Supporting Information

π-Bridge Strategy for Asymmetric Small Molecule Acceptors in Organic Photovoltaics

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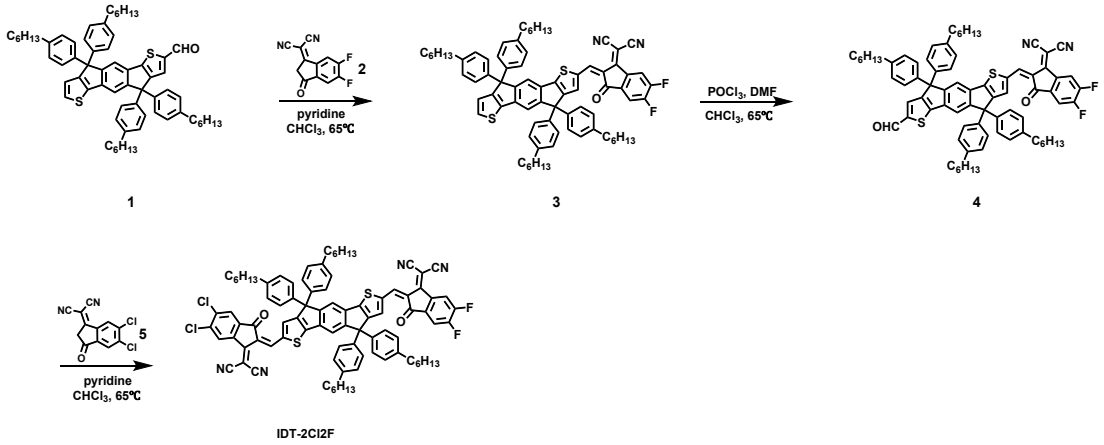
Experimental Section

1.Materials.

All chemicals and solvents were of reagent grade and were purchased from Alfa Aesar, J&K and Aldrich, respectively. The molecular structures and synthetic routes of **IDT-2Cl2F**, **IDT-S-2Cl2F**, **IDT-S-2F2Cl** and **IDT-S-4F** are shown in Scheme S1, Scheme S2 and Scheme S3, as follows:



Scheme S1. The synthetic route and molecular structure of **IDT-2Cl2F**.

Compound 3

A mixture of compound **1** (200 mg, 0.21 mmol) and compound **2** (72.5 mg, 0.315 mmol) in chloroform (CF, 15 mL) was charged into a two-necked flask equipped with a magnetic stirrer. The system was degassed via argon purging (bubbling) for 20 min, followed by rapid addition of pyridine (1 mL) under continuous argon flow. The mixture was further purged with argon for 10 min and then heated at 65°C in a thermostated oil bath. Reaction progress was monitored by TLC. After removal of the solvent under reduced pressure, the residue was purified by means of column chromatography on silica gel using a mixed solvent as eluent (CH_2Cl_2 / petroleum ether, v/v 1:3) to give compound **3** (162.23 mg, yield=67.3%).

Compound 4

$POCl_3$ (6.5 mL) and DMF (9.75 mL) were sequentially injected via syringe into a dry 100 mL two-necked flask under anhydrous conditions. The mixture was maintained at ice-water bath with vigorous stirring for 30 min. A solution of compound **3** (150 mg, 0.13 mmol) in CF was then introduced through the side neck using syringe transfer. The reaction vessel was immersed in a thermostated oil bath and heated at 65°C with continuous reflux for 18 h. The cooled reaction mixture was quenched with distilled water and extracted with CF. After removal of the solvent under reduced pressure, the residue was purified by means of column chromatography on silica gel using a mixed solvent as eluent (CH_2Cl_2 / petroleum ether, v/v 1:3) to give compound **4** (128.86 mg, yield=84.3%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 9.85 (s, 1H), 9.05 (d, *J* = 61.9 Hz, 2H), 8.28 (s, 1H), 7.75 (d, *J* = 2.7 Hz, 2H), 7.64 (d, *J* = 52.5 Hz, 2H), 7.18 – 7.06 (m, 16H), 2.62 – 2.52 (m, 8H), 1.58 (dd, *J* = 11.9, 7.2 Hz, 8H), 1.31 (dd, *J* = 17.2, 7.9 Hz, 24H), 0.87 (t, *J* = 6.2 Hz, 12H).

