Supporting Information

Cyano-Substituted Benzochalcogenadiazole-Based Polymer Semiconductors for Balanced Ambipolar Organic Thin-Film Transistors†

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† Electronic supplementary information (ESI) available.

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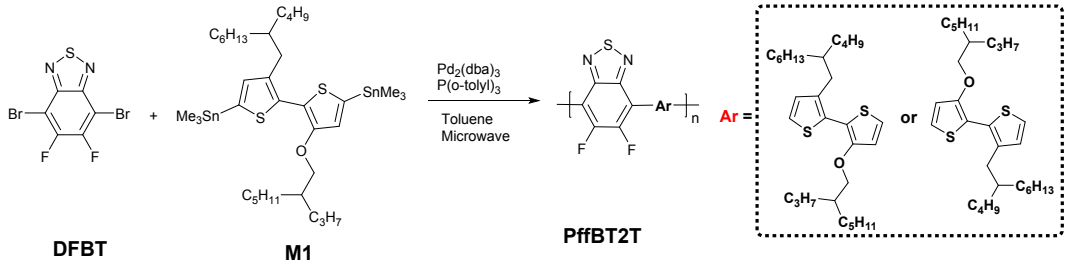
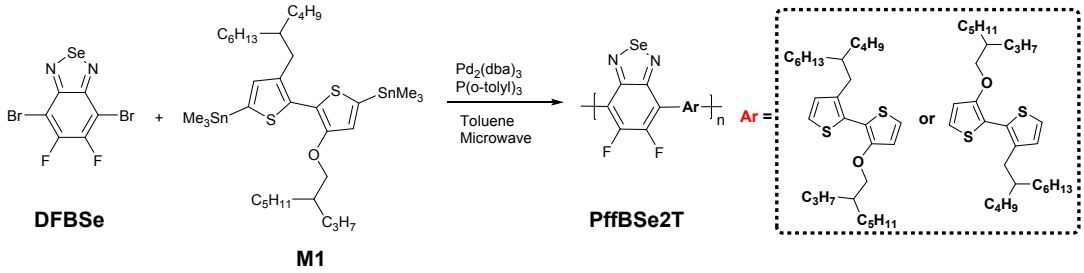
1. Synthesis of PffBT2T and PffBSe2T polymers.



PffBT2T: The polymer was synthesized according to the literature report.[1] M_n = 35.5 kDa, M_w = 58.0 kDa, PDI = 1.63.



PffBSe2T: To a 5 mL microwave vial was added 4,7-dibromo-5,6-fluorobenzo[c][1,2,5] selenadiazole[2] (54.0 mg, 0.14 mmol), the distannylated monomer M1 (118.2 mg, 0.14 mmol), tris(dibenzylideneacetone)dipalladium(0) (1.5 mol%), tri(*o*-tolyl)phosphine (12 mol%), and 2.5 mL anhydrous toluene. The microwave vial and its contents were subjected to 3 pump/purge cycles with argon, then sealed under argon flow. It was then stirred at 80 ºC for 10 min, 100 ºC for 10 min, and 140 ºC for 4.5 h under microwave irradiation. Then, 50 uL of 2-(tributylstanny)thiophene was added and the reaction mixture was stirred under microwave irradiation at 140 ºC for 20 min. Finally, 100 uL of 2-bromothiophene was added and the reaction mixture was stirred at 140 ºC 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 1 h, 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 chloroform fraction was concentrated to ~5 mL then dripped into 150 mL methanol under vigorous stirring. The precipitate was collected by filtration and dried under reduced pressure to afford a deep colored solid as the final product polymer (yield: 70.8%). ^{1}H NMR (400 MHz, 80 ºC, 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 $C_{36}H_{48}F_2N_2OS_2Se$ (%): 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.

