Supporting Information

A Chlorinated Nonacyclic Carbazole-Based Acceptor Affords over 15% Efficiency in Organic Solar Cells

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Contents

S1. Chemical structures

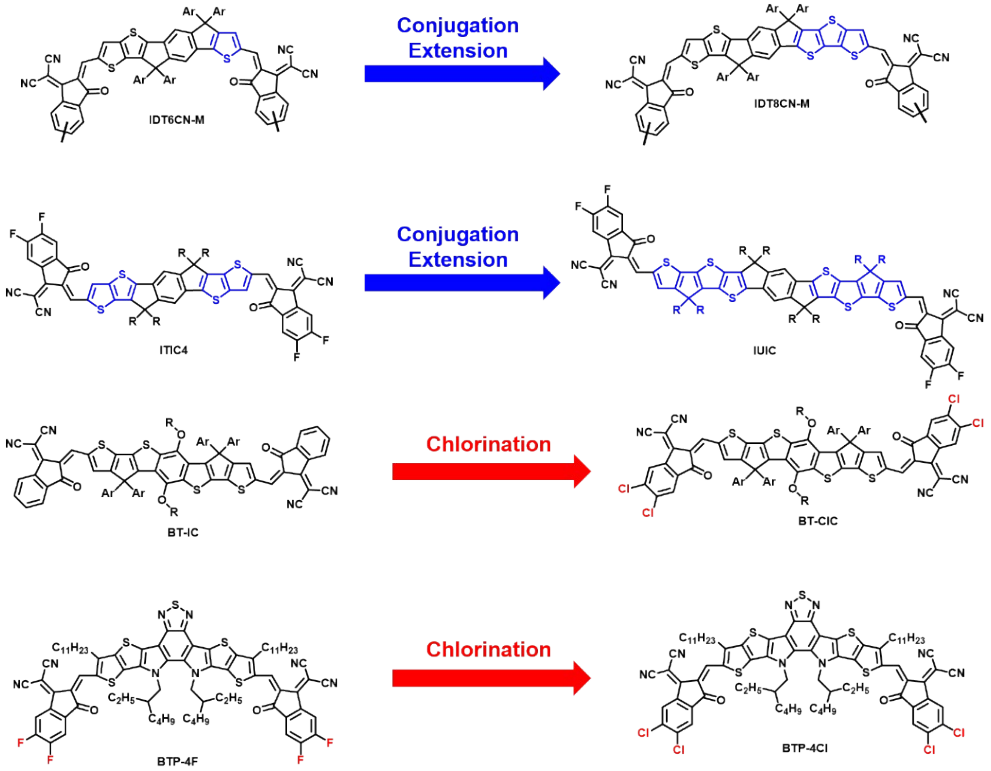


Figure S1. NFAs mentioned in introduction.

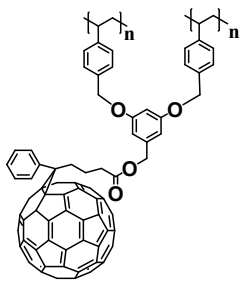


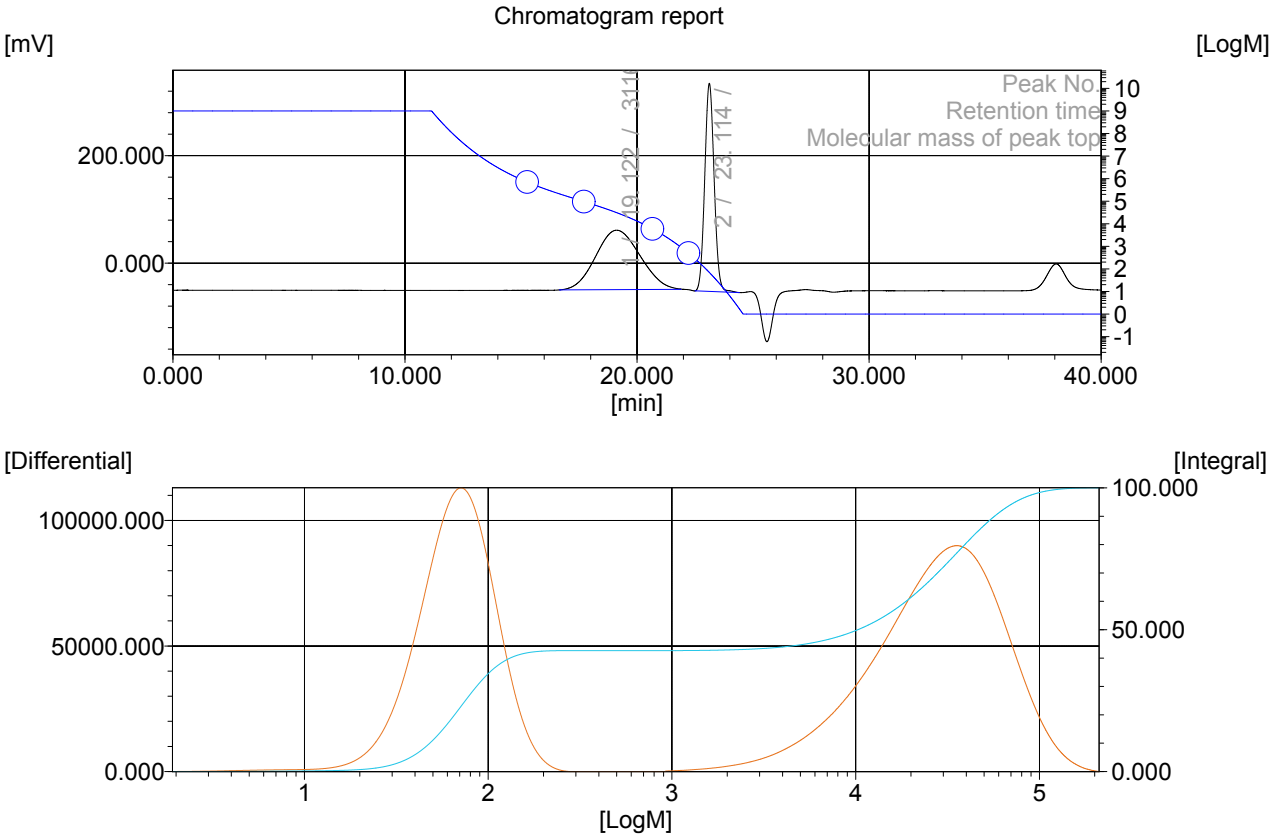
Figure S2. C-PCBSD

S2. Other studies about conjugation extension and chlorination

Table S1. Previous efforts in conjugation extension and chlorination with PCE improvement

