
		d -spacing [Å]	17.0	16.5
		CCL [Å]	56.7	57.6
q_z profile (010)		q [Å ⁻¹]	1.57	1.57
		d -spacing [Å]	4.0	4.0
PffBT-3		q_{xy} profile (100)	q [Å ⁻¹]	0.35
	d -spacing [Å]		18.0	17.5
	CCL [Å]		204.2	160.7
	q_z profile (100)	q [Å ⁻¹]	0.35	0.37
		d -spacing [Å]	18.0	17.0
		CCL [Å]	101.4	76.6
	q_z profile (010)	q [Å ⁻¹]	1.59	1.60
		d -spacing [Å]	4.0	3.9
	PffBSe-2	q_{xy} profile (100)	q [Å ⁻¹]	0.37
d -spacing [Å]			17.0	17.0
CCL [Å]			211.1	162.2
q_z profile (100)		q [Å ⁻¹]	0.37	0.38
		d -spacing [Å]	17.0	16.5
		CCL [Å]	172.5	107.0
q_z profile (010)		q [Å ⁻¹]	1.57	-
		d -spacing [Å]	4.0	-
PffBSe-3		q_{xy} profile (100)	q [Å ⁻¹]	0.35
	d -spacing [Å]		18.0	17.5
	CCL [Å]		201.3	186.7
	q_z profile (100)	q [Å ⁻¹]	0.35	0.37
		d -spacing [Å]	18.0	17.0
		CCL [Å]	190.4	155.0
	q_z profile (010)	q [Å ⁻¹]	1.59	-
		d -spacing [Å]	4.0	-

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