Compound IDT-2Cl2F

A mixture of compound **4** (110 mg, 0.093 mmol) and compound **5** (36.56 mg, 0.139 mmol) in chloroform (20 mL) was charged into a two-necked flask equipped with a magnetic stirrer. The system was degassed via argon purging (bubbling) for 20 min, followed by rapid addition of pyridine (1 mL) under continuous argon flow. The mixture was further purged with argon for 10 min and then heated at 65°C in a thermostated oil bath. Reaction progress was monitored by TLC. After removal of the solvent under reduced pressure, the residue was purified by means of column

chromatography on silica gel using a mixed solvent as eluent (CH_2Cl_2 / petroleum ether, v/v 1:3) to give **IDT-2Cl2F** (88.94 mg, yield=67.3%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.90 (d, *J* = 3.1 Hz, 1H), 8.77 (d, *J* = 3.1 Hz, 1H), 7.93 (d, *J* = 4.1 Hz, 1H), 7.76 – 7.71 (m, 3H), 7.65 (d, *J* = 34.3 Hz, 1H), 7.18 – 7.05 (m, 19H), 2.57 (q, *J* = 6.3, 5.1 Hz, 8H), 1.63 – 1.58 (m, 8H), 1.34 – 1.27 (m, 24H), 0.87 (t, *J* = 6.6 Hz, 12H).

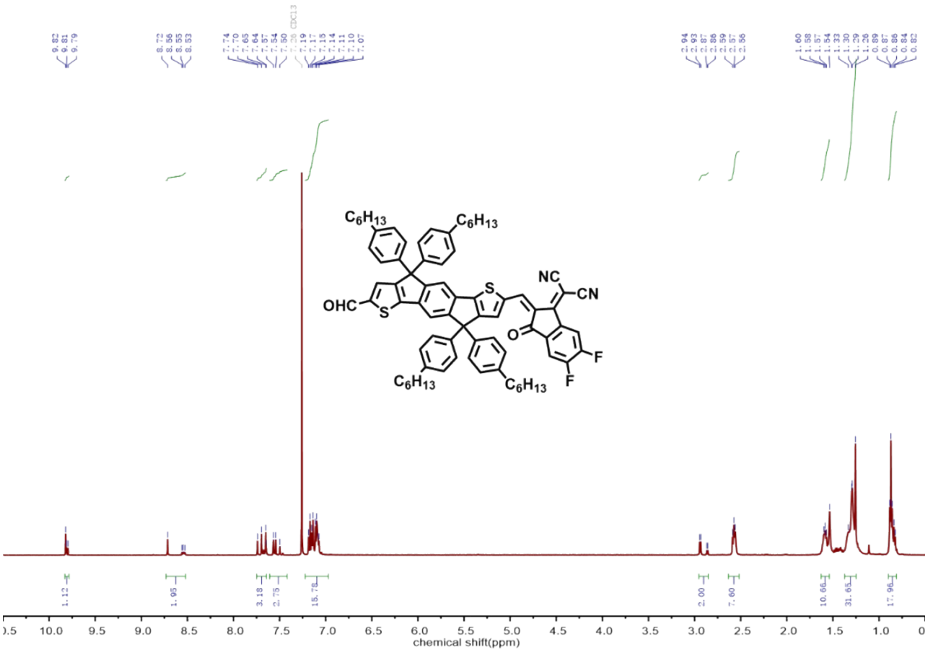


Figure S1. ^{1}H NMR of IDT-2F-CHO in $CDCl_3$.

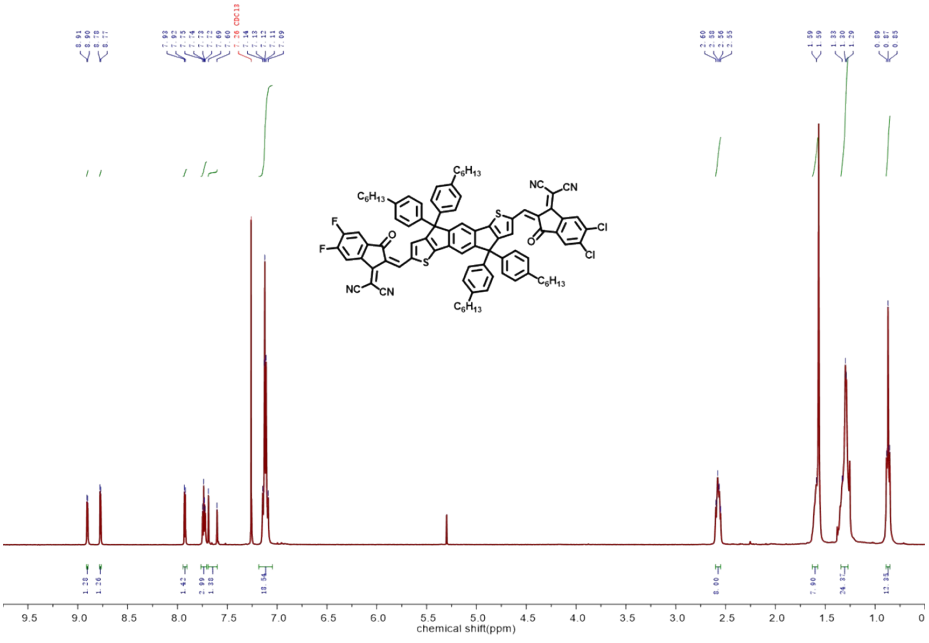


Figure S2. ^{1}H NMR of **IDT-2Cl2F** in $CDCl_3$.