2. NMR and HRMS Spectra.

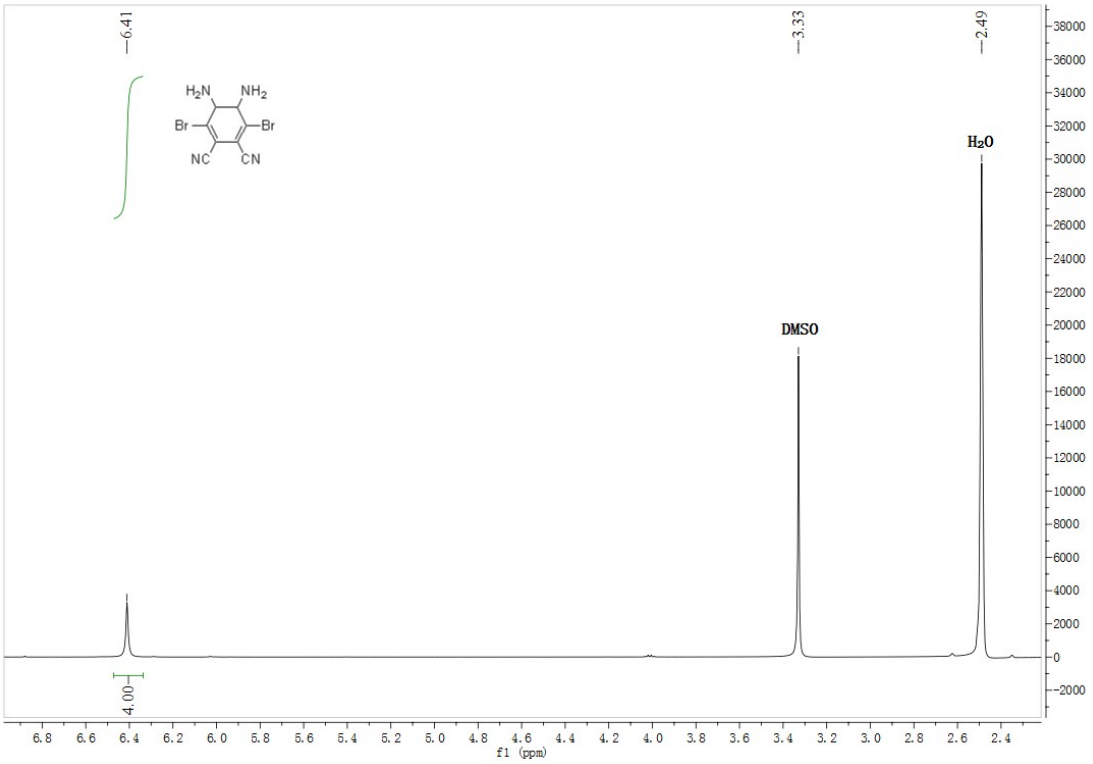


Figure S1. ^{1}H NMR spectrum of compound DCNBr (r.t., in DMSO-d_6).

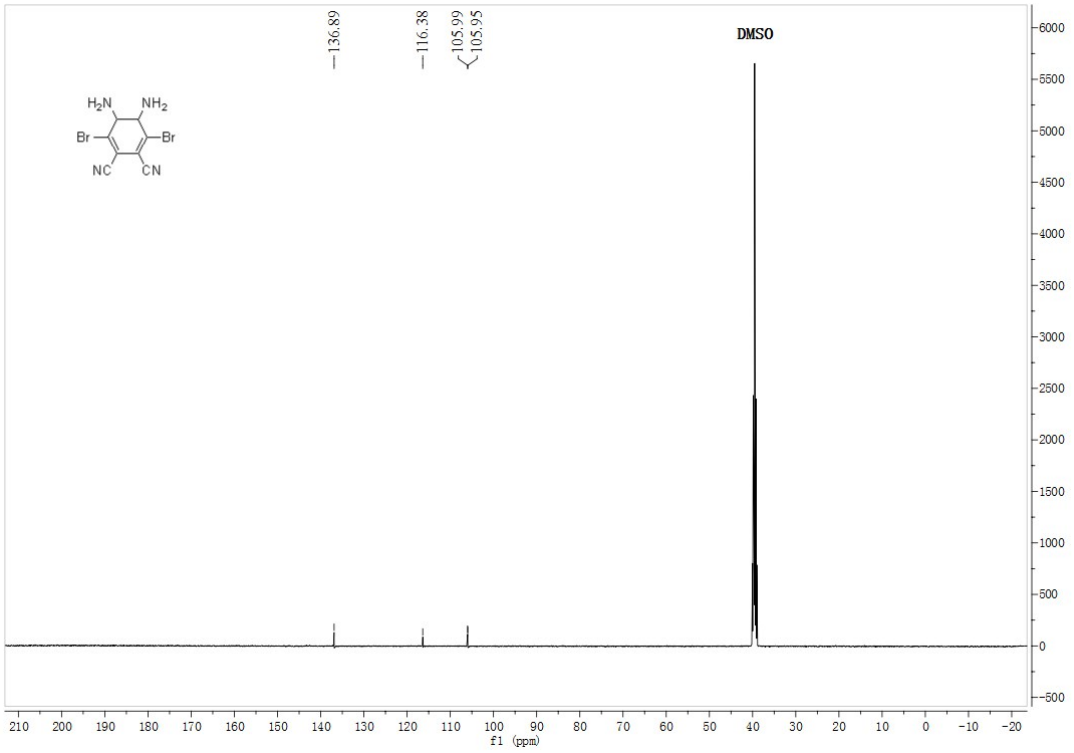


Figure S2. ^{13}C NMR spectrum of compound DCNBr (r.t., in DMSO-d_6).

