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Electronic Supplementary Information (ESI)

Tuning LUMO Levels of Nonfullerene Acceptors via Extension of π-Conjugated Cores for Organic Solar Cells

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Materials

All chemicals and reagent were purchased from commercial sources and used without further purification. All reactions were proceeded under nitrogen atmosphere. Tetrahydrofuran (THF), chloroform (CF), cholorobenzene (CB) and 1-Chloronaphthalene (CN) were purchased from Sigma–Aldrich. PBDB-T, DTBT-2Br and 2FIC were purchased from Derthon Optoelectronic Materials Science Technology Co. Ltd.. BT(SOMe)-Br, CPDT-$Sn(CH_3)_3$, BT-4F were synthesized according to previous method.[s1, s2]

Device Fabrication

OSC devices were fabricated in an conventional structure with ITO/PEDOT:PSS/PBDB-T:NFAs/PDINN/Ag. Pre-patterned ITO-coated glass substrates were cleaned by performing sequential sonication in soapy water, deionized water, acetone, and 2-propanol for 20 min each. The cleaned substrates were further treated with UV-ozone for 15 min to increase the wettability. The PEDOT:PSS solution was spin-coated on the ITO-coated glass at 4000 rpm for 60 s, then annealed in ambient air at 120 °C for 30 min. The PBDB-T and NFAs (BT-4F and BTST-4F) were dissolved in CF with a weight ratio of 45:55 wt% with the donor concentration of 7 mg mL^{-1}, then stirred at 50 °C for 3 h in a nitrogen-filled glovebox. The PBDB-T and DTBT-4F was dissolved in CB with a weight ratio of 45:55 wt% with the donor concentration of 9 mg mL^{-1}, then stirred at 90 °C for 12 h in a nitrogen-filled glovebox. PBDB-T:NFAs blend solution was spin-coated on ITO/PEDOT:PSS substrate at 4000 rpm for BT-4F- and BTST-4F-based blends and at 2000 rpm for DTBT-4F-based blends in a nitrogen-filled glovebox. ITO/PEDOT:PSS/PBDB-T:NFAs were annealed for 10 mins at 140 °C. Then, PDINN dissolved in methanol with concentration of 1 mg mL^{-1} was spin-coated at 3000 rpm for 30 s. Finally, a 100 nm Ag layer for the top electrode were deposited using thermal evaporation at a pressure of less than 4×10^{-6} Torr.

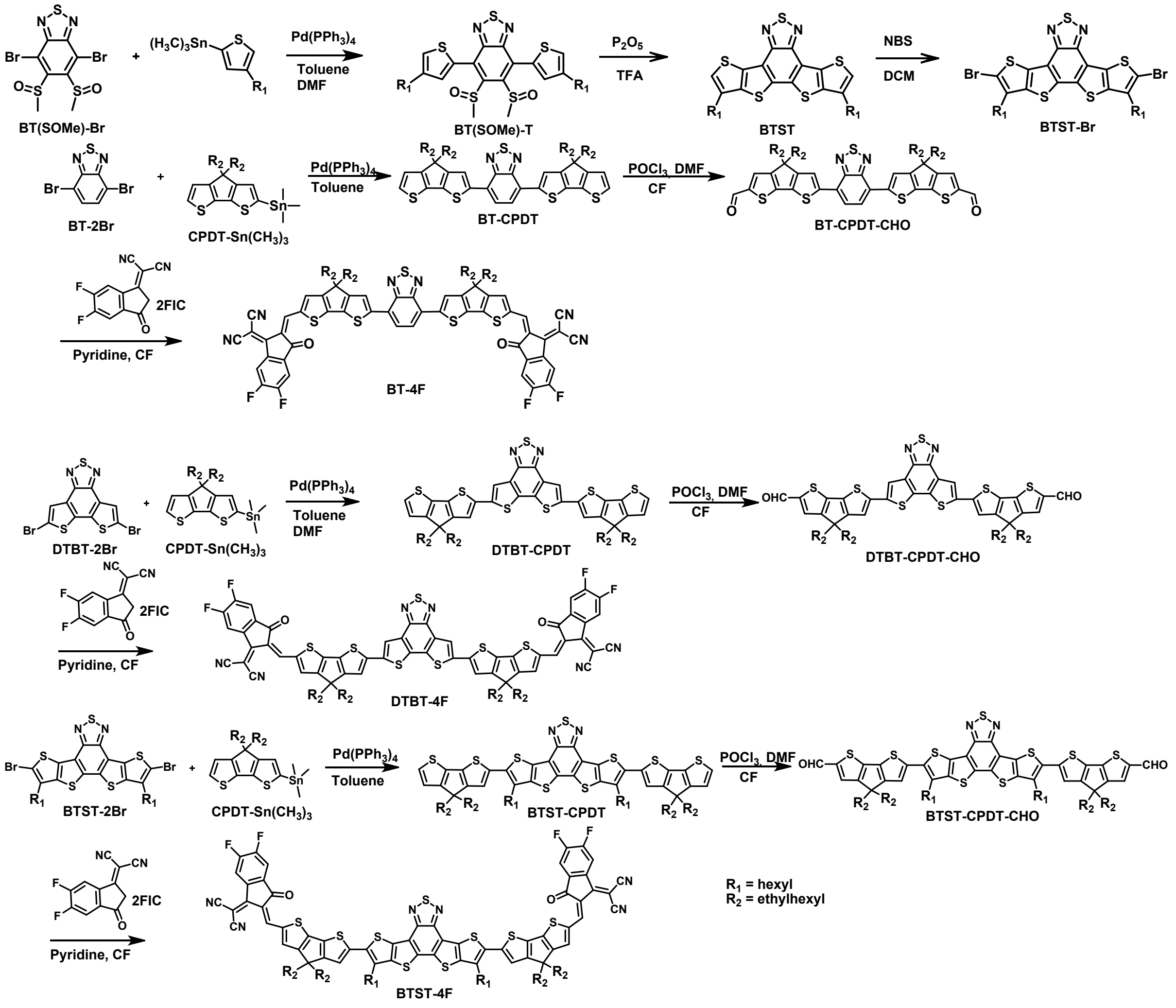
Characterization of OSC devices

J–V characteristics were recorded using a solar simulator (Newport, Oriel Class A) and a source meter (Keithley 4200) in a nitrogen-filled glove box. The illumination was set to AM 1.5G and calibrated to 100 mW cm^{-2} by using a Reference Cell PVM 132 calibrated at the US National Renewable Energy Laboratory. The EQE spectra were measured using a photomodulation spectroscopic setup (Merlin, Oriel) with monochromatic light from a Xenon lamp. The device area of devices was 0.0555 cm^2.

Characterization of Thin Films

For the measurements of thin films, materials were spin-coated onto substrates under identical solutions to those used to fabricate OSC devices. The UV–vis–NIR absorption was recorded using a Varian CARY-5000 UV–Vis spectrophotometer. 2D-GIWAXS measurements were performed using an In-Vacuum Undulator 20B source (11.08 keV) and a 2D CCD Detector (Rayonix SX165, USA) at the 3C beamlines of the Pohang Accelerator Laboratory (PAL) in Korea. The incidence critical angle was around 0.11˚. The AFM images were characterized using Digital Instruments Multimode 8-HR AFM (Bruker).

Synthesis of BT-4F, DTBT-4F and BTST-4F.



Scheme S1. Synthesis routes for BT-4F, DTBT-4F and BTST-4F.