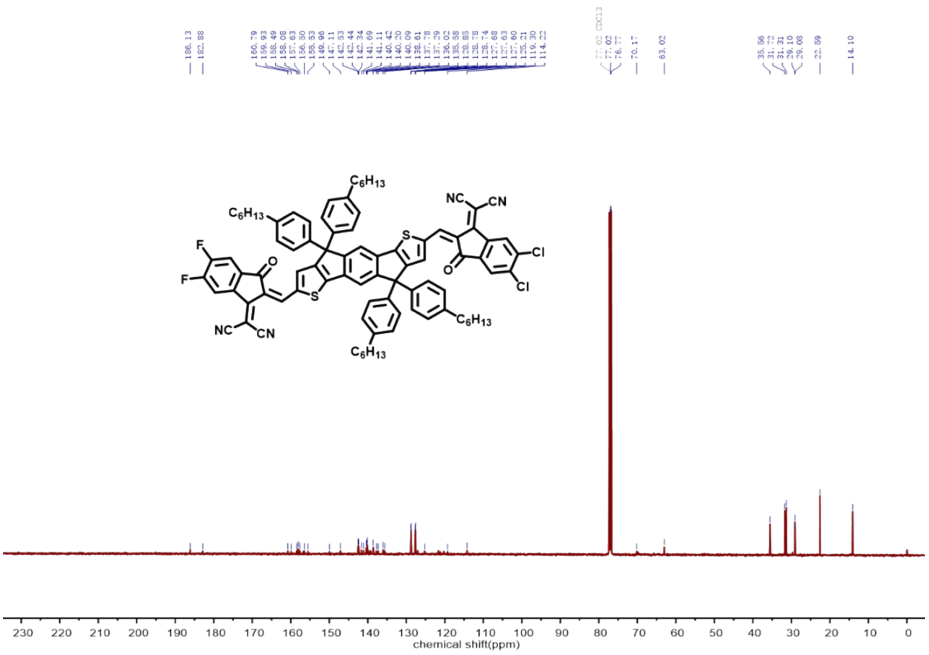


Figure S3. ^{13}C NMR of **IDT-2Cl2F** in $CDCl_3$.

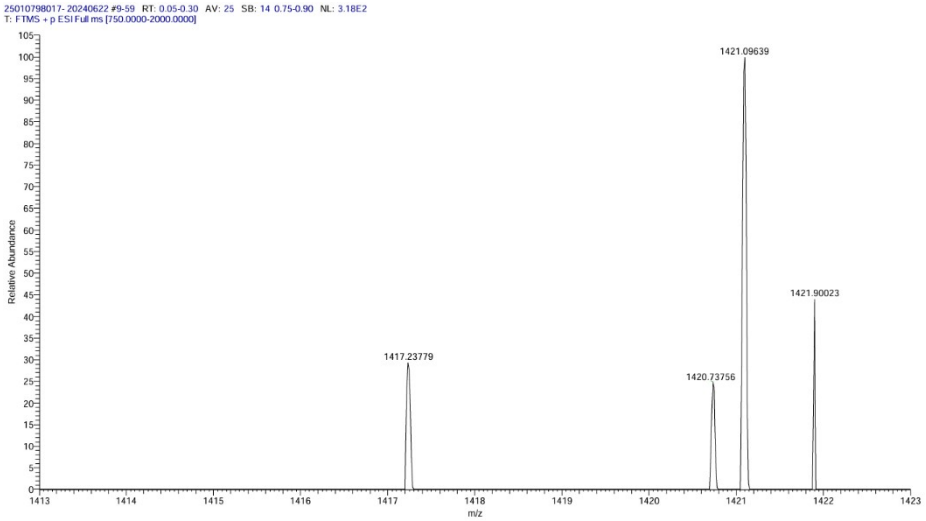
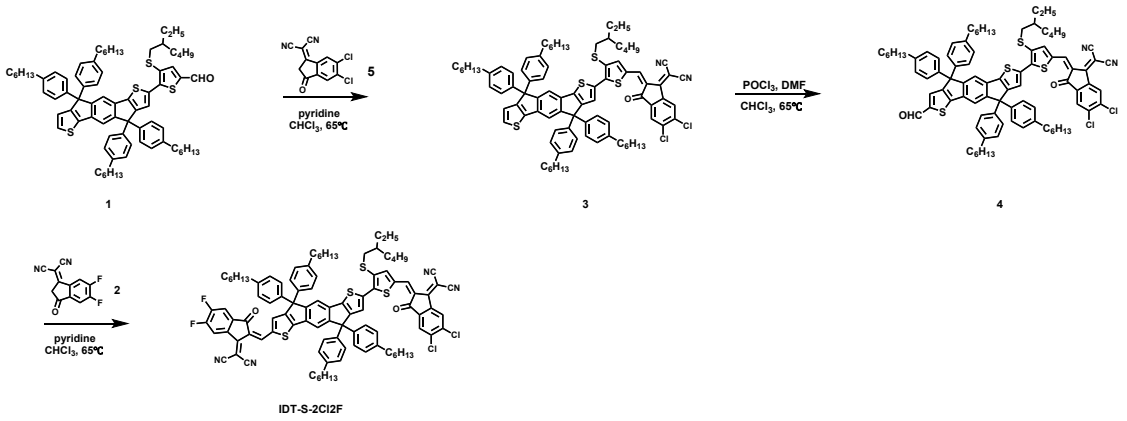