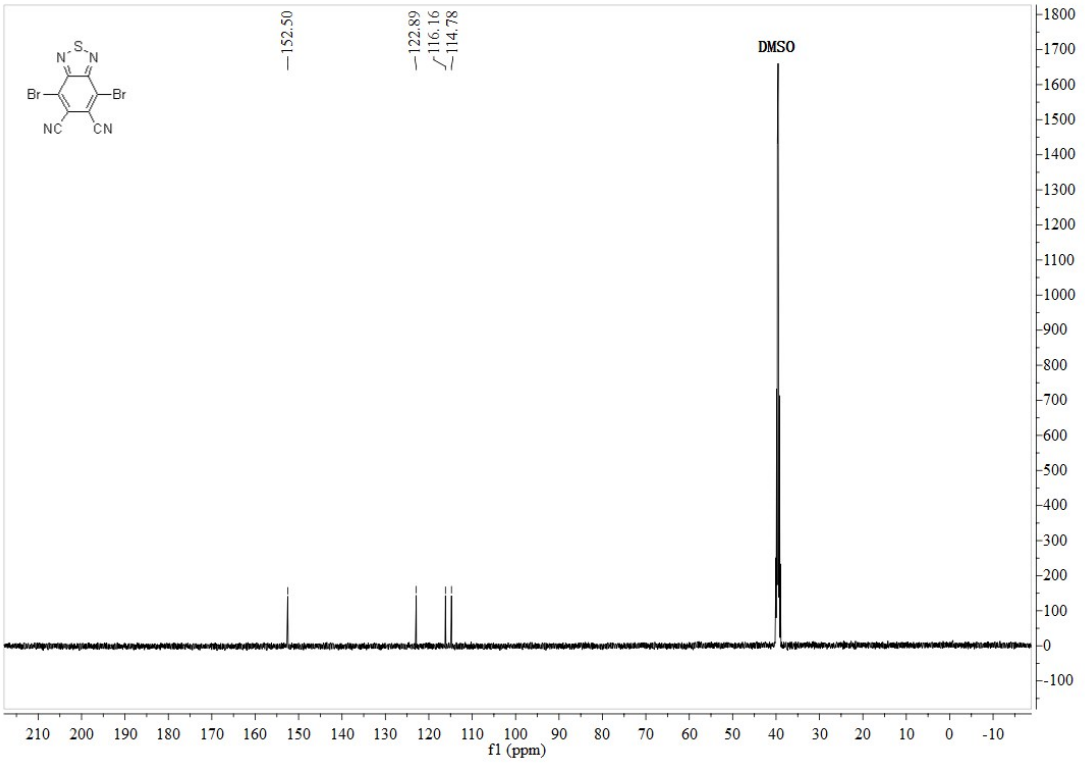


Figure S3. ^{13}C NMR spectrum of monomer DCNBT (r.t., in DMSO-d_6).

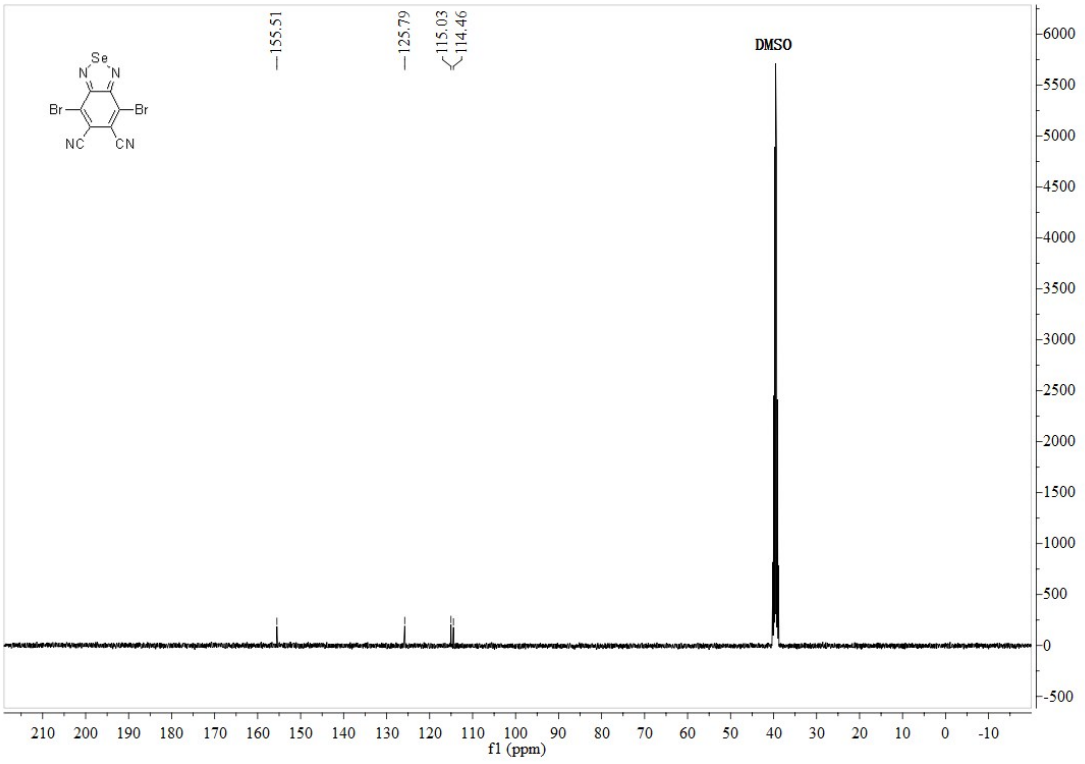


Figure S4. ^{13}C NMR spectrum of monomer DCNBSe (r.t., in DMSO-d_6).