Synthesis of BT(SOMe)-T

A mixture of BT(SOMe)-Br (1,648 mg, 3.94 mmol), (4-hexylthienyl)(trimethyl)stannane (3,000 mg, 9.06 mmol) and Pd(PPh$_3$)$_4$ was dissolved in 40 mL of toluene and 10 mL under nitrogen protection. The reaction mixture was stirred at 110 °C for 15 h. After cooling to room temperature, the reaction mixture was poured into D.W. and extracted with dichloromethane three times. The organic layer was dried over anhydrous MgSO$_4$ and filtered. After the filtrate was concentrated in vacuum, the crude product was purified by silica gel column chromatography (hexane:ethylacetate = 1:3) to afford the product (1,705 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.17 (s, 2H), 7.09 (s, 2H), 3.19 (d, 6H), 2.64 (t, 4H), 1.64 (m, 4H), 1.36-1.20 (b, 12H), 0.85-0.81 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 143.03, 132.61, 132.06, 123.49, 41.52, 31.67, 31.56, 30.45, 30.33, 29.00, 22.64, 14.19.

Synthesis of BTST

To 100 mL round bottom flask, BT(SOMe)-T (500 mg, 0.84 mmol) was put under nitrogen protection and then P_2O_5 (1.192 mg, 8.40 mmol) was added quickly. Trifluoroacetic acid was added to the mixture and stirred at 50 °C for 15 h. After cooling to room temperature, the reaction mixture was poured into crushed ice and stirred vigorously to afford a solid. The crude solid was filtered and dried. The crude solid was purified by silica gel column chromatography (hexane:dichloromethane = 1:2) to afford the product (312 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ δ 6.81 (s, 2H), 2.41 (t, 4H), 1.62 (m, 4H), 1.37-1.32 (b, 12H), 0.95-0.91 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 147.77, 137.07, 136.50, 134.60, 133.94, 123.58, 120.37, 31.69, 29.39, 29.23, 28.56, 22.71, 14.18.

Synthesis of BTST-Br

To a dry 100 mL two-necked round bottom flask, BTST (1,058 mg, 2.0 mmol) was added and dissolved in 30 mL of dichloromethane. The reaction mixture was cooled to 0 °C and N-bromsuccinimide (890 mg, 5.0 mmol) was added in small portions. The reaction mixture was slowly allowed to room temperature and stirred overnight. The reaction mixture was poured into D.W. and extracted with dichloromethane three times. The organic layer was dried over anhydrous $MgSO_4$ and filtered. After the filtrate was concentrated in vacuum, the crude product was purified by silica gel column chromatography (hexane:dichloromethane = 1:3) to afford the product (1,263 mg, 92 %). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 2.54 (t, 4H), 1.64 (m, 4H), 1.44-1.34 (b, 12H), 0.98-0.95 (m, 6H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 147.20, 135.40, 134.73, 133.83, 132.27, 119.67, 113.11, 31.62, 29.22, 28.92, 28.11, 22.69, 14.20.

Synthesis of DTBT-CPDT

A mixture of DTBT-2Br (300 mg, 0.74 mmol) and CPDT-$Sn(CH_3)_3$ (922 mg, 1.63 mmol) was dissolved in 50 mL of toluene under nitrogen protection. After $Pd(PPh_3)_4$ (46 mg, 0.04 mmol) was added into the mixture, the mixture was purged with nitrogen gas for 30 min. The reaction mixture was stirred at 110 °C for 18 h. After cooling to room temperature, the reaction mixture was poured into DW and extracted with dichloromethane three times. The organic layer was dried over anhydrous $MgSO_4$ and filtered. After the filtrate was concentrated in vacuum, the crude product was purified by silica gel column chromatography with hexane/dichloromethane (8/1) as eluent to afford the product (574 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.97 (s, 2H), 7.22 (m, 4H), 6.98 (m, 2H), 1.95 (m, 8H), 1.06-0.98 (b, 36H), 0.88-0.78 (b, 12H), 0.69-0.64 (b, 12H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 158.39, 158.20, 150.06, 138.22, 137.88, 136.58, 132.64, 132.62, 129.37, 125.49, 122.39, 120.26, 118.16, 53.85, 43.33, 35.23, 34.35, 34.22, 31.63, 28.67, 27.52, 27.43, 22.90, 22.85, 22.70, 14.20, 14.16, 10.80.

Synthesis of DTBT-CPDT -CHO

DTBT-CPDT (315 mg, 0.30 mmol) was dissolved in 50 mL of dichloroethane under nitrogen protection. The solution was cooled to 0 °C and then DMF (1 mL) and $POCl_3$ (0.25 mL) was added dropwise. The mixture was stirred at 0 °C for 2 h, room temperature for 30 min and then at 80 °C for 15 h. After cooling to room temperature, the reaction mixture poured into 20 mL of 1 M NaOH solution and extracted with dichloromethane. The organic layer was washed with brine and dried anhydrous $MgSO_4$. The crude product was purified by silica gel column chromatography with Hexane/EA (6/1) as eluent to afford the product (274 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.87 (s, 2H), 7.94 (s, 2H), 7.61 (s, 2H), 7.28 (s, 2H), 2.00 (m, 8H), 1.12 -0.95 (b, 36H), 0.90-0.80 (b, 12H), 0.76-0.69 (b, 12H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 182.41, 158.01, 150.05, 146.88, 143.93, 140.05, 137.53, 136.47, 133.27, 130.42, 129.79, 120.22, 119.63, 54.36, 43.12, 35.38, 34.33, 34.22, 28.59, 27.53, 27.43, 22.79, 14.09, 10.70.

Synthesis of DTBT-4F

A mixture of DTBT-CPDT-CHO (250 mg, 0.23 mmol), 2FIC (267 mg, 1.16 mmol), pyridine (1.0 mL) and chloroform (40 mL) was stirred at 65 °C for 15 h. After cooling to room temperature, the reaction mixture was concentrated in vacuum. The crude product was purified by silica gel column chromatography with chloroform as eluent to afford the product (244 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.79 (s, 2H), 8.39 (s, 2H), 8.02 (s, 2H), 7.69 (s, 2H), 7.57 (s, 2H), 7.40 (s, 2H). 2.13-2.00 (m, 8H), 1.20-0.96 (b, 36H), 0.86-0.69 (m, 24H). ^{13}C NMR(400 MHz, $CDCl_3$, ppm): δ. 185.79, 166.01, 159.66, 157.34, 155.19, 153.40, 150.21, 143.67, 139.39, 137.98, 137.59, 137.15, 134.49, 130.46, 120.86, 120.48, 119.94, 114.86, 114.71, 114.41, 112.38, 112.25, 68.51, 54.41, 43.42, 43.33, 35.79, 35.73, 34.38, 34.24, 29.62, 28.63, 28.57, 27.55, 27.45, 22.78, 13.92, 13.88, 10.57, 10.52,

MS (MALDI-TOF): Calcd. For $C_{86}H_{80}F_4N_6O_2S_7$ (M+H): 1528.43, Found: 1529.18

Synthesis of BTST-CPDT

A mixture of BTST-2Br (1,000 mg, 1.46 mmol) and CPDT-$Sn(CH_3)_3$ (1,894 mg, 3.35 mmol) was dissolved in 60 mL of toluene under nitrogen protection. After $Pd(PPh_3)_4$ (84 mg, 0.07 mmol) was added into the mixture, the mixture was purged with nitrogen gas for 30 min. The reaction mixture was stirred at 110 °C for 18 h. After cooling to room temperature, the reaction mixture was poured into DW and extracted with dichloromethane three times. The organic layer was dried over anhydrous $MgSO_4$ and filtered. After the filtrate was concentrated in vacuum, the crude product was purified by silica gel column chromatography with hexane/dichloromethane (10/1) as eluent to afford the product (1,447 mg, 78%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.21 (m, 4H), 7.00 (m, 2H), 2.98 (t, 4H), 1.97 (m, 8H), 1.85 (m, 4H), 1.51 (m, 4H), 1.60 (m, 8H), 1.16-0.91 (b, 42H), 0.85-0.75 (b, 12H), 0.74-0.63 (b, 12H).