Figure S4. HRMS of **IDT-2Cl2F**. MS (HRMS) m/z: Calcd for $C_{90}H_{78}Cl_2F_2N_4O_2S_2$: 1418.49;



Scheme S2. The synthetic route and molecular structure of **IDT-S-2Cl2F**.

Compound 3

A mixture of compound **1** (200 mg, 0.17 mmol) and compound **5** (67.08 mg, 0.255 mmol) in CF (15 mL) was charged into a two-necked flask equipped with a magnetic stirrer. The system was degassed via argon purging (bubbling) for 20 min, followed by rapid addition of pyridine (1 mL) under continuous argon flow. The mixture was further purged with argon for 10 min and then heated at 65°C in a thermostated oil bath. Reaction progress was monitored by TLC. After removal of the solvent under reduced pressure, the residue was purified by means of column chromatography on silica gel using a mixed solvent as eluent (CH_2Cl_2 / petroleum ether, v/v 1:3) to give compound **3** (153.7 mg, yield=64.3%). ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.74 (d, *J* = 20.4 Hz, 2H), 7.93 (s, 1H), 7.74 (s, 1H), 7.72 (s, 1H), 7.52 (s, 1H), 7.44 (s, 1H), 7.30 (d, *J* = 4.9 Hz, 1H), 7.20 – 7.00 (m, 17H), 2.93 (d, *J* = 6.2 Hz, 2H), 2.62 – 2.50 (m, 8H), 1.62 – 1.54 (m, 11H), 1.33 – 1.25 (m, 30H), 0.86 (q, *J* = 7.9, 7.4 Hz, 19H).

Compound 4

$POCl_3$ (6.5 mL) and DMF (9.75 mL) were sequentially injected via syringe into a dry

100 mL two-necked flask under anhydrous conditions. The mixture was maintained at ice-water bath with vigorous stirring for 30 min. A solution of compound **3** (140 mg, 0.099 mmol) in CF was then introduced through the side neck using syringe transfer. The reaction vessel was immersed in a thermostatic oil bath and heated at 65°C with continuous reflux for 18h. The cooled reaction mixture was quenched with distilled water and extracted with CF. After removal of the solvent under reduced pressure, the residue was purified by means of column chromatography on silica gel using a mixed solvent as eluent (CH_2Cl_2 / petroleum ether, v/v 1:3) to give compound **4** (115.4 mg, yield=81.3%). ^{1}H NMR (500 MHz, Chloroform-d) δ 9.83 – 9.79 (m, 1H), 8.76 (d, J = 19.4 Hz, 2H), 7.94 (s, 1H), 7.76 – 7.63 (m, 3H), 7.59 – 7.44 (m, 3H), 7.20 – 7.00 (m, 15H), 2.90 (dd, J = 39.8, 6.2 Hz, 2H), 2.64 – 2.48 (m, 8H), 1.65 – 1.54 (m, 11H), 1.38 – 1.26 (m, 30H), 0.89 – 0.82 (m, 18H).