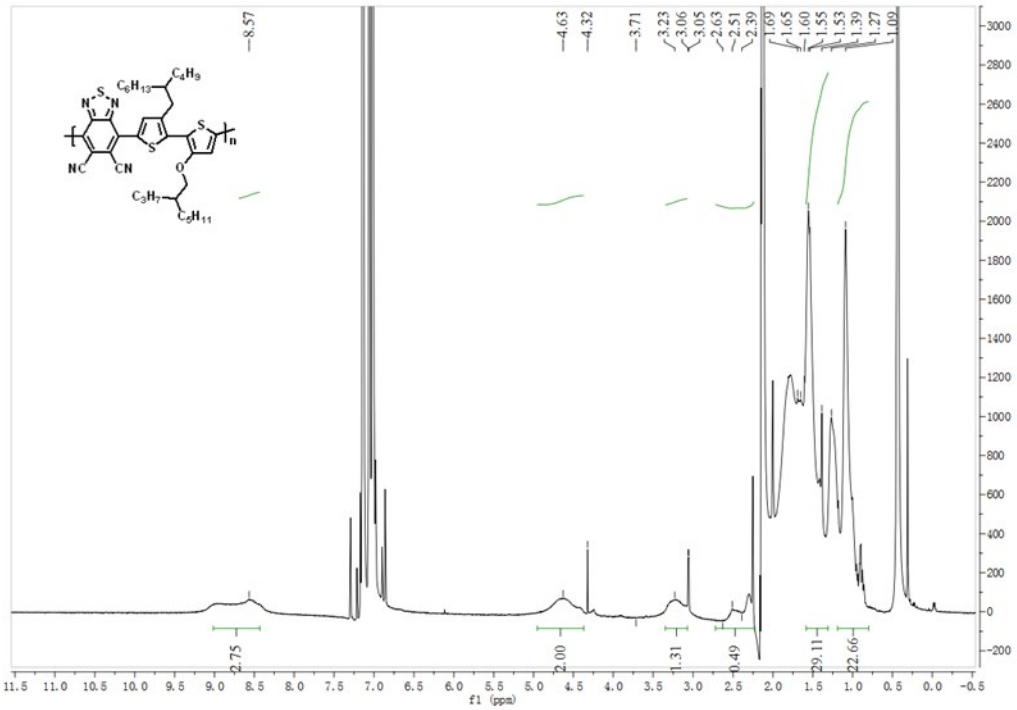


Figure S5. ^{1}H NMR spectrum of polymer PDCNBT2T (80 ºC in Toluene-d_8).

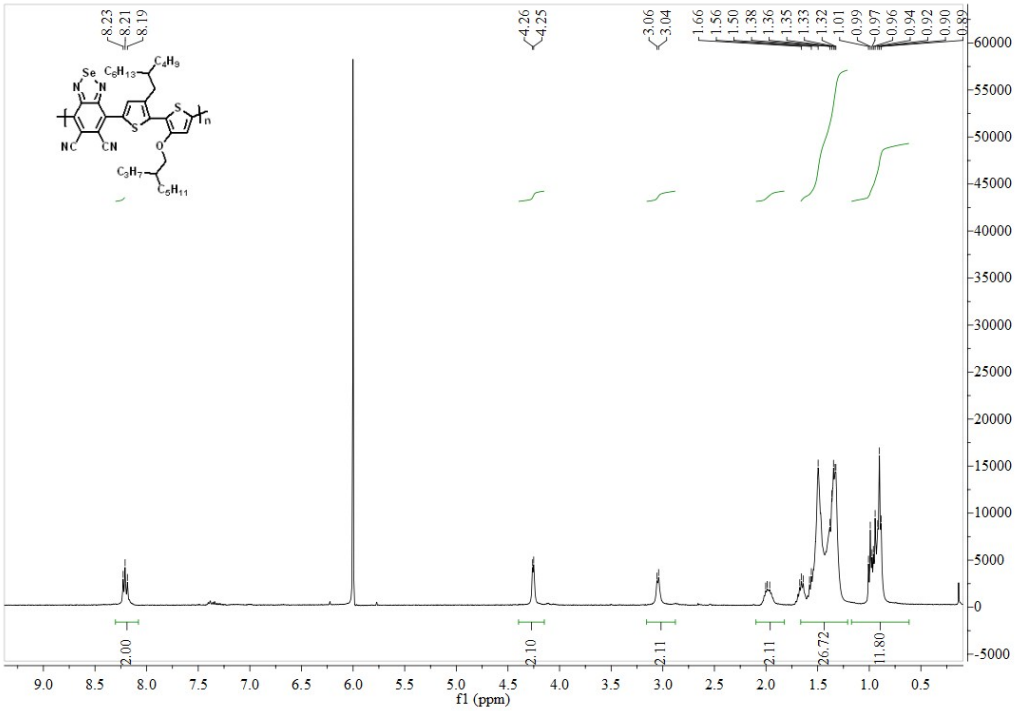


Figure S6. ^{1}H NMR spectrum of polymer PDCNBSe2T (80 ºC in $C_2D_2Cl_4$).