Synthesis of BTST-CPDT -CHO

BTST-CPDT (350 mg, 0.27 mmol) was dissolved in 50 mL of dichloroethane under nitrogen protection. The solution was cooled to 0 °C and then DMF (1 mL) and $POCl_3$ (0.20 mL) was added dropwise. The mixture was stirred at 0 °C for 2 h, room temperature for 30 min and then at 80 °C for 15 h. After cooling to room temperature, the reaction mixture poured into 20 mL of 1 M NaOH solution and extracted with dichloromethane. The organic layer was washed with brine and dried anhydrous $MgSO_4$. The crude product was purified by silica gel column chromatography with Hexane/EA (6/1) as eluent to afford the product (245 mg, 67%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 9.88 (s, 2H), 7.63 (s, 2H), 7.24 (s, 2H), 2.91 (t, 4H), 2.09-1.94 (m, 8H), 1.85-1.74 (m, 4H), 1.52-1.43 (m, 4H), 1.42-1.32 (m, 8H), 1.18-0.87 (b, 42H), 0.83-0.75 (b, 12H), 0.74-0.64 (b, 12H). ^{13}C NMR(400 MHz, $CDCl_3$, ppm): δ. 182.41 162.25 162.15 162.06, 157.70, 148.23, 147.31, 143.60, 140.08, 139.70, 139.67, 136.73, 136.55, 135.43, 132.35, 131.79, 130.55, 121.57, 120.94, 54.31, 43.21, 35.40, 35.36, 34.34, 31.64, 29.56, 29.10, 28.71, 28.70, 28.59, 27.51, 27.39, 22.89, 22.87, 22.81, 22.67, 14.18, 14.14, 14.10, 10.85, 10.65

Synthesis of BTST-4F

A mixture of BTST-CPDT-CHO (250 mg, 0.19 mmol), 2FIC (258 mg, 1.12 mmol), pyridine (1.0 mL) and chloroform (40 mL) was stirred at 65 °C for 15 h. After cooling to room temperature, the reaction mixture was concentrated in vacuum. The crude product was purified by silica gel column chromatography with chloroform as eluent to afford the product (231 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.48 (s, 2H), 8.28 (s, 2h) 7.60-7.47 (m, 4H), 7.33 (s, 2H), 3.0-2.90 (b, 4H), 2.15-1.96 (b, 8H), 1.92-1.82 (b, 4H), 1.60-1.52 (b, 4H), 1.49-1.39 (b, 8H), 1.26-1.05 (b, 36H), 1.03-0.94 (m, 6H), 0.90-0.74 (m, 24H). ^{13}C NMR(400 MHz, $CDCl_3$, ppm): δ. 185.42, 165.83, 159.50, 158.27, 157.84, 155.04, 153.36, 148.63, 144.36, 140.50, 139.24, 138.12, 137.56, 137.23, 137.14, 136.28, 135.71, 134.28, 133.23, 132.84, 121.50, 119.21, 114.41, 112.13, 67.90, 54.27, 43.43, 35.75, 34.44, 34.32, 31.61, 29.58, 29.50, 29.07, 28.70, 28.58, 27.50, 22.89, 22.56, 13.97, 10.68, 10.47. MS (MALDI-TOF): Calcd. For $C_{102}H_{104}F_4N_6O_2S_9$ (M+H): 1808.56, Found: 1809.17.

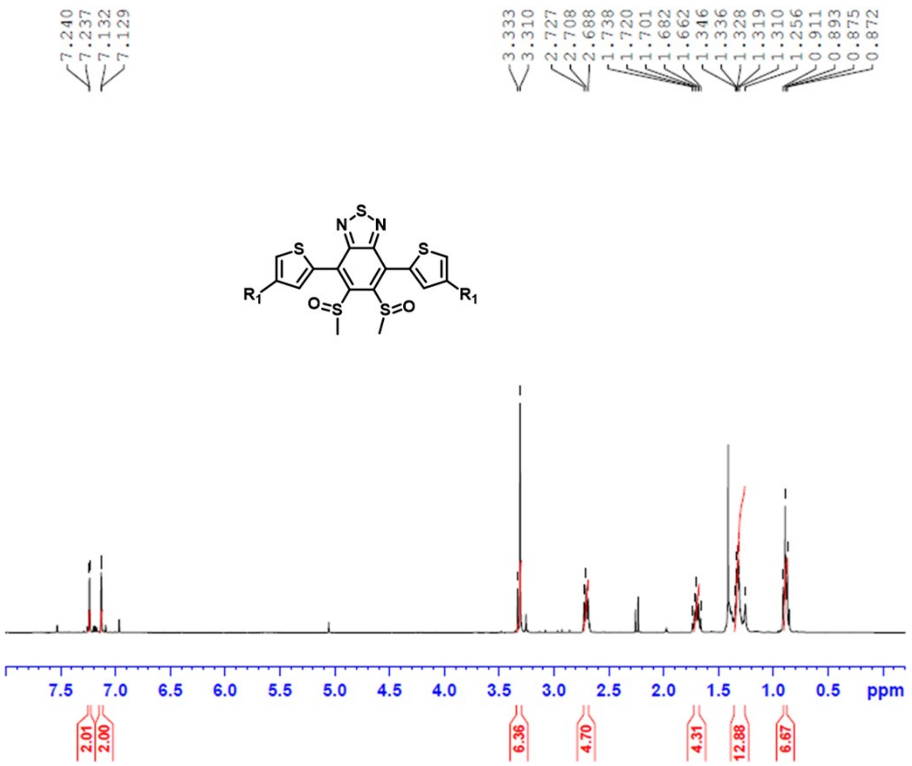


Fig. S1. ^{1}H NMR spectra of BT(SOMe)-T in $CDCl_3$.

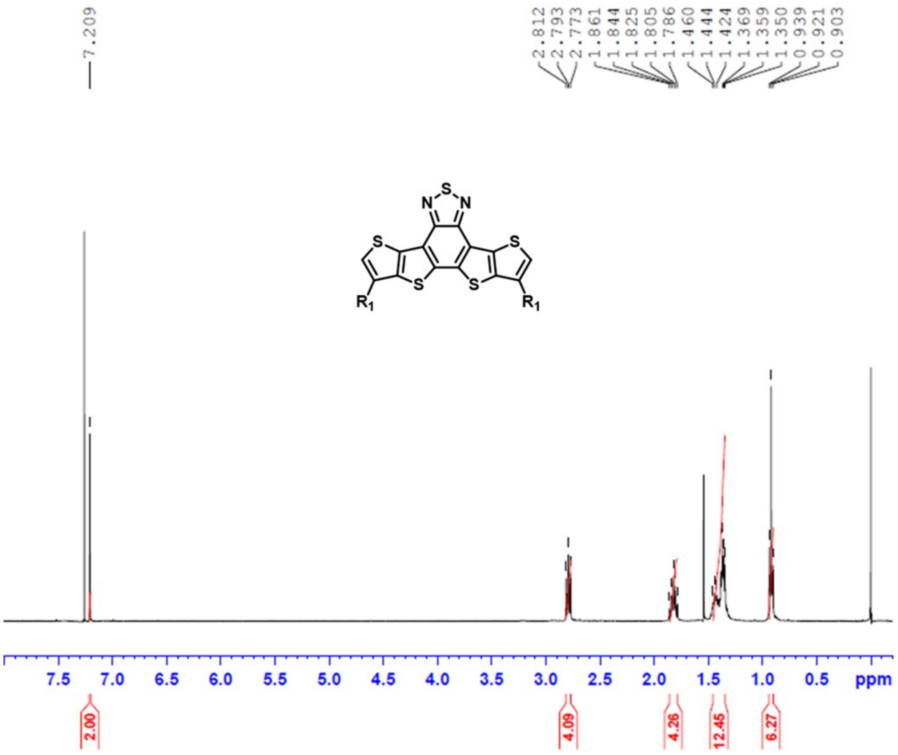


Fig. S2. ^{1}H NMR spectra of BTST in $CDCl_3$.