Compound IDT-S-2Cl2F

A mixture of compound **4** (110 mg, 0.076 mmol) and compound **2** (26.24 mg, 0.114 mmol) in CF (20 mL) was charged into a two-necked flask equipped with a magnetic stirrer. The system was degassed via argon purging (bubbling) for 20 min, followed by rapid addition of pyridine (1 mL) under continuous argon flow. The mixture was further purged with argon for 10 min and then heated at 65°C in a thermostatic oil bath. Reaction progress was monitored by TLC. After removal of the solvent under reduced pressure, the residue was purified by means of column chromatography on silica gel using a mixed solvent as eluent (CH_2Cl_2 / petroleum ether, v/v 1:3) to give **IDT-S-2Cl2F** (78.86 mg, yield=63.1%). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.90 (d, J = 3.1

Hz, 1H), 8.77 (d, J = 3.1 Hz, 1H), 7.93 (d, J = 4.1 Hz, 1H), 7.76 – 7.71 (m, 3H), 7.65 (d, J = 34.3 Hz, 1H), 7.18 – 7.05 (m, 19H), 2.57 (q, J = 6.3, 5.1 Hz, 8H), 1.63 – 1.58 (m, 8H), 1.34 – 1.27 (m, 24H), 0.87 (t, J = 6.6 Hz, 12H).

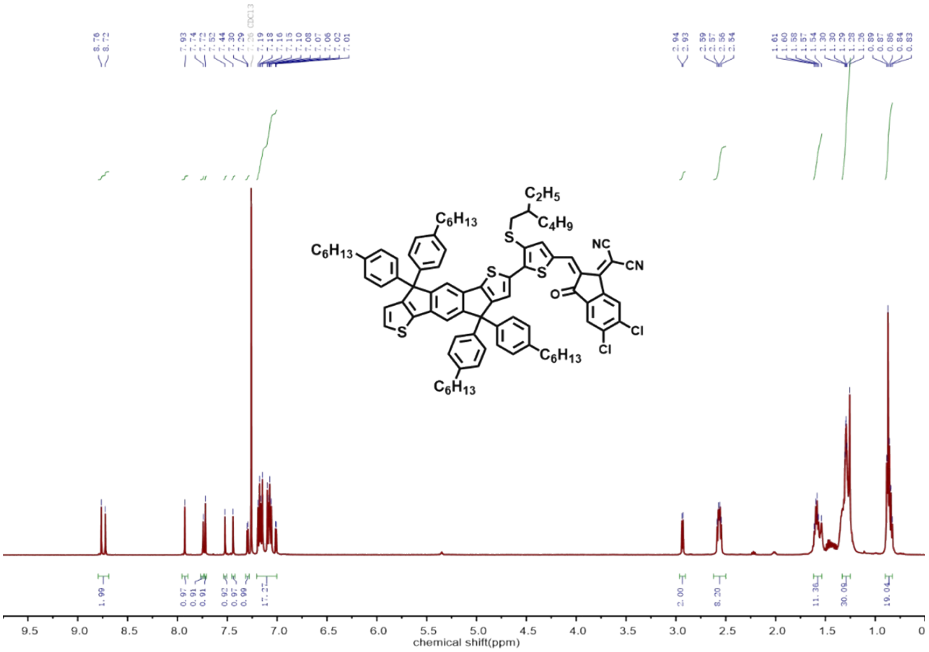


Figure S5. ^{1}H NMR of **IDT-S-2Cl** in $CDCl_3$.

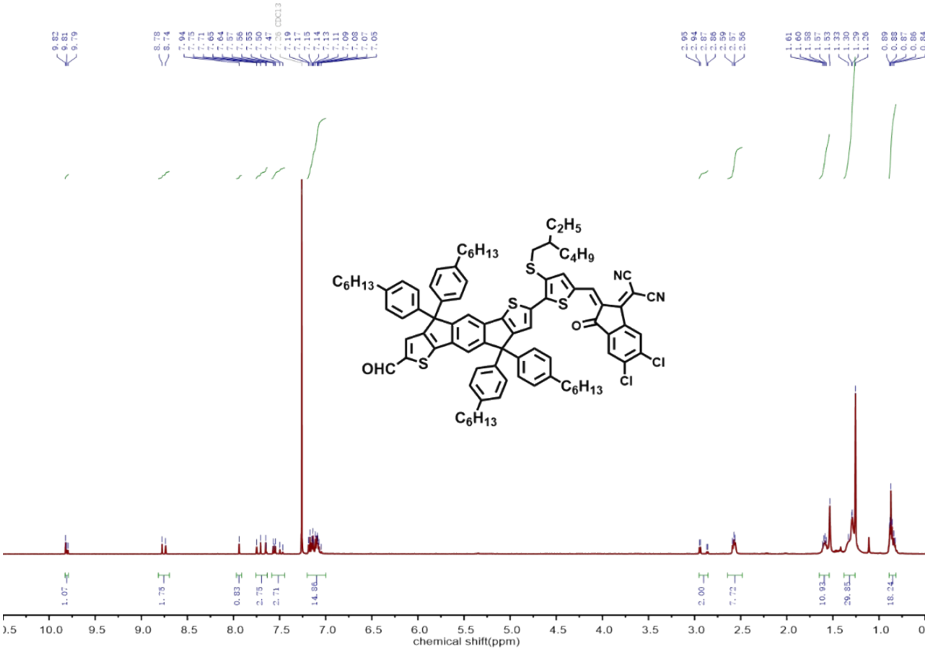


Figure S6. ^{1}H NMR of **IDT-S-2Cl-CHO** in $CDCl_3$.