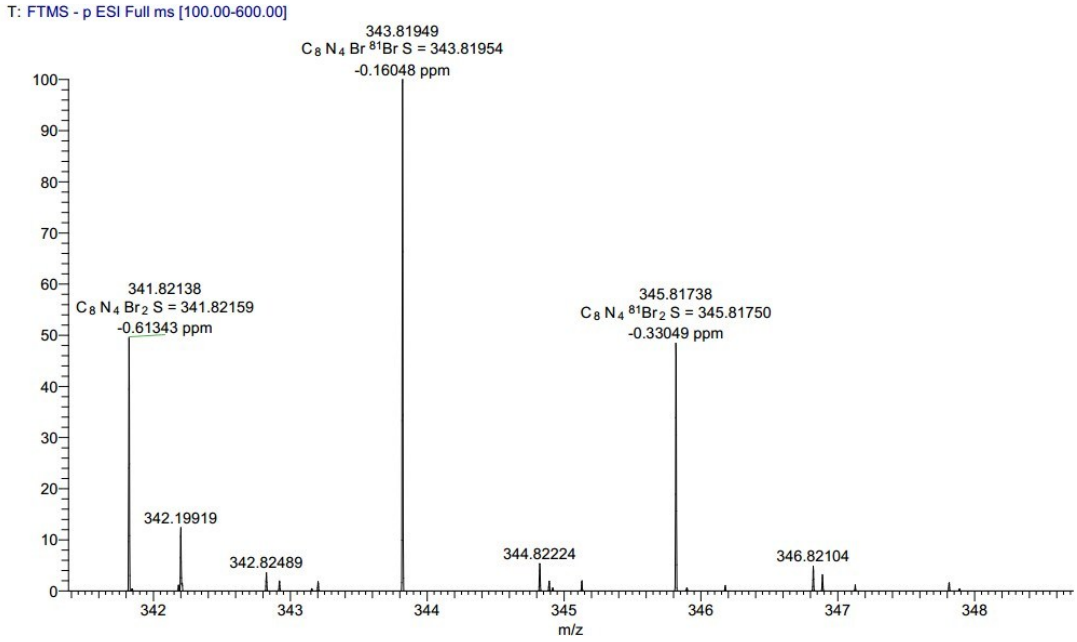


Figure S7. HRMS spectrum of monomer DCNBT.

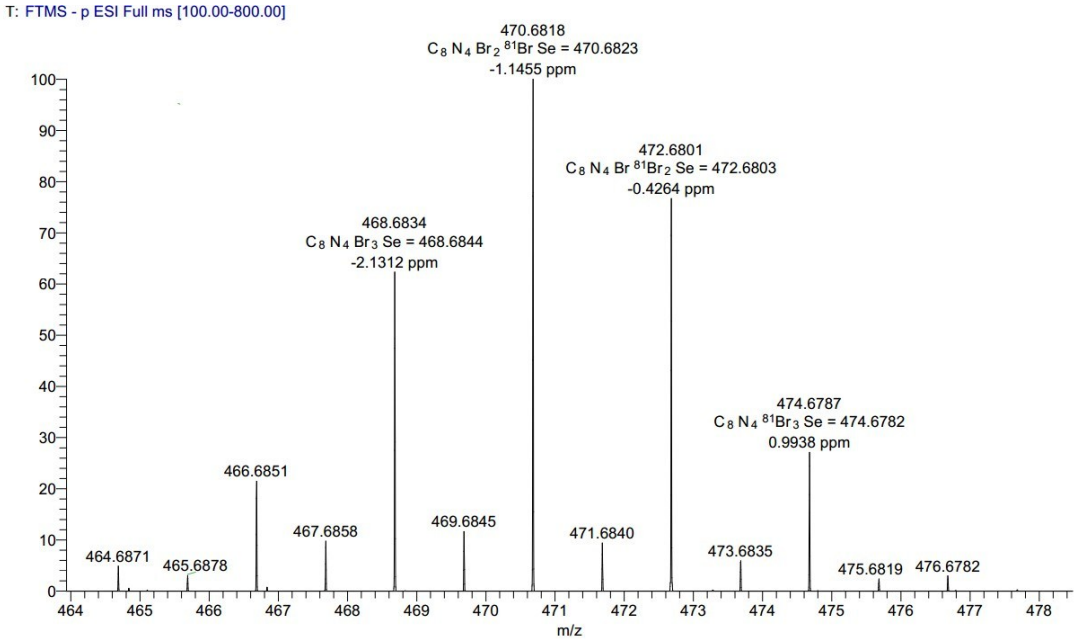


Figure S8. HRMS spectrum of monomer DCNBSe.

3. Other supporting experiment data.

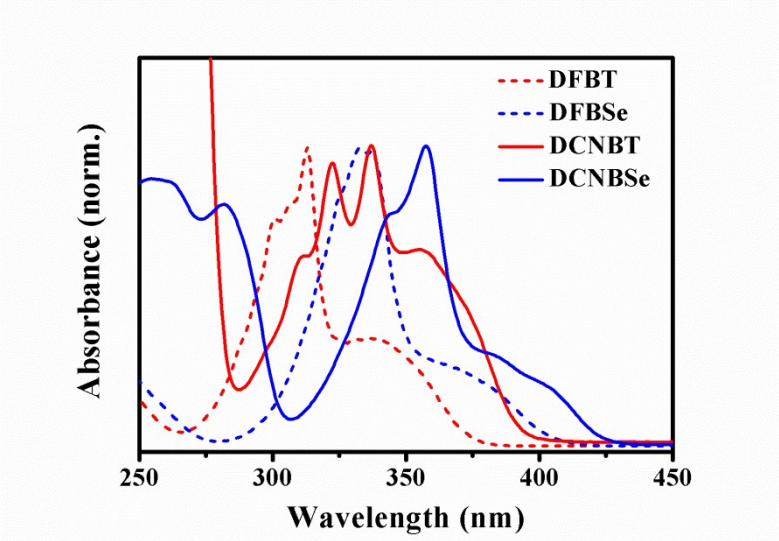


Figure S9. UV-Vis absorption spectra of the monomers (DFBT, DFBSe, DCNBT, and DCNBSe) in diluted solutions (10^{-5} M in dichloromethane).