Strategy	Modification	PCE improvement	Reference
Conjugation extension	F6IC to SN6IC-4F	7.1% to 13.2%	*Chem. Mater.* 2018, **30**, 5429−5434
	IDTIC to IDTTIC	5.7% to 11.2%	*Adv. Funct. Mater.*2018, **28**, 1802895
	IDTO-TT-4F to IDTO-T-4F	10.2% to 12.6%	*Adv. Energy Mater*. 2018, **8**, 1801618
Chlorination	PBDB-T-2F to PBDB-T-2Cl	13.2% to 14.4%	*Adv. Mater*. 2018, **30**, 1800868
	IDIC-4H to IDIC-4Cl	4.6% to 9.2%	*ACS Appl. Mater. Interfaces* 2018, **10**, 39992-40000
	BTP-4F to BTP-4Cl	15.6% to 16.5%	*Nature Communication*. 2019, **10**, 2515-2523

S3. Experimental section



Molecular mass calculation result (RI)

Peak 1 Base Peak

	[min]	[mV]	[mol]		
Peak start	16.664	-49.730	210,878	Mn	18,008
Peak top	19.122	61.417	31,160	Mw	35,497
Peak end	21.887	-48.208	923	Mz	54,851
				Mz+1	74,039
				Mv	35,497
Height [mV]			110.670	Mp	35,726
Area [mV*s]			14648.413	Mz/Mw	1.545
Height% [%]			22.228	Mw/Mn	1.971
[eta]			35497.19164	Mz+1/Mw	2.086

Peak 2 Base Peak

	[min]	[mV]	[mol]		
				Mn	56

Peak start	22.506	-51.432	277	Mw	73
Peak top	23.114	334.743	69	Mz	89
Peak end	24.373	-54.581	1	Mz+1	105
				Mv	73
Height [mV]			387.213	Mp	71
Area [mV*s]			10883.595	Mz/Mw	1.212
Height% [%]			77.772	Mw/Mn	1.302
[eta]			73.36626	Mz+1/Mw	1.429

Molecular mass calculation result (RI)

Total

	[min]	[mV]	[mol]		
Peak start	16.664	-49.730	210,878	Mn	132
Peak top	23.114	334.743	69	Mw	20,397
Peak end	24.373	-54.581	1	Mz	54,767
				Mz+1	74,039
Height [mV]			497.882	Mv	20,397
Area [mV*s]			25532.008	Mp	71
Height% [%]			100.000	Mz/Mw	2.685
[eta]			20396.96694	Mw/Mn	154.950
				Mz+1/Mw	3.630

Figure S3. High temperature gel permeation chromatography analysis of PM6

Materials and Instruments: PM6 was synthesized in accord to the literature precedents.[1] Other chemicals were purchased from Aldrich or Acros and used as received. C-PCBSD and Compound **1** was synthesized in accord to our previous publications.[2-4] ^{1}H and ^{13}C NMR spectra were measured using a Varian 400 MHz instrument spectrometer. Differential scanning calorimeter (DSC) was measured on a TA Q200 Instrument and thermogravimetric analysis (TGA) was recorded on a Perkin Elmer Pyris under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Solution/film absorption spectra were collected on a HP8453 UV-vis spectrophotometer. The electrochemical cyclic voltammetry (CV) was conducted on a CH Instruments Model 611D. A carbon glass coated with a thin polymer film was used as the working electrode and Ag/Ag^{+} electrode as the reference electrode, while 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) in dichloromethane was used as the electrolyte. CV curves were calibrated using ferrocene as the standard, whose oxidation potential is set at –4.8 eV with respect to zero vacuum level. The HOMO/LUMO energy levels were obtained from the equation of HOMO = – ($E_{ox}^{onset} - E_{ferrocene}^{onset} + 4.8$) eV and LUMO = – ($E_{red}^{onset} - E_{ferrocene}^{onset} + 4.8$) eV. Electron/hole mobility were obtained from SCLC method as the equation $J = 9\,\mu\,\varepsilon_0\,\varepsilon_r\,V^2/(8\,L^3)$ noted. GIWAXS measurement was conducted at TLS13A beamline in NSRRC. The coherence length was obtained from the FWHM of (010) signal using Scherrer equation. EQE_{EL} measurements were carried out by applying external voltage/current sources through the devices (ELCT-3010, Enlitech) from 1 to 2 V. ΔE_3 was acquired from the equation $\Delta E_3 = -kT\ \ln(EQE_{EL})$. High Temperature EcoSEC GPC system (HLC-8321GPC HT) was calibrated using polystyrene standard.