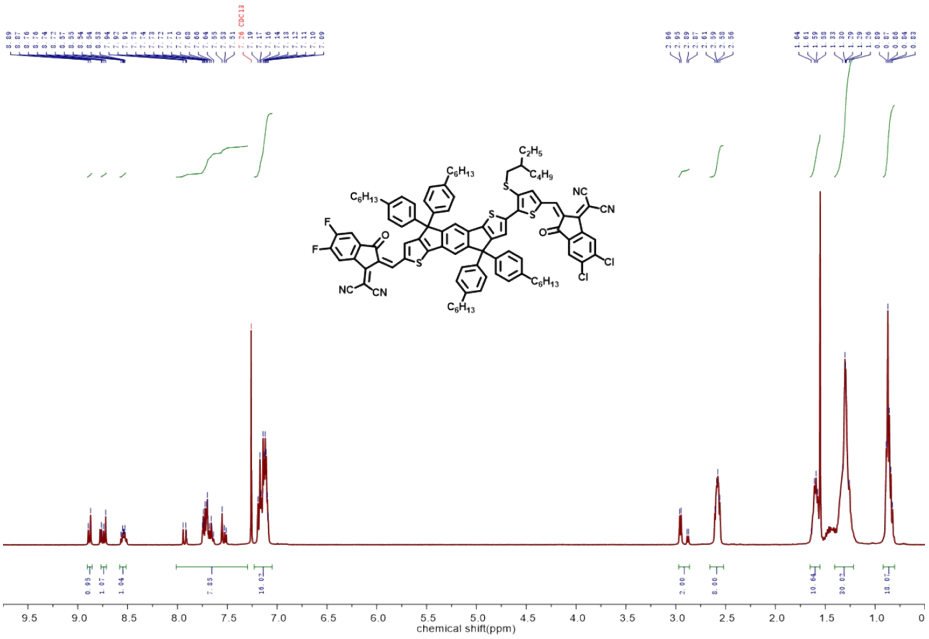


Figure S7. ^{1}H NMR of **IDT-S-2Cl2F** in $CDCl_3$.

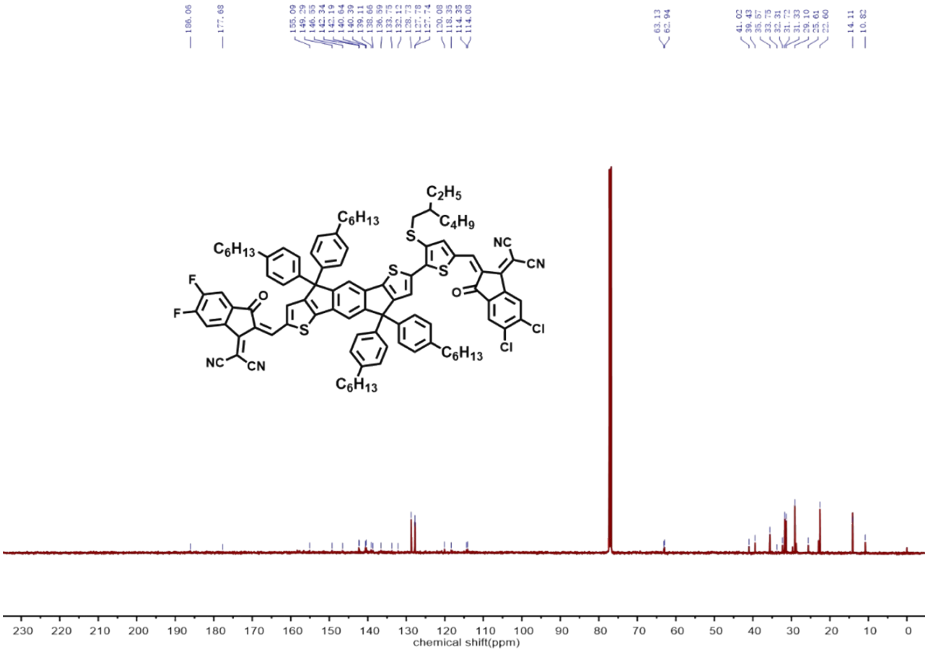


Figure S8. ^{13}C NMR of **IDT-S-2Cl2F** in $CDCl_3$.