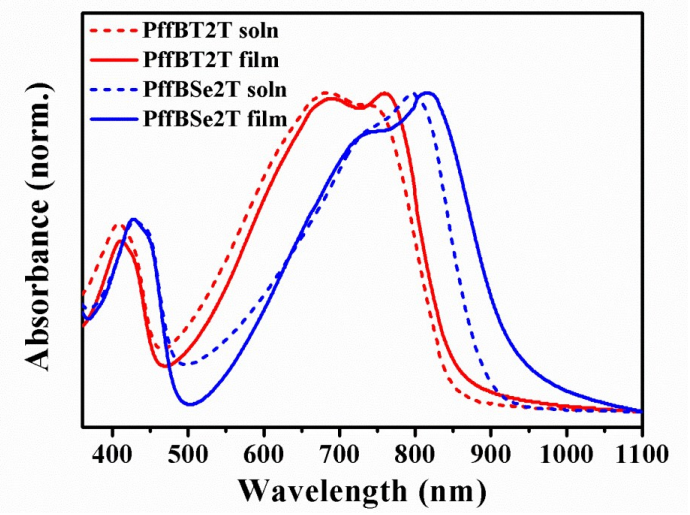


Figure S10. UV-Vis absorption spectra of polymers PffBT2T and PffBSe2T in diluted solutions (10^{-5} M in *o*-DCB) and at thin-film state (spin-coated on glass from 5 mg mL^{-1} *o*-DCB solutions).

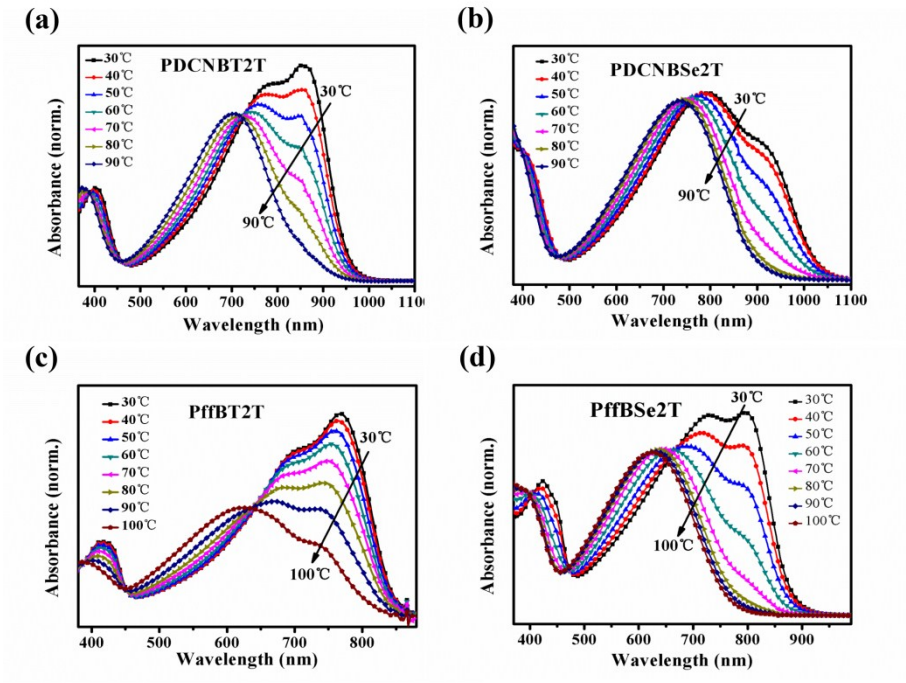


Figure S11. Temperature-dependent UV-Vis absorption spectra of polymers PDCNBT2T, PDCNBSe2T, PffBT2T, and PffBSe2T in diluted solutions (10^{-5} M in *o*-DCB).

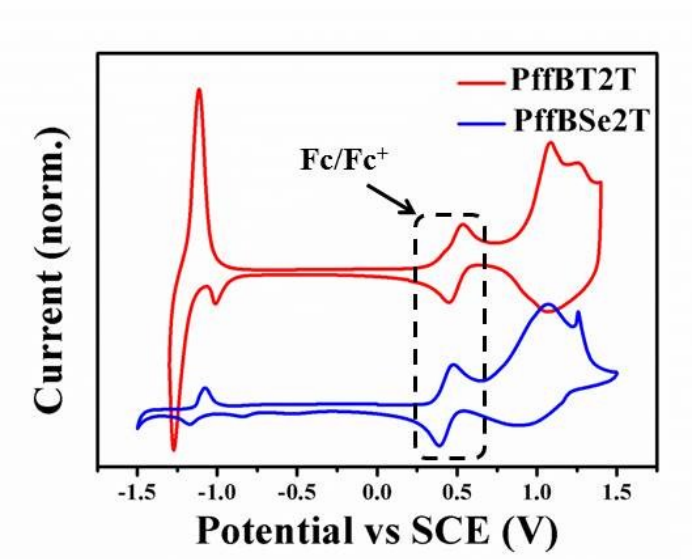


Figure S12. Cyclic voltammograms of PffBT2T and PffBSe2T thin films measured in 0.1 M $(n\text{-Bu})_4\text{N}\cdot\text{PF}_6$ acetonitrile solutions at scan rate of 50 mV s^{-1}.