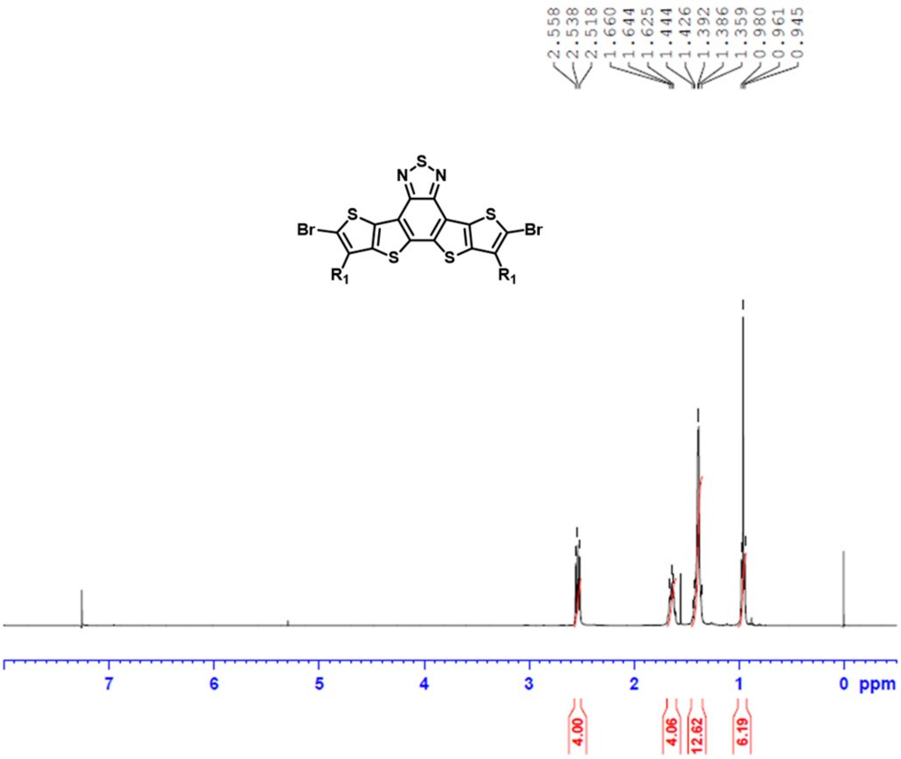


Fig. S3. ^{1}H NMR spectra of BTST-Br in $CDCl_3$.

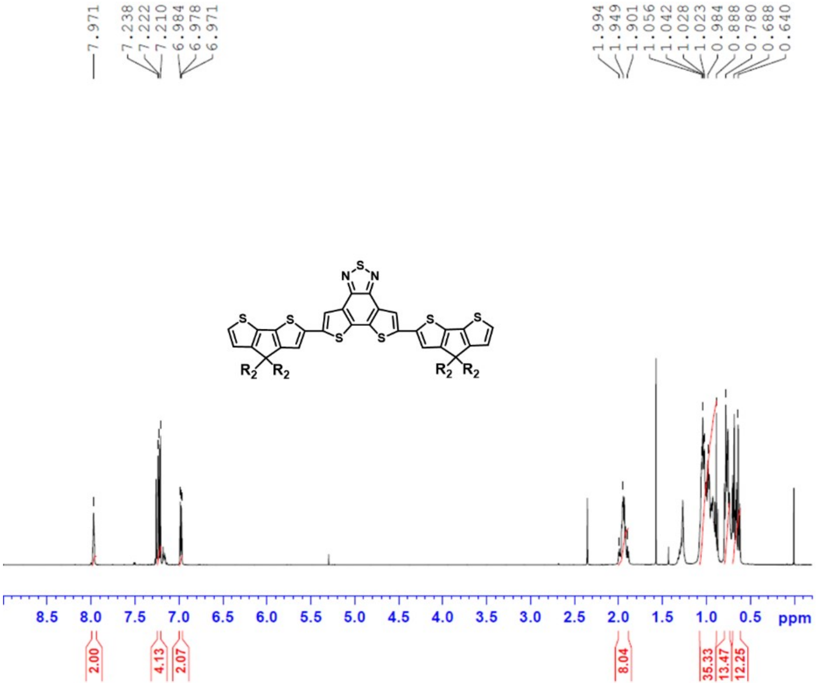


Fig. S4. ^{1}H NMR spectra of DTBT-CPDT in $CDCl_3$.

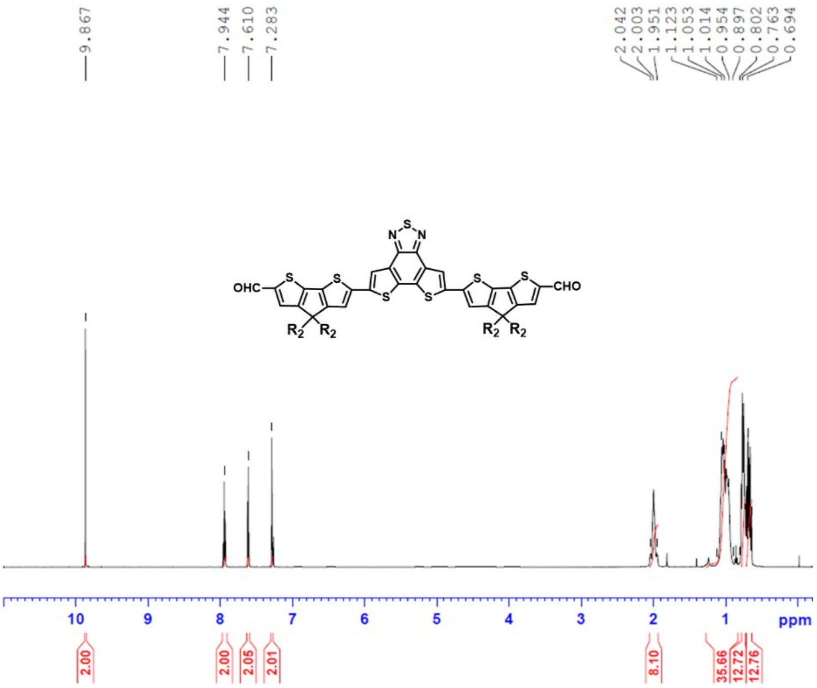


Fig. S5. ^{1}H NMR spectra of DTBT-CPDT-CHO in CDCl$_3$.

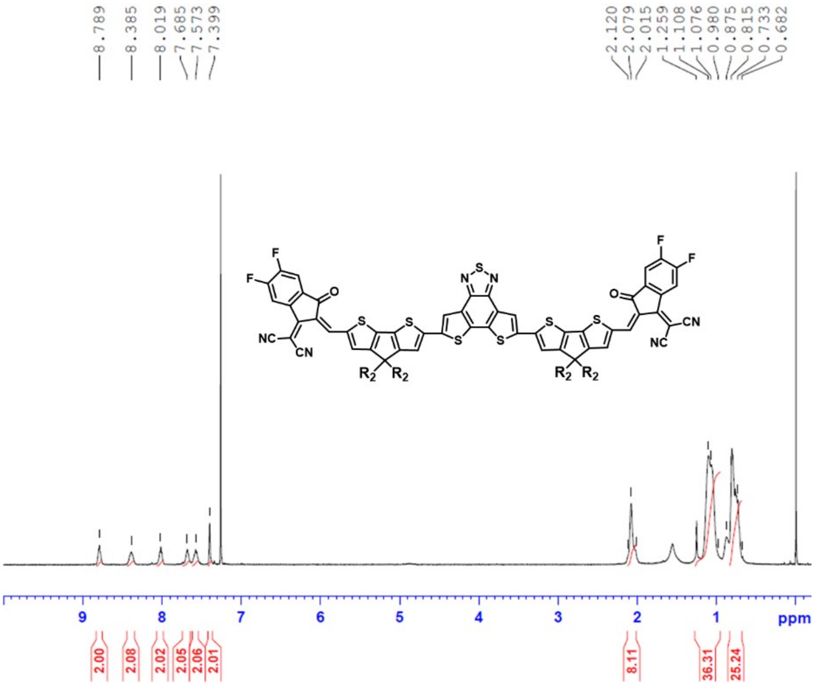


Fig. S6. ^{1}H NMR spectra of DTBT-4F in CDCl$_3$.