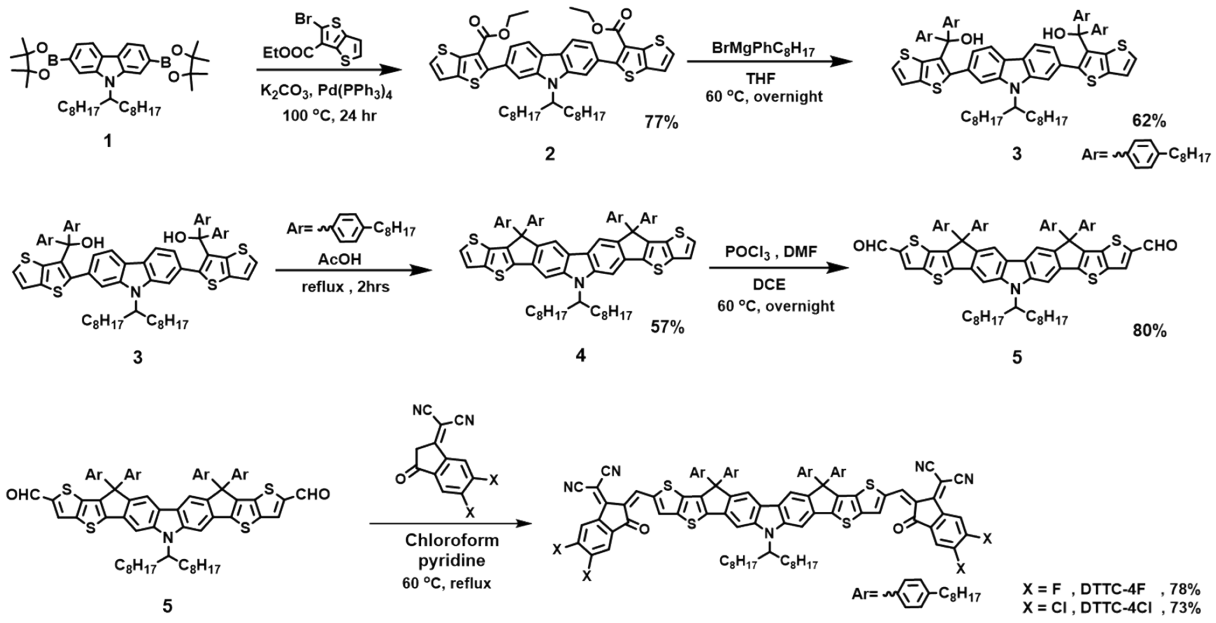


Figure S4. Synthetic scheme of DTTC-4F and DTTC-4Cl

Synthesis of compound 2: **Compound 1** was synthesized in accord to our previous work.[2,3] A mixture of **compound 1** (0.5 g, 0.76 mmol), ethyl 2-bromothieno[3,2-b] thiophene-3-carboxylate (0.49 g, 1.68 mmol), K_2CO_3(0.63 g, 4.56 mmol), $Pd(PPh_3)_4$ (0.088 g, 0.08 mmol), Aliquat 336 (0.1 ml) was added in 6.2 ml degased toluene and 1.25 ml deionized water and then refluxed in 100 °C over 24 hours. After the mixture was cooled to room temperature, the mixture was poured into $NH_4Cl_{(aq)}$ and extracted with ethyl acetate (EA), and then dried over anhydrous $MgSO_4$. After the removal of solvent, the residue was purified by column chromatography on silica gel using n-hexane/EA (20:1) as eluent to give **compound 2** as a yellow solid (480 mg, 77%).

^{1}H NMR (400MHz, $CDCl_3$): δ/ppm: 8.133 (br, 2H), 7.818 (s, 1H), 7.609 (s, 1H), 7.475 (br, 4H), 7.285 (d, J = 5.6Hz, 2H), 4.567 (m, 1H), 4.289 (br, 4H), 2.284 (m, 2H), 1.936 (m, 1H), 1.242-1.062 (m, 32H), 0.803 (t, J = 6.8 Hz, 6H)

HRMS (FAB) Calcd for $C_{47}H_{55}NO_4S_4$ $[M]^+$: 825.3008 ; found: 825.3009.

Synthesis of compound 3: **Compound 2** (1 g, 1.21 mmol) was fire-dried over 3 times repeatedly in vacuum. Anhydrous THF (5 ml) was then injected with 4-octylphenyl magnesium bromide (12.1 mmol) was slowly added as Grignard reagent. The reaction was controlled in 70 °C and refluxed overnight. The reaction was quenched by methanol and extracted with $NH_4Cl_{(aq)}$/EA. To remove the residual 4-octylbenzene, column chromatography was conducted

using silica gel with n-hexane/EA (20:1) as eluent to give **compound 3** as a yellow liquid (1.12 g, 0.74 mmol).

Synthesis of compound 4: A mixture of **Compound 3** (1.44 g, 0.964 mmol) and acetic acid (50 ml) was heated in 120 °C and refluxed for 2 hours. After extracted by EA:NaOH, the mixture was purified by silica column chromatography exploiting n-hexane/EA (50:1) as eluent. Recrystallization with methanol and EA was carried out to acquire **compound 4** as a yellow solid (1 g, 57%)

^{1}H NMR ($CDCl_3$, 400 MHz): δ/ ppm: 7.615 (d, J = 7.615, 2H), 7.518 (s, 1H), 7.383 (s, 1H), 7.310 (d, J = 5.2 Hz, 2H), 7.269 (d, J = 6.8 Hz, 2H), 7.197 (d, J = 8.4 Hz, 8H), 7.041 (d, J = 8.4 Hz, 8H), 4.595 (m, 1H), 2.522 (t, J = 8Hz, 8H), 2.327 (m, 2H), 2.015 (m, 2H), 1.275-1.969 (m, 75H), 0.857 (t, J = 6.8 Hz, 12H), 0.784 (t, J = 6.8 Hz, 6H)

^{13}C NMR ($CDCl_3$, 400 MHz) : δ/ ppm : 146.497 , 144.751 , 143.973 , 142.440 , 141.537 , 141.499 , 138.915 , 135.958 , 135.522 , 134.118 , 128.452 , 128.209 , 126.403 , 122.771 , 122.337 , 120.449 , 117.640 , 117.291 , 102.074 , 99.489 , 62.599 , 57.051 , 35.739 , 33.951 , 32.020 , 31.894 , 31.439 , 29.674 , 29.587 , 29.488 , 29.375 , 29.352 , 27.192 , 22.809 , 22.722 , 14.252 , 14.187 (multiple carbon peaks result from phenomenon of atropisomerism)

HRMS (FAB) calcd for $C_{99}H_{127}NS_4$ $[M]^+$: 1457.8846; found: 1457.8856

Synthesis of compound 5: A mixture of **compound 4** (1 g, 0.68 mmol) and 1,2-dichloroethane (20 ml) was deoxygenated with nitrogen for 30 min and then added a solution of $POCl_3$ (0.31 ml, 3.43 mmol) in DMF (4.72 mL, 61 mmol) at 0 °C. After being stirred at 60 °C for 24 hours, the mixture was poured into $Na_2CO_{3(aq)}$ and extracted with CH_2Cl_2. The organic layer was washed with water, and then dried over anhydrous $MgSO_4$. After the removal of solvent, the residue was purified by column chromatography on silica gel using n-hexane/CH_2Cl_2 (1:2) as eluent to give **compound 5** as an orange solid (0.8 g, 88%).

^{1}H NMR ($CDCl_3$, 400MHz): δ/ ppm: 9.889 (s, 2H), 7.982 (m, 4H), 7.605 (s,1H), 7.472 (s, 1H), 7.160 (d, J= 8 Hz, 8H), 7.055 (d, J= 8 Hz, 8H), 4.620 (m, 1H) , 2.523 (t, J= 7.8 Hz, 8H), 2.325 (m, 1H), 2.022 (m, 1H), 1.275-1.161 (m, 75H), 0.855 (t, J = 7 Hz, 12H), 0.775 (t, J = 6.4 Hz, 6H)

^{13}C NMR ($CDCl_3$, 400MHz): δ/ ppm: 182.935, 150.717, 146.68, 145.742, 144.155, 142.763, 142.049, 141.386, 140.759, 140.508, 139.222, 135.268, 134.850, 129.970, 128.702, 127.989, 123.928, 122.513, 118.130, 117.796, 103.155, 100.628, 62.690, 57.263, 35.704, 33.936,

32.004, 31.864, 31.420, 29.629, 29.595, 29.560, 29.454, 29.344, 29.302, 27.132, 22.787, 22.699, 14.237, 14.165 (multiple carbon peaks result from phenomenon of atropisomerism)

HRMS (FAB) calcd for $C_{101}H_{127}NO_2S_4$ $[M]^+$: 1513.8744; found: 1513.8748

Synthesis of DTTC-4F and DTTC-4Cl: A mixture of **compound 5** (0.2 g, 0.11 mmol), 2-(5,6-difluoro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (0.12 g, 0.54 mmol) or 2-(5,6-dichloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (0.14 g, 0.54 mmole) in $CHCl_3$ (11 ml) was deoxygenated with nitrogen for 30 minutes. Pyridine (0.11 ml) was added and then refluxed for 5 hours. After the mixture was cooled to room temperature, the mixture was poured into water and extracted with CH_2Cl_2. The organic layer was washed with water, and then dried over anhydrous $MgSO_4$. After removal of solvent, the residue was purified by column chromatography on silica gel using n-hexane/CH_2Cl_2 (1:2) as eluent and recrystallized by methanol and CH_2Cl_2 to give DTTC-4F/DTTC-4Cl as dark blue solid (DTTC-4F: 0.2 g, 78%; DTTC-4Cl: 0.19 g, 73%).