Table S1. Molecular weights, electrochemical and optical properties of polymer PffBT2T and PffBSe2T.

Polymer	M_n [kDa][a)]	PDI	λ_{max} (soln) [nm][b)]	λ_{max}(film) [nm][c)]	E_g^{opt} [eV][c)]	E_{HOMO} [eV][d)]	E_{LUMO} [eV][d)]	E_{LUMO} [eV][e)]
PffBT2T	35.5	1.63	748	759	1.46	−5.20	−3.44	−3.74
PffBSe2T	17.2	1.56	799	820	1.33	−5.12	−3.61	−3.79

a) High-temperature GPC at 150 °C, versus polystyrene standards using trichlorobenzene as the eluent; [b)] Diluted *o*-DCB solution (10^{-5} M); [c)] As-cast thin-film from *o*-DCB solution, $E_g^{opt} = 1240/\lambda_{onset}$ eV. [d)] $E_{HOMO} = -e(E_{ox}^{onset} + 4.80)$ eV, $E_{LUMO} = -e\ (E_{red}^{onset} + 4.8)$ eV, E_{ox}^{onset} and E_{red}^{onset} determined electrochemically using Fc/Fc^+ internal standard. [e)] $E_{LUMO}^{cal} = E_{HOMO} + E_g^{opt}$.

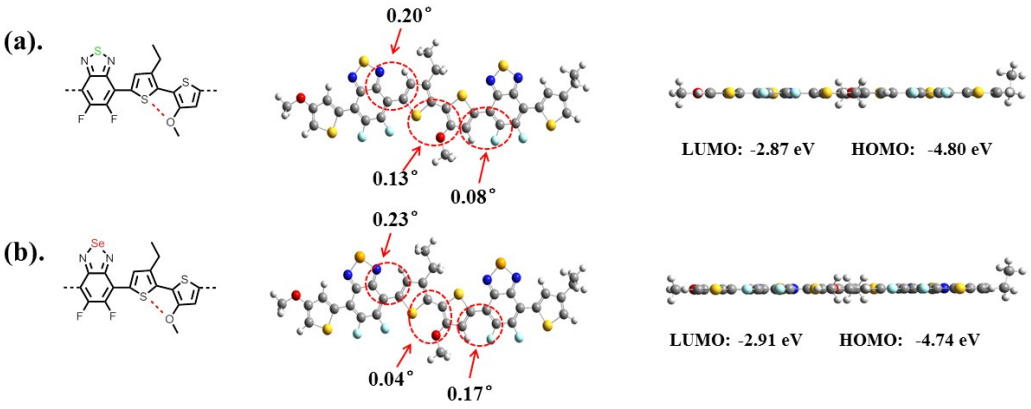


Figure S13. DFT optimized geometries of the dimers for (a) PffBT2T and (b) PffBSe2T at the B3LYP/6-31G (d, p) level. The dihedral angles are indicated in the red circles. The alkyl substituents are truncated for simplicity.

Table S2. TG/BC OTFT performance parameters of PffBT2T and PffBSe2T.

Polymer	T_{anneal} (°C)	μ_{lin} ($cm^2\ V^{-1}\ s^{-1}$) [a)]	μ_{sat} ($cm^2\ V^{-1}\ s^{-1}$) [a)]	V_{th} (V)	I_{on}/I_{off}
PffBT2T [1]	r. t	0.19 (0.18)	0.53 (0.32)	−20	10^3
	250	0.36 (0.32)	0.69 (0.53)	−19	10^4
PffBSe2T	250	0.13 (0.09)	0.28 (0.21)	−28	10^5

[a)] Maximum mobility with average value from at least 5 devices shown in the parentheses.

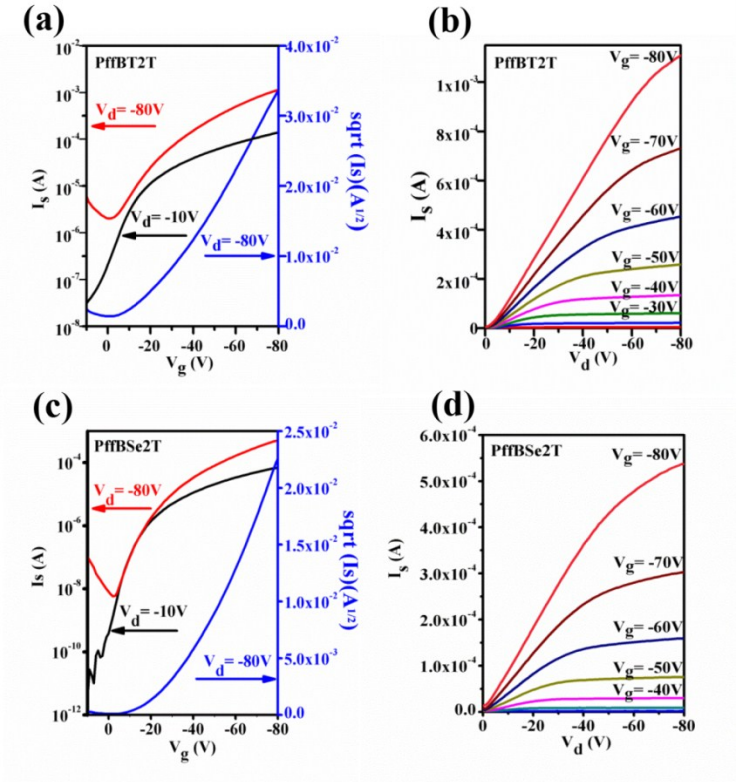


Figure S14. Transfer and output characteristics of (a, b) PffBT2T and (c, d) PffBSe2T-based OTFT devices (L = 10 μm, W = 5 mm) fabricated under the optimal condition. The fabrication and characterization of polymer PffBT2T and PffBSe2T-based OTFTs were according to the literature report.[1]