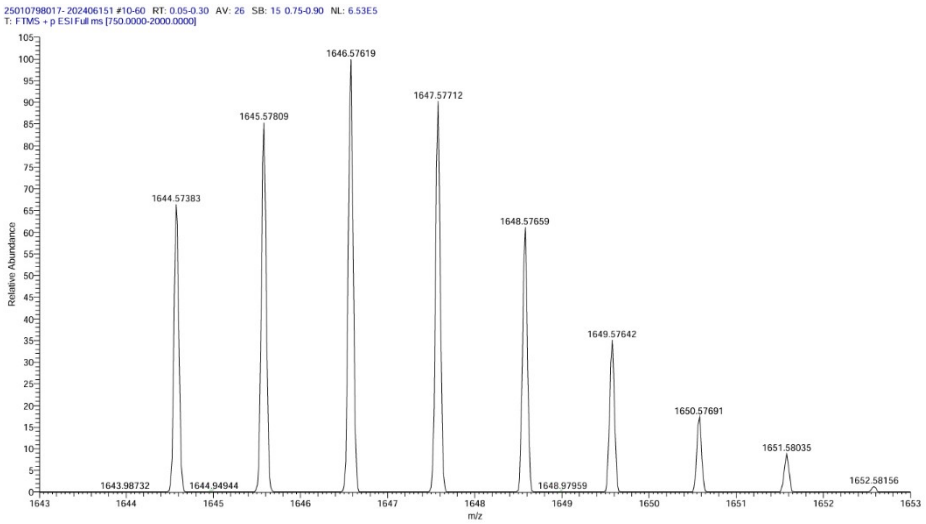
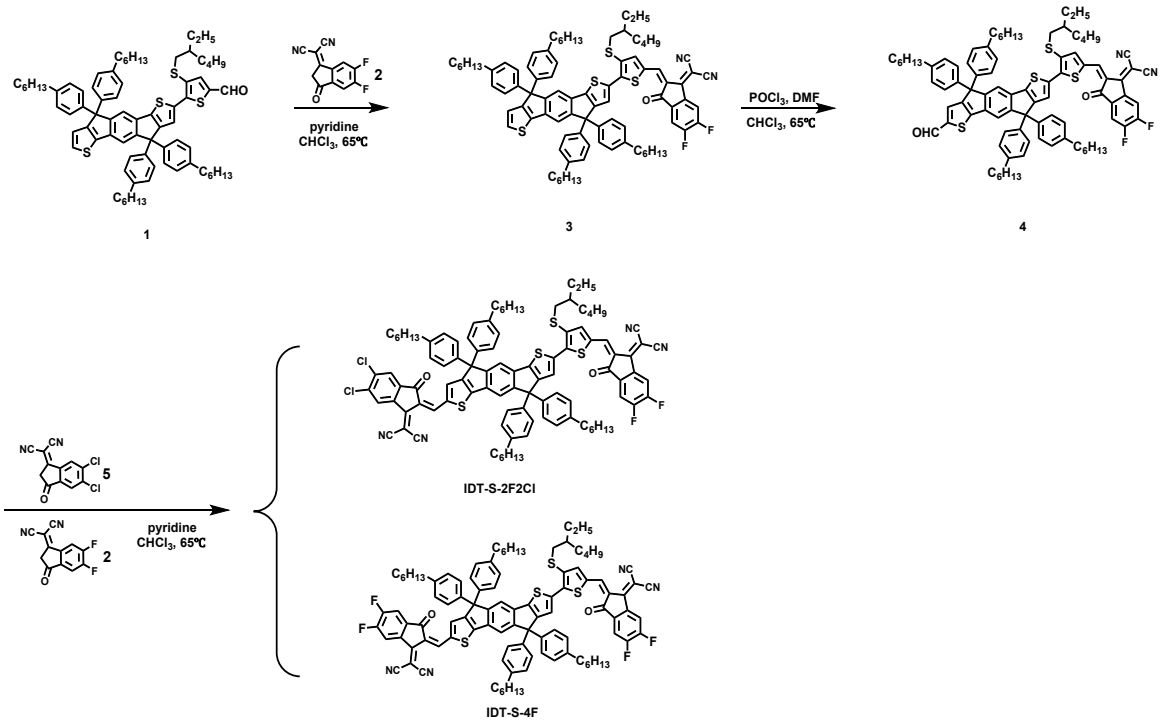


Figure S9. HRMS of **IDT-S-2Cl2F**. MS (HRMS) m/z: Calcd for $C_{102}H_{96}Cl_2F_2N_4O_2S_4$: 1647.05;



Scheme S3. The synthetic route and molecular structure of **IDT-S-2F2Cl**.