DTTC-4F

^{1}H NMR ($CDCl_3$, 400MHz) : δ/ ppm : 8.869 (s , 2H) , 8.535 (m , 2H) , 8.275 (s , 2H) , 8.014 (d , J = 12.8 Hz , 2H) , 7.680 (m , 3H) , 7.553 (s , 1H) , 7.243 (d , J = 7.6 Hz , 8H) , 7.118 (d , J = 7.2 Hz , 8H) , 4.648 (m , 1H) , 2.552 (t , J = 7.6 Hz , 8H) , 2.347 (m , 2H) , 2.047 (m , 2H) , 1.295-1.175 (m , 71H) , 0.857 (t , J = 6.4 Hz , 12H) , 0.787 (t , J = 6.4 Hz , 6H)

^{13}C NMR ($CDCl_3$, 400MHz) : δ/ ppm : 185.937 , 185.485 , 155.912 , 155.772 , 155.491 , 153.316 , 153.180 , 148.576 , 147.563 , 146.835 , 143.635 , 143.210 , 142.311 , 140.137 , 139.658 , 139.241 , 138.603 , 137.746 , 136.702 , 135.196 , 134.786 , 134.653 , 134.592 , 128.850 , 128.008 , 124.927 , 123.530 , 121.352 , 118.456 , 118.115 , 115.181 , 114.961 , 114.506 , 114.418 , 112.817 , 112.635 , 103.842 , 101.364 , 69.460 , 62.800 , 57.468 , 35.739 , 33.928 , 32.008 , 31.864 , 31.428 , 29.841 , 29.689 , 29.576 , 29.454 , 29.363 , 29.295 , 27.139 , 24.244 , 22.794 , 22.703 , 14.233 , 14.172

HRMS (FAB) calcd for $C_{125}H_{131}F_4N_5O_2S_4$ $[M]^+$: 1937.9116 ; found : 1937.9112

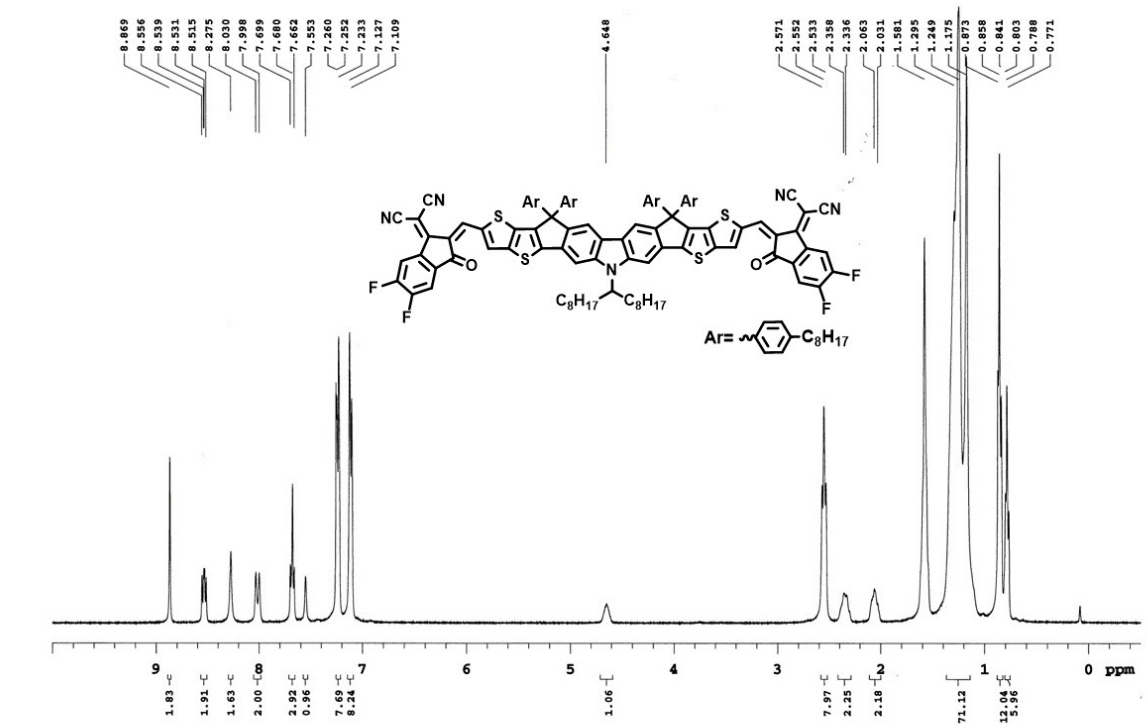
DTTC-4Cl

^{1}H NMR ($CDCl_3$, 400MHz) : δ/ ppm : 8.882 (s , 2H) , 8.757 (s , 2H) , 8.273 (d , 2H) , 8.01 (d , J = 13.2 Hz , 2H) , 7.939 (s , 1H) , 7.677 (s , 1H) , 7.548 (s , 1H) , 7.233 (d , J = 8.4 Hz , 8H) , 7.112 (d , J = 8.4 Hz , 8H) , 4.641 (m , 1H) , 2.545 (t , J = 7.8 Hz , 8H) , 2.335 (m , 2H) , 2.058 (m , 1H) , 1.303-1.097 (m , 75H) , 0.851 (t , J = 6.8 Hz , 12H) , 0.781 (t , J = 6.8 Hz , 6H)