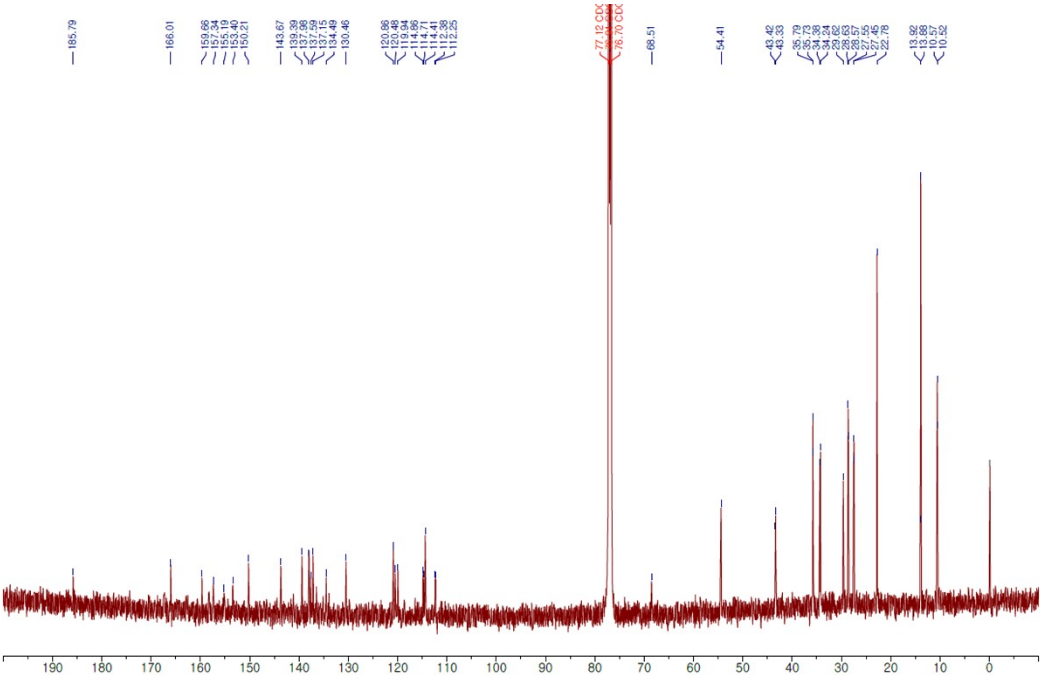


Fig. S7. ^{13}C NMR spectra of DTBT-4F in CDCl$_3$.

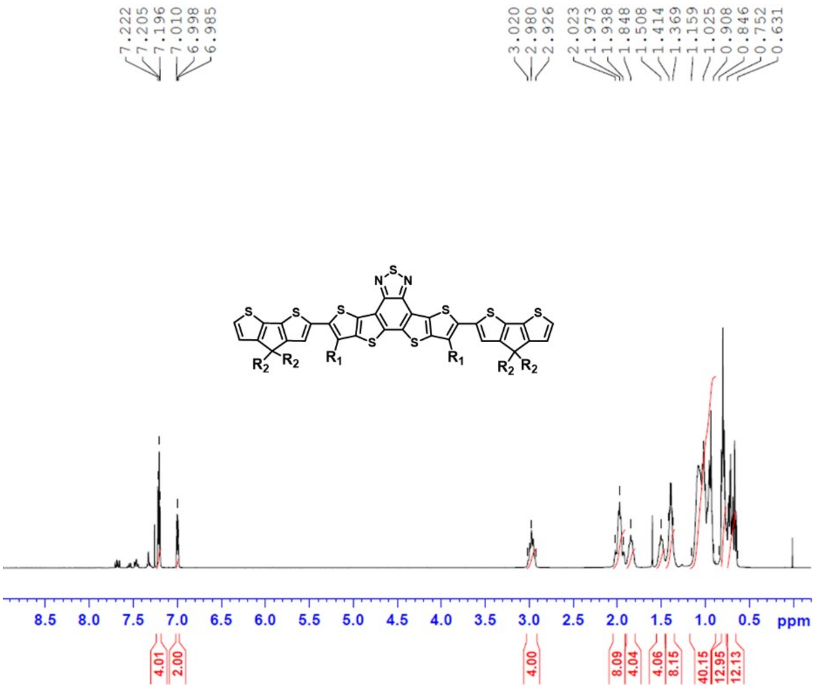


Fig. S8. ^{1}H NMR spectra of BTST-CPDT in CDCl$_3$.

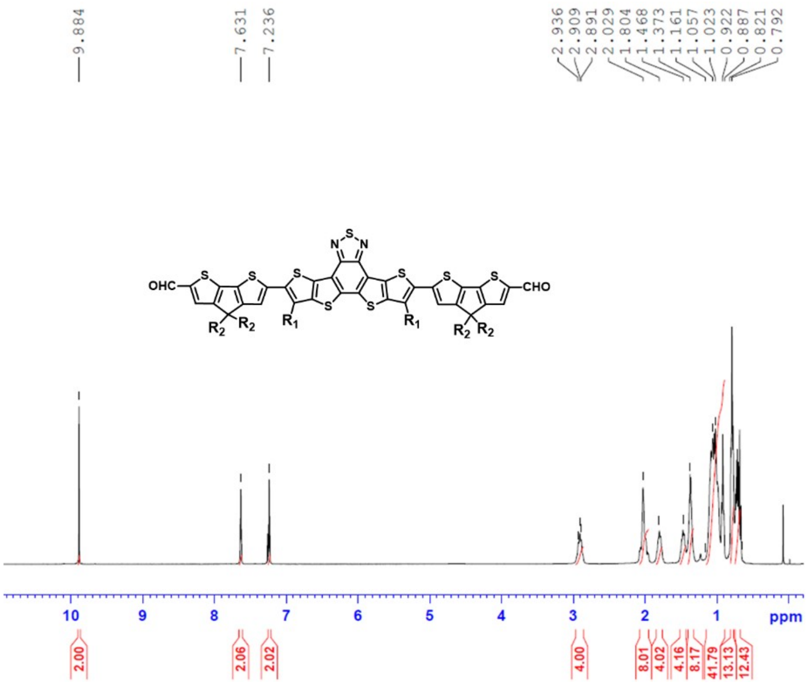


Fig. S9. ^{1}H NMR spectra of BTST-CPDT-CHO in $CDCl_3$.