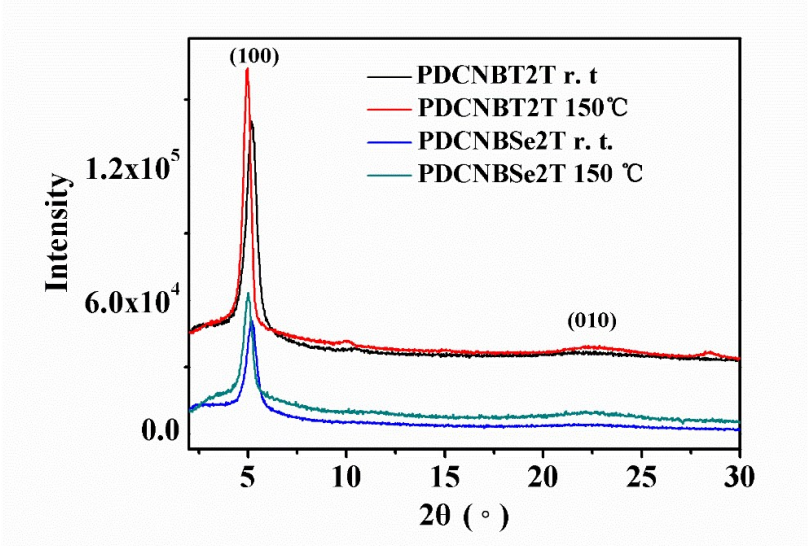


Figure S15. Out-of-plane 2θ XRD measurement of PDCNBT2T and PDCNBSe2T films annealed at room temperature (r. t.) and 150 °C.

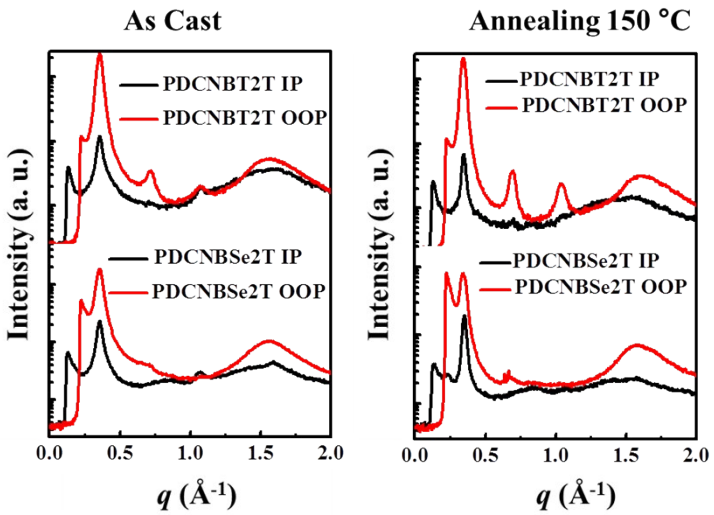


Figure S16. In-plane (IP) and out-of-plane (OOP) line-cut profiles of 2D-GIXD measurements.

Table S3. Summary of the lamellar distances, the π-π-stacking distances, and CCLs of as-cast polymer films and thermal annealed polymer films.

Polymer	Crystallographic parameters		As-cast	Thermal Annealed
PDCNBT2T	q_z profile (100)	q(Å^{-1})	0.36	0.36
		d-spacing (Å)	17.44	17.44
		Correlation length (nm)	12.67	14.76
	q_{xy} profile (100)	q (Å^{-1})	0.36	0.36
		d-spacing (Å)	17.44	17.44
		Correlation length (nm)	11.97	19.55
	q_z profile (010)	q (Å^{-1})	1.56	1.60
		d-spacing (Å)	4.03	4.03
PDCNBSe2T	q_z profile (100)	q(Å^{-1})	0.35	0.35
		d-spacing (Å)	17.94	17.94
		Correlation length (nm)	11.41	11.90
	q_{xy} profile (100)	q(Å^{-1})	0.35	0.35
		d-spacing (Å)	17.94	17.94
		Correlation length (nm)	12.61	18.7
	q_z profile (010)	q(Å^{-1})	1.56	1.56
		d-spacing (Å)	4.03	4.03

Reference

1. S. Shi, Q. Liao, Y. Tang, H. Guo, X. Zhou, Y. Wang, T. Yang, Y. Liang, X. Cheng, F. Liu and X. Guo, *Adv. Mater*., 2016, **28**, 9969-9977.

2. X. He, B. Cao, T. C. Hauger, M. Kang, S. Gusarov, E. J. Luber and J. M. Buriak, *ACS. Appl. Mater. Interfaces*., 2015, **7**, 8188-8199.