^{13}C NMR ($CDCl_3$, 400MHz) : δ/ ppm : 186.036 , 158.394 , 155.832 , 148.895 , 147.616 , 146.910 , 143.783 , 143.245 , 142.338 , 140.102 , 139.757 , 139.453 , 139.165 , 138.812 , 137.913 , 136.140 , 135.222 , 134.801 , 128.866 , 128.004 , 127.052 , 125.276 , 125.006 , 123.617 , 121.348 , 118.471 , 118.156 , 114.506 , 103.907 , 101.428 , 69.502 , 62.804 , 57.483 , 35.742 , 33.932 , 32.012 , 31.868 , 31.428 , 29.693 , 29.579 , 29.454 , 29.367 , 29.299 , 27.143 , 22.798 , 22.707 , 14.240 , 14.176

HRMS (FAB) calcd for $C_{125}H_{131}Cl_4N_5O_2S_4$ $[M]^+$: 2001.7934; found: 2001.7945

Fabrication of Inverted OSC devices: Inverted devices were fabricated in the structure of ITO/ZnO/C-PCBSD/active layer/MoO_3/Al. The ITO-coated glass was cleaned sequentially by detergent, DI water, acetone and isopropyl alcohol. The zinc acetate precursor was dissolved in 2-methoxy ethanol with ethanol amine to enhance the solubility. A thin ZnO film was deposited on a clean ITO-coated glass by spin-coating the precursor solution at 4000 rpm for 30 seconds and thermal annealing at 170 °C for 30 minutes in air. Next, the device was transferred into a nitrogen-filled glovebox for C-PCBSD deposition. The C-PCBSD *o*-DCB solution was prepared in a concentration of 7 mg/ml and stirred at 65 °C over 8 hours. The C-PCBSD solution was then filtered before deposition. The C-PCBSD layer was spin-coated at 8000 rpm for 30 seconds and thermal annealed at 160 °C for 15 minutes as cross-linking process. Also, the PM6:NFA chlorobenzene (CB) solutions were prepared in a PM6 concentration of 10 mg/ml with NFA concentration of 12 (DTC-4F), 11 (DTTC-4F) and 10 (DTTC-4Cl) mg/ml. Besides, 0.1v% of DIO, 0.5v% of DPE and 0.5v% of DIO were added into the PM6:DTC-4F, PM6:DTTC-4F and PM6:DTTC-4Cl solutions, respectively. The active layer was deposited under an optimal spin-coating condition of 1400 rpm for 60 seconds and thermal annealed at their optimal conditions of 100 °C (PM6:DTC-4F), 140 °C (PM6:DTTC-4F) and 90 °C (PM6:DTTC-4Cl) for 10 minutes. Last, 7 nm of MoO_3 and 100 nm of Al was sequentially deposited and the fabrication of inverted OSC device was complete.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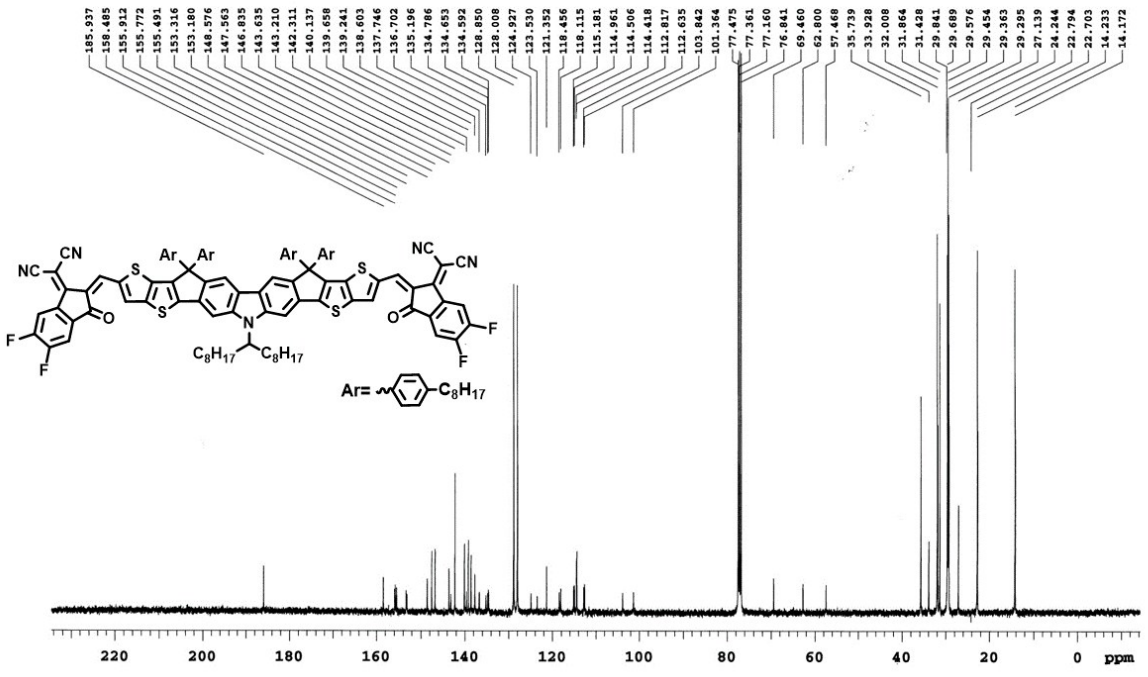
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ppm