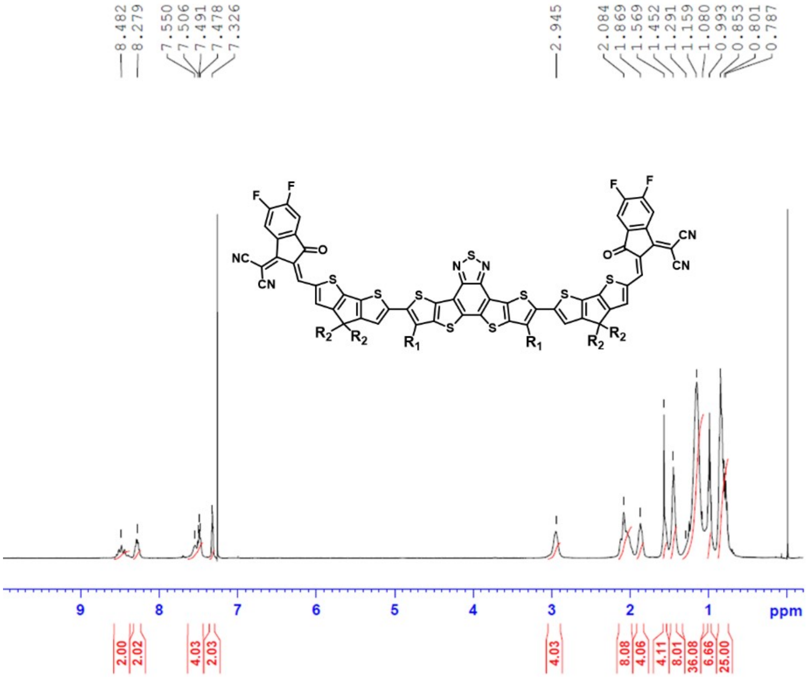


Fig. S10. ^{1}H NMR spectra of BTST-4F in $CDCl_3$.

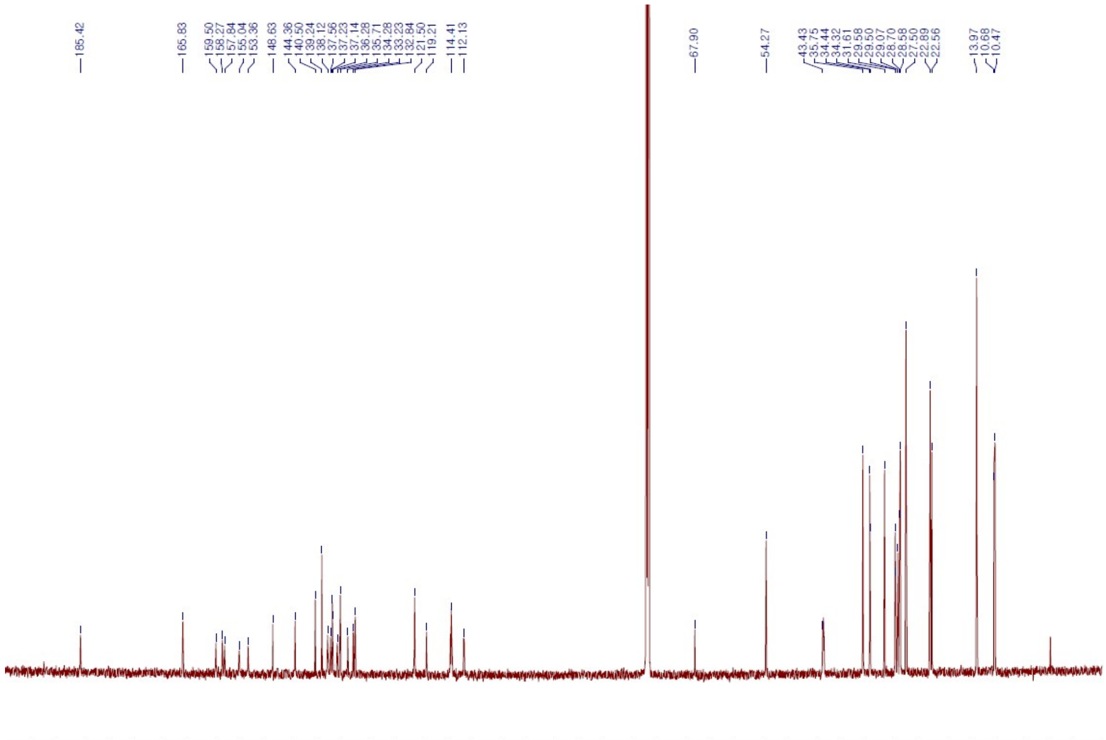


Fig. S11. ^{13}C NMR spectra of BTST-4F in $CDCl_3$.

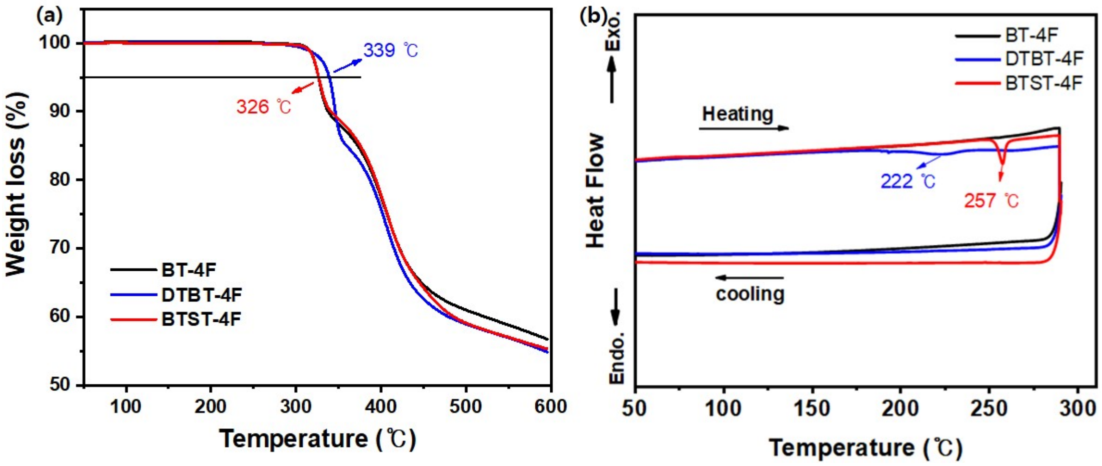


Fig. S12. TGA and DSC curves of BT-4F, DTBT-4F and BTST-4F.

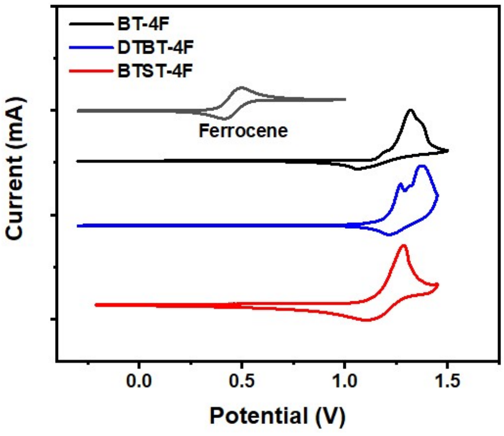


Fig. S13. CV curves of BT-4F, DTBT-4F and BTST-4F.

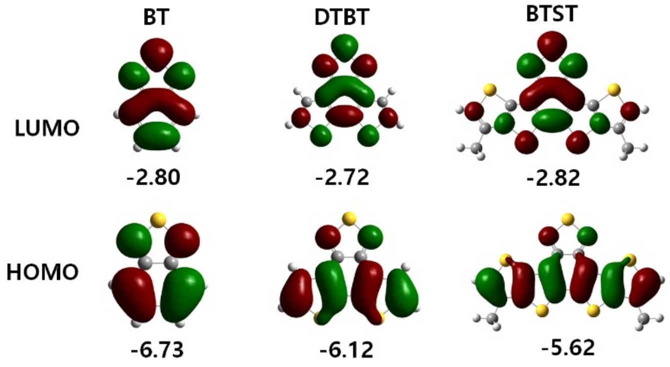


Fig. S14. Molecular frontier orbitals of HOMO and LUMO for BT, DTBT and BTST as the central core.

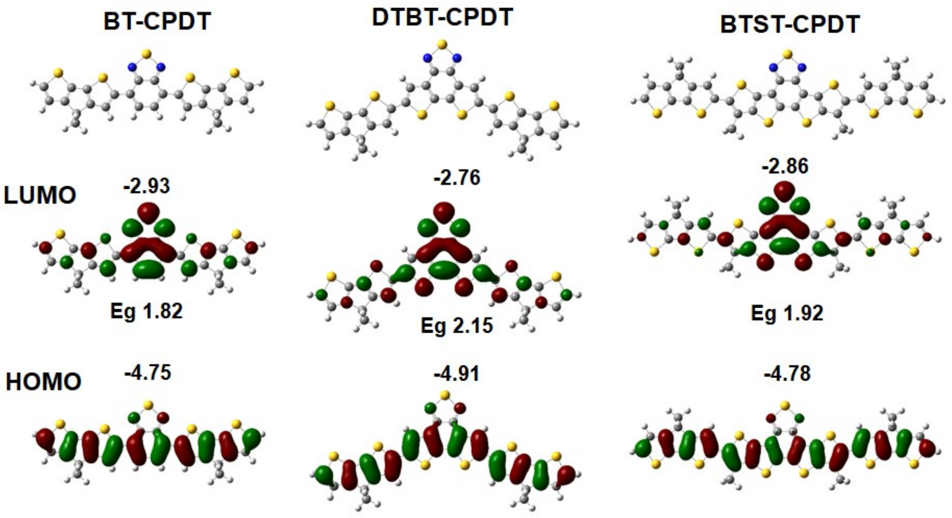


Fig. S15. Optimized molecular geometries and frontier molecular orbitals of HOMO and LUMO for the BT-CPDT, DTBT-CPDT and BTST-CPDT.

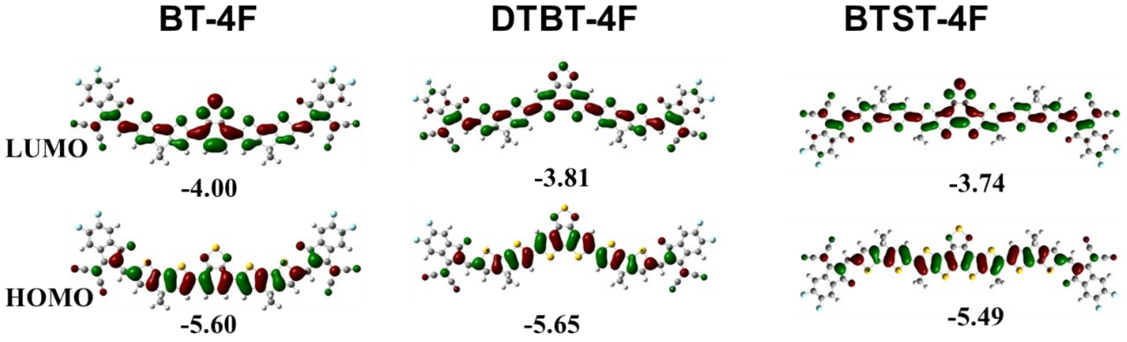


Fig. S16. Molecular frontier orbitals of HOMO and LUMO for the three NFAs.

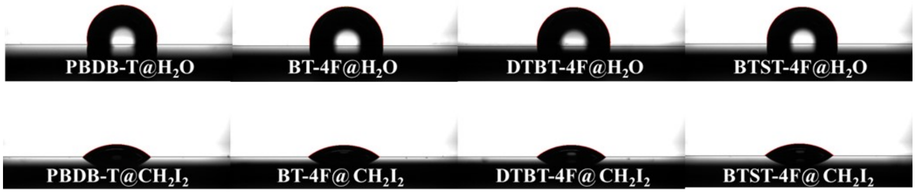


Fig. S17. Contact angles of water and diiodomethane on PBDB-T, BT-4F, DTBT-4F and BTST-4F neat films

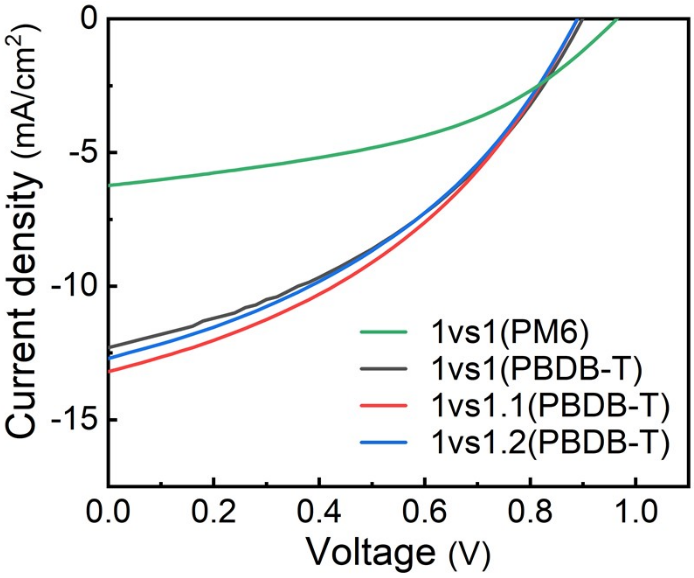


Fig. S18. Detailed *J–V* characteristics curve of PM6:BTST-4F and PBDB-T:BTST-4F OSC devices with different D:A ratio.

Table S1. Photovoltaic parameters of PM6:BTST-4F and PBDB-T:BTST-4F OSC devices with different D:A ratio

Donor polymer	D:A ratio	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF [%]	PCE [%]
PBDB-T	1:1	12.30	0.899	39.8	4.39(4.13 ± 0.19)
	1:1.1	13.20	0.890	39.4	4.62(4.33 ± 0.20)
	1:1.2	12.70	0.889	39.0	4.40(4.13 ± 0.18)
PM6	1:1	6.23	0.964	44.0	2.64(2.42 ± 0.13)

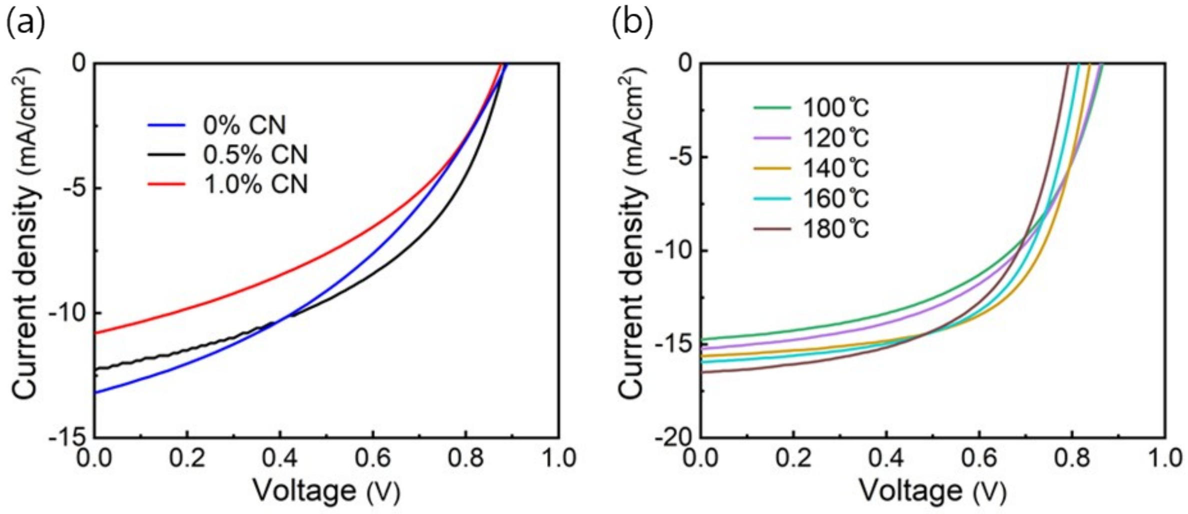


Fig. S19. Detailed *J–V* characteristics curve of PBDB-T:BTST-4F OSC devices with (a) different CN vol% and (b) different thermal annealing temperature.