Figure S5. ^{1}H NMR and ^{13}C NMR spectra of DTTC-4F

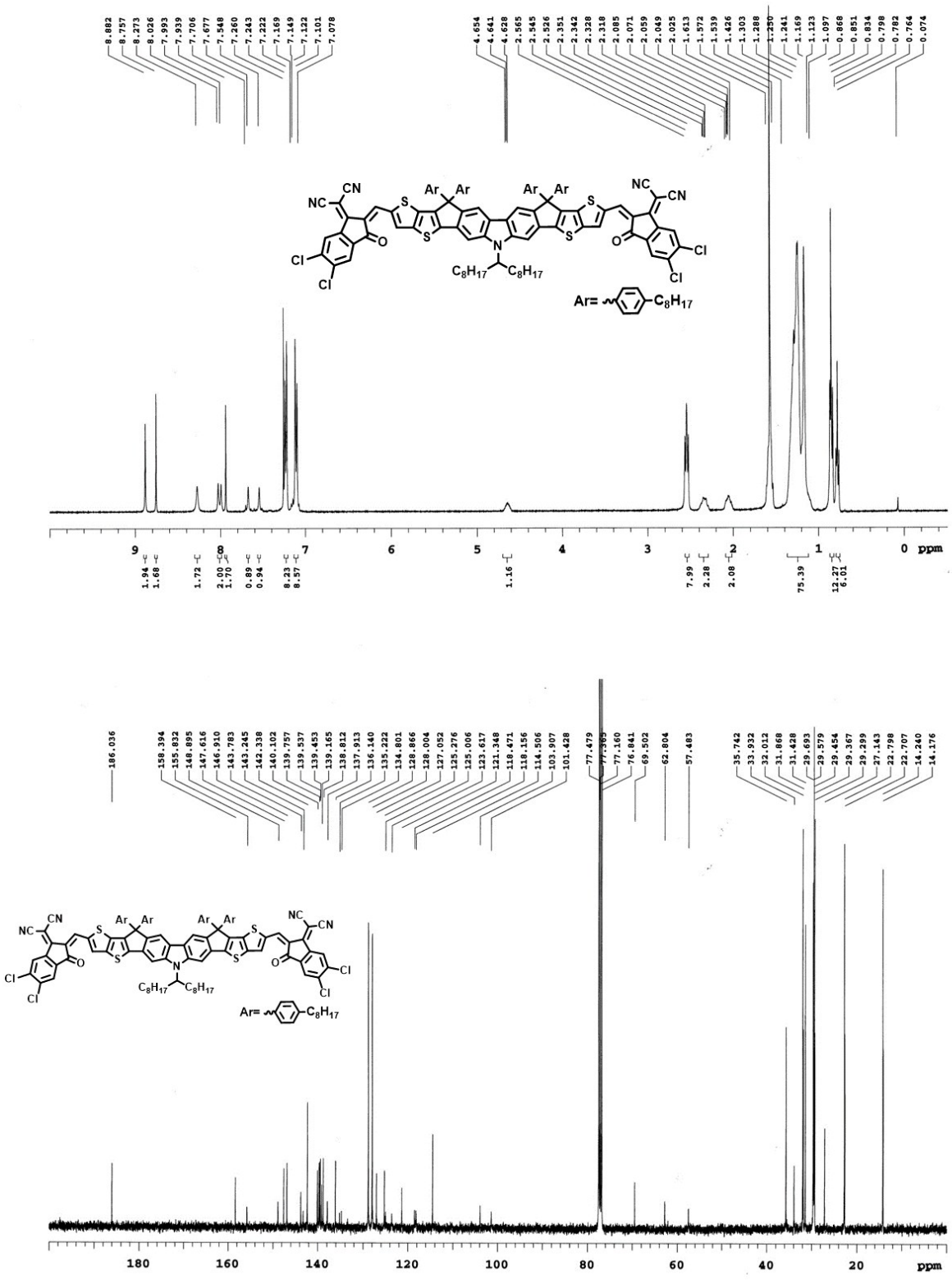


Figure S6. ^{1}H NMR and ^{13}C NMR spectra of DTTC-4Cl

S4. Thermal properties of DTTC-4F and DTTC-4Cl

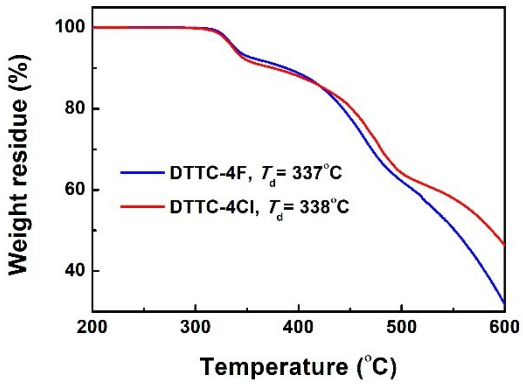


Figure S7. TGA traces of DTTC-4F and DTTC-4Cl. The T_d values of DTTC-4F and DTTC-4Cl are 337 and 338 °C, respectively.

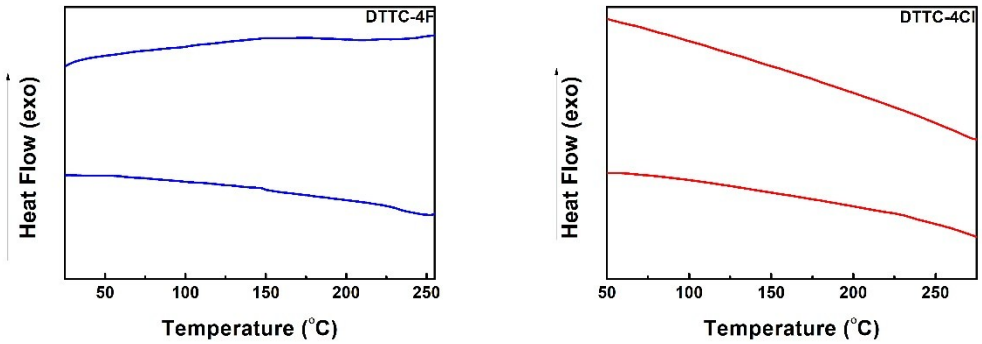


Figure S8. DSC diagrams of DTTC-4F and DTTC-4Cl.

S5. Structural simulation

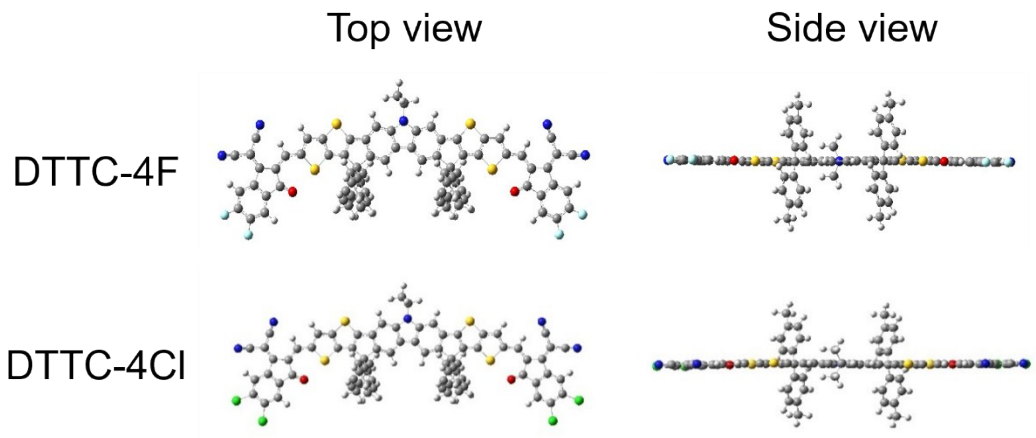


Figure S9. B3LYP/6-31G(d,p) DFT calculation of DTTC-4F and DTTC-4Cl.

S6. Electronic property of DTC-4F, DTTC-4F and DTTC-4Cl

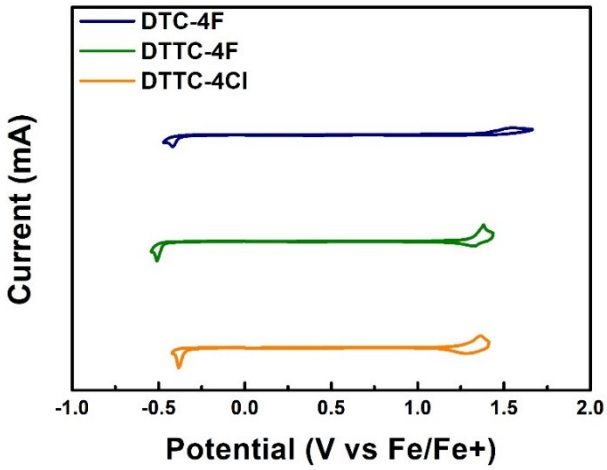


Figure S10. CV diagrams of DTC-4F, DTTC-4F and DTTC-4Cl neat films. The HOMO/LUMO of DTC-4F, DTTC-4F and DTTC-4Cl are -5.79/-3.92, -5.69/-3.91 and -5.72/-4.03 eV, respectively.

S7. UV-vis absorption measurement

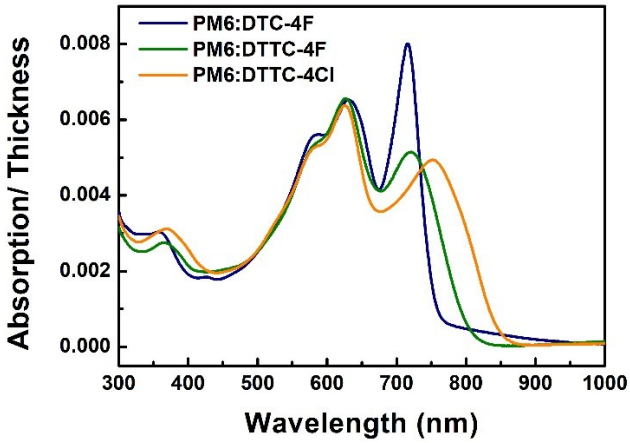


Figure S11. The UV-vis absorption spectrum of PM6:DTC-4F, PM6:DTTC-4F and PM6:DTTC-4Cl blends.

S8. Electron/hole mobility obtained from SCLC method

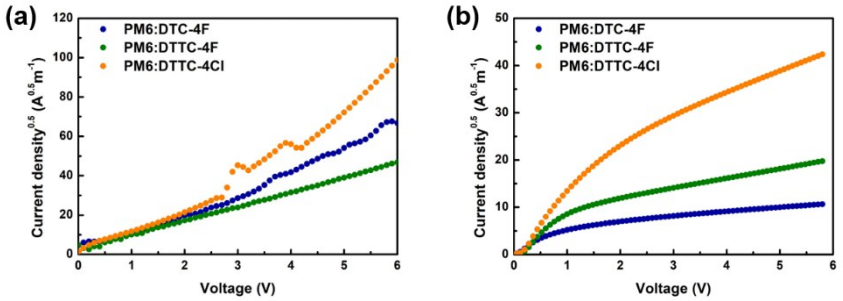


Figure S12. (a) Electron-only and (b) hole-only measurements of PM6:DTC-4F, PM6:DTTC-4F and PM6:DTTC-4Cl devices.

Table S2. Summary of electron/hole mobility of PM6:DTC-4F, PM6:DTTC-4F and PM6:DTTC-4Cl devices.

Blend	μ_e ($cm^2\ V^{-1}\ s^{-1}$)	μ_h ($cm^2\ V^{-1}\ s^{-1}$)
PM6:DTC-4F	3.51×10^{-4}	2.56×10^{-4}
PM6:DTTC-4F	3.02×10^{-4}	2.70×10^{-4}
PM6:DTTC-4Cl	7.91×10^{-4}	6.22×10^{-4}

S9. Non-radiative energy loss measurement

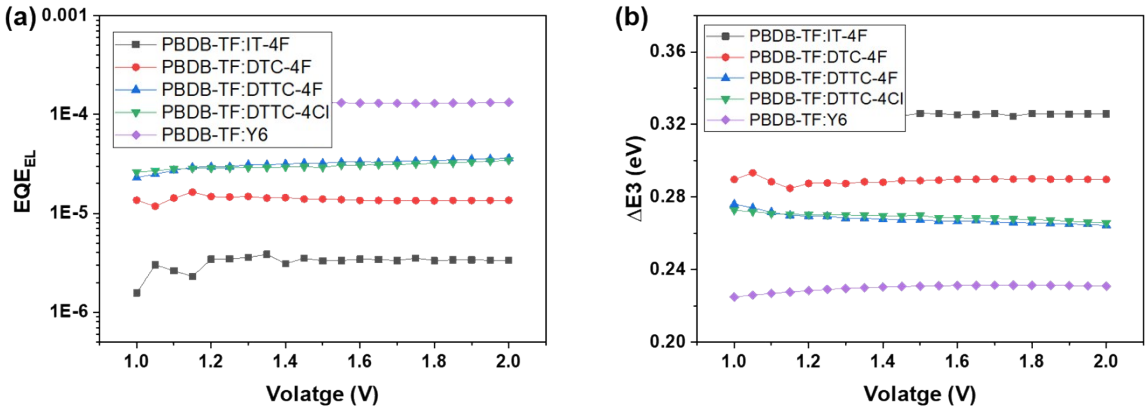


Figure S13. (a) EQE_{EL} measurement and (b) ΔE_3 measurement of PM6 (also known as PBDB-TF)-based devices.

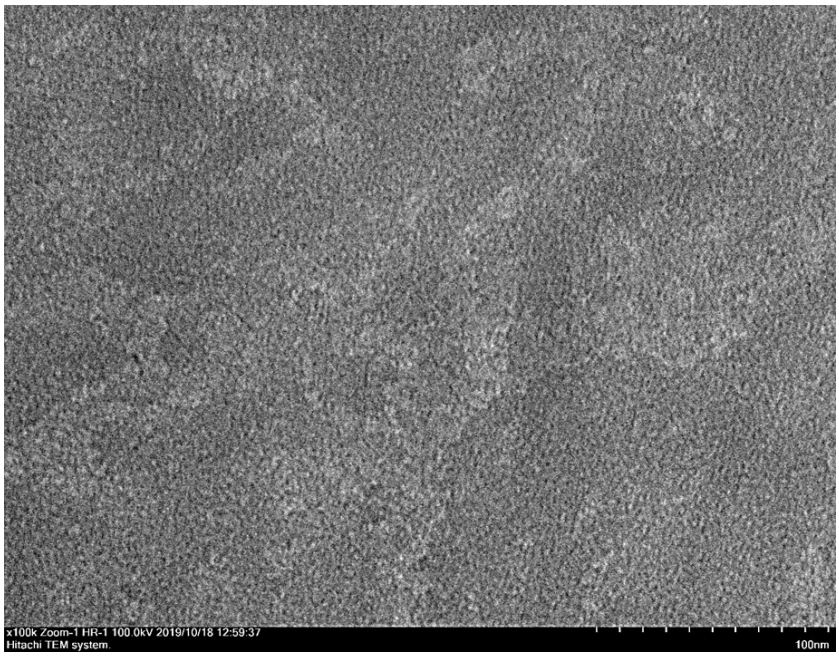
Table S3. Summary of EQE_{EL} and ΔE_3 afforded by PM6-based devices.