Table S2. Photovoltaic parameters of PBDB-T:BTST-4F OSC devices with different CN vol% and different thermal annealing temperature.

Additive [vol%]	Annealing temperature	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF [%]	PCE [%]
CN [0]	-	13.20	0.890	39.4	4.62(4.33 ± 0.20)
CN[0.5]	-	12.30	0.885	46.8	5.07(4.63 ± 0.26)
	100 °C	14.70	0.866	53.2	6.79(6.33 ± 0.30)
	120 °C	15.30	0.861	54.0	7.09(6.88 ± 0.35)
	140 °C	15.60	0.840	62.8	8.23(8.07 ± 0.13)
	160 °C	15.90	0.815	61.4	7.97(7.80 ± 0.14)
	180 °C	16.51	0.792	58.6	7.66(7.40 ± 0.24)
CN[1.0]	-	10.80	0.877	41.5	3.93 (3.58 ± 0.17)

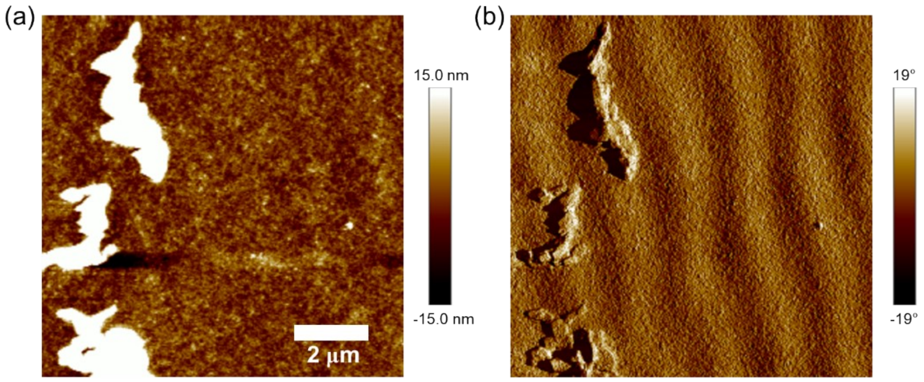


Fig. S20. AFM (a) height and (b) phase images of PBDB-T:DTBT-4F blends optimized using CF solutions.

Table S3. Photovoltaic parameters of PBDB-T:DTBT-4F devices optimized using CF solutions.

Donor polymer	D:A ratio	J_{SC} [mA cm^{-2}]	V_{OC} [V]	FF [%]	PCE [%]
PBDB-T	1:1.1	10.80	0.495	44.7	2.38 (2.14 ± 0.22)

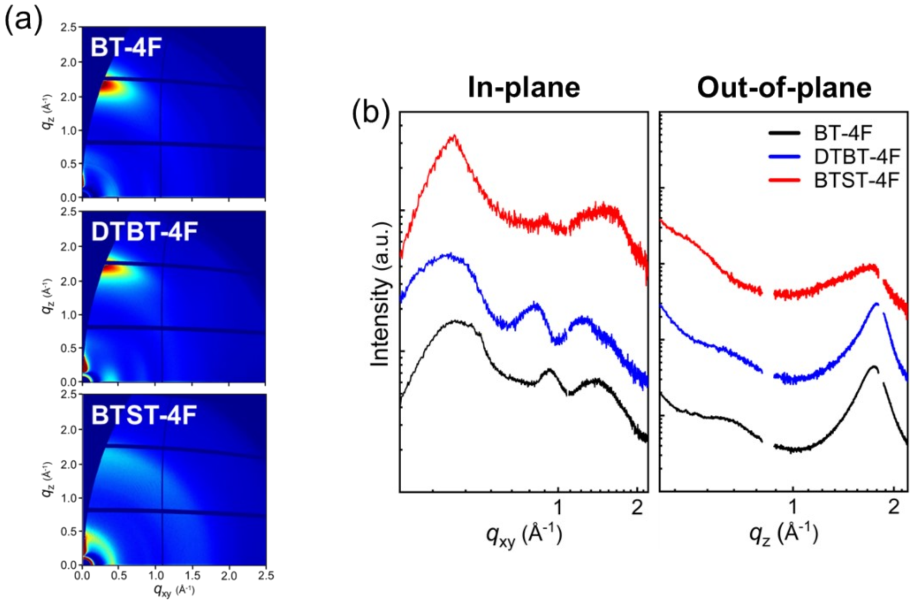


Fig. S21. Crystalline ordering of as-cast BT-4F, DTBT-4F and BTST-4F films. (a) 2D-GIWAXS images and (b) 1D-GIWAXS profiles.

Table S4. Morphological parameters extracted from GIWAXS measurements of pristine BT-4F, BTST-4F and DTBT-4F films.

Crystallographic parameters			BT-4F	DTBT-4F	BTST-4F
In-plane	Lamellar packing (100)	*q* [Å^{-1}]	0.403	0.382	0.399
		d-spacing [Å]	15.59	16.45	15.74
		FWHM	0.201	0.208	0.118
		Coherence length [Å]	28.13	27.19	47.92
Out-of-plane	π-π stacking (010)	*q* [Å^{-1}]	1.751	1.765	1.721
		d-spacing [Å]	3.59	3.56	3.65
		FWHM	0.282	0.272	0.432
		Coherence length [Å]	20.05	20.79	13.09

Table S5. Morphological parameters extracted from GIWAXS measurements of pristine BT-4F, BTST-4F and DTBT-4F films after 10 min of annealing at 150°C.

Crystallographic parameters			BT-4F	DTBT-4F	BTST-4F
In-plane	Lamellar packing (100)	q [Å^{-1}]	0.480	0.401	0.395
		d-spacing [Å]	13.09	15.67	15.91
		FWHM	0.033	0.081	0.072
		Coherence length [Å]	171.36	69.81	78.54
Out-of-plane	π-π stacking (010)	q [Å^{-1}]	1.723	1.751	1.765
		d-spacing [Å]	3.65	3.59	3.56
		FWHM	0.106	0.135	0.264
		Coherence length [Å]	53.35	41.89	21.42
	Long π-π stacking (010)	q [Å^{-1}]	0.662	0.608	-
		d-spacing [Å]	9.49	10.33	-
		FWHM	0.059	0.072	-
		Coherence length [Å]	95.85	78.54	-

Table S6. Morphological parameters extracted from GIWAXS measurements of PBDB-T:BT-4F, PBDB-T:DTBT-4F and PBDB-T:BTST-4F films.

Crystallographic parameters			PBDB-T: BT-4F	PBDB-T: DTBT-4F	PBDB-T: BTST-4F
In-plane	PBDB-T lamellar packing (100)	q [Å^{-1}]	0.295	0.303	0.304
		d-spacing [Å]	21.30	20.74	20.67
		FWHM	0.050	0.079	0.056
		Coherence length [Å]	113.10	71.58	100.98
	NFAs lamellar packing (100)	q [Å^{-1}]	0.480	0.417	0.410
		d-spacing [Å]	13.09	15.07	15.32
		FWHM	0.047	0.070	0.074
		Coherence length [Å]	120.32	80.78	76.42
Out-of-plane	π-π stacking (010)	q [Å^{-1}]	1.684	1.713	1.706
		d-spacing [Å]	3.73	3.67	3.68
		FWHM	0.144	0.252	0.262
		Coherence length [Å]	39.27	22.44	21.58
	Long π-π stacking (010)	q [Å^{-1}]	0.634	0.645	-
		d-spacing [Å]	9.91	9.74	-
		FWHM	0.085	0.097	-
		Coherence length [Å]	66.53	58.30	-

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