Blend	EQE_{EL} (%)	ΔE_3 (eV)
PBDB-TF:IT-4F	3.34×10^{-6}	0.326
PBDB-TF:DTC-4F	1.35×10^{-5}	0.289

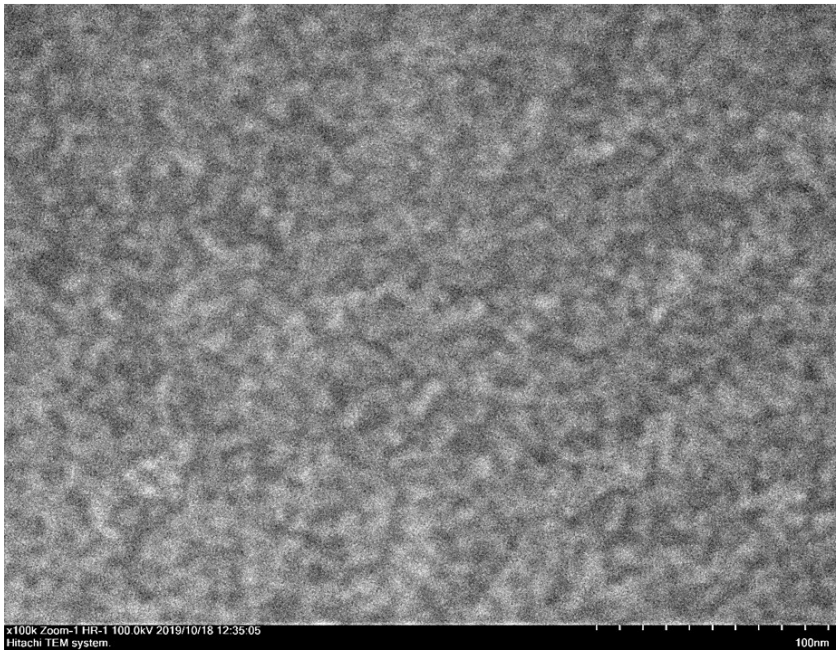
PBDB-TF:DTTC-4F	3.30×10^{-5}	0.267
PBDB-TF:DTTC-4Cl	3.07×10^{-5}	0.269
PBDB-TF:Y6	1.29×10^{-4}	0.231

S10. TEM measurements

(a) PM6:DTC-4F



(b) PM6:DTTC-4F



(c) PM6:DTTC-4Cl

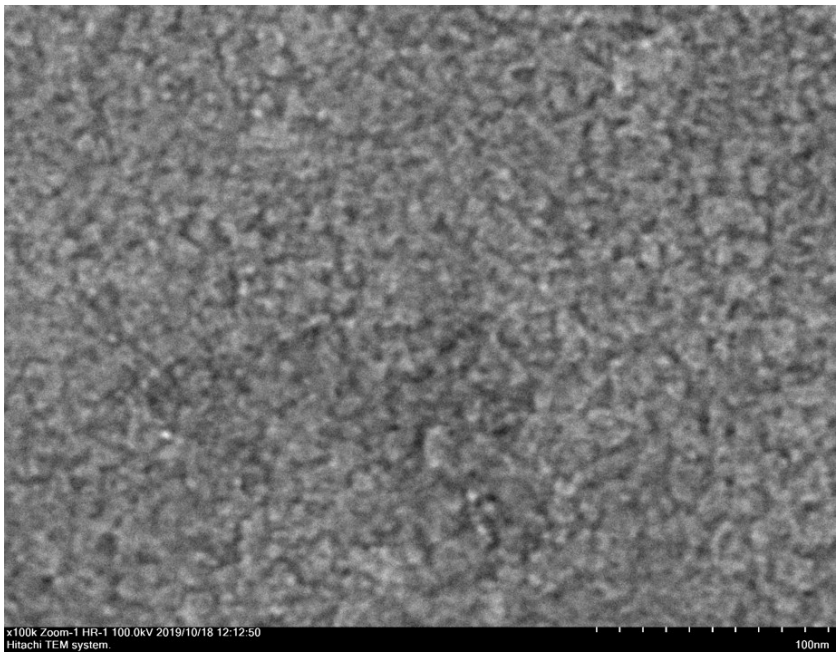


Figure S14. TEM images of (a) PM6:DTC-4F, (b) PM6:DTTC-4F and (c) PM6:DTTC-4Cl blends.

S11. GIWAXS data obtained from 1D linecuts

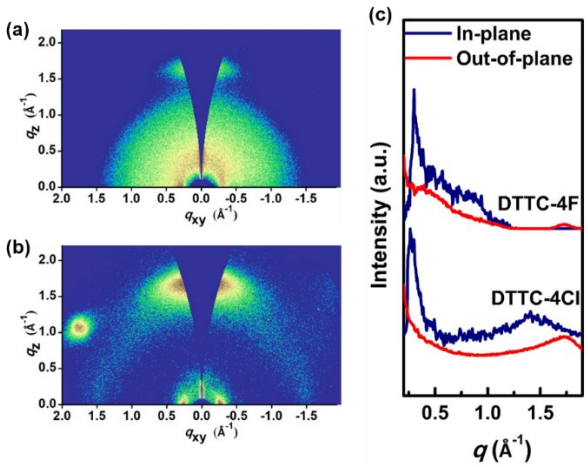


Figure S15. 2D GIWAXS patterns of (a) DTTC-4F and (b) DTTC-4Cl neat films with (c) their corresponding 1D linecuts.

Table S4. D-spacing of PM6, DTC-4F, DTTC-4F and DTTC-4Cl neat films and PM6:DTC-4F, PM6:DTTC-4F and PM6:DTTC-4Cl blends.

Composition	(010)		Note
	d-spacing (Å)	CL (Å)	
PM6	3.76	-	Ref. 3
DTC-4F	4.27	-	Ref. 3
DTTC-4F	3.61	-	This work
DTTC-4Cl	3.59	-	This work
PM6:DTC-4F	3.87	26.27	Ref. 3
PM6:DTTC-4F	3.69	30.20	This work
PM6:DTTC-4Cl	3.51	43.33	This work

S12. References

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