Compound 3

A mixture of compound **1** (200 mg, 0.17 mmol) and compound **2** (58.69 mg, 0.255 mmol) in CF (15 mL) was charged into a two-necked flask equipped with a magnetic

stirrer. The system was degassed via argon purging (bubbling) for 20 min, followed by rapid addition of pyridine (1 mL) under continuous argon flow. The mixture was further purged with argon for 10 min and then heated at 65°C in a thermostatic oil bath. Reaction progress was monitored by TLC. After removal of the solvent under reduced pressure, the residue was purified by means of column chromatography on silica gel using a mixed solvent as eluent (CH_2Cl_2 / petroleum ether, v/v 1:3) to give compound **3** (145.7 mg, yield=62.4%).^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.70 (s, 1H), 8.53 (dd, *J* = 9.9, 6.5 Hz, 1H), 7.72 – 7.63 (m, 2H), 7.52 (s, 1H), 7.44 (s, 1H), 7.29 (d, *J* = 4.9 Hz, 1H), 7.17 (dd, *J* = 14.5, 8.3 Hz, 8H), 7.13 – 6.98 (m, 10H), 2.92 (s, 2H), 2.61 – 2.52 (m, 8H), 1.58 (dt, *J* = 14.4, 7.9 Hz, 11H), 1.35 – 1.25 (m, 30H), 0.89 – 0.83 (m, 18H).

Compound 4

$POCl_3$ (6.5 mL) and DMF (9.75 mL) were sequentially injected via syringe into a dry 100 mL two-necked flask under anhydrous conditions. The mixture was maintained at ice-water bath with vigorous stirring for 30 min. A solution of compound **3** (140 mg, 0.1 mmol) in CF was then introduced through the side neck using syringe transfer. The reaction vessel was immersed in a thermostatic oil bath and heated at 65°C with continuous reflux for 18h. The cooled reaction mixture was quenched with distilled water and extracted with CF. After removal of the solvent under reduced pressure, the residue was purified by means of column chromatography on silica gel using a mixed solvent as eluent (CH_2Cl_2 / petroleum ether, v/v 1:3) to give compound **4** (120.43 mg, yield=85.9%). ^{1}H NMR (500 MHz, Chloroform-d) δ 9.83 – 9.79 (m, 1H), 8.73 – 8.52

(m, 2H), 7.75 – 7.64 (m, 3H), 7.61 – 7.42 (m, 3H), 7.22 – 6.97 (m, 16H), 2.90 (dd, J = 38.2, 6.2 Hz, 2H), 2.63 – 2.52 (m, 8H), 1.63 – 1.54 (m, 11H), 1.37 – 1.25 (m, 30H), 0.90 – 0.81 (m, 18H).

Compound IDT-S-2F2Cl and IDT-S-4F

A mixture of compound **4** (① 110 mg, 0.078 mmol; ② 100 mg, 0.07mmol) and compound **5** (30.77 mg, 0.117 mmol) or compound **2** (24.16 mg, 0.105 mmol) in CF (20 mL) was charged into a two-necked flask equipped with a magnetic stirrer. The system was degassed via argon purging (bubbling) for 20 min, followed by rapid addition of pyridine (1 mL) under continuous argon flow. The mixture was further purged with argon for 10 min and then heated at 65°C in a thermostated oil bath. Reaction progress was monitored by TLC. After removal of the solvent under reduced pressure, the residue was purified by means of column chromatography on silica gel using a mixed solvent as eluent (CH_2Cl_2 / petroleum ether, v/v 1:3) to give **IDT-S-2F2Cl** (82.69 mg, yield=64.4%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.88 (d, *J* = 9.1 Hz, 1H), 8.81 – 8.48 (m, 3H), 8.01 – 7.36 (m, 8H), 7.21 – 7.09 (m, 16H), 2.92 (dd, *J* = 30.8, 6.1 Hz, 2H), 2.63 – 2.53 (m, 8H), 1.58 (s, 11H), 1.37 – 1.23 (m, 30H), 0.86 (td, *J* = 12.7, 10.9, 4.7 Hz, 18H).

IDT-S-4F (70.41 mg, yield=62.3%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.87 (s, 1H), 8.72 (s, 1H), 8.54 (dt, *J* = 9.9, 6.4 Hz, 2H), 7.76 – 7.54 (m, 7H), 7.21 – 7.06 (m, 16H), 2.95 (d, *J* = 6.1 Hz, 2H), 2.58 (dq, *J* = 8.2, 4.2 Hz, 8H), 1.61 (dt, *J* = 12.8, 7.7 Hz, 11H), 1.37 – 1.24 (m, 30H), 0.90 – 0.82 (m, 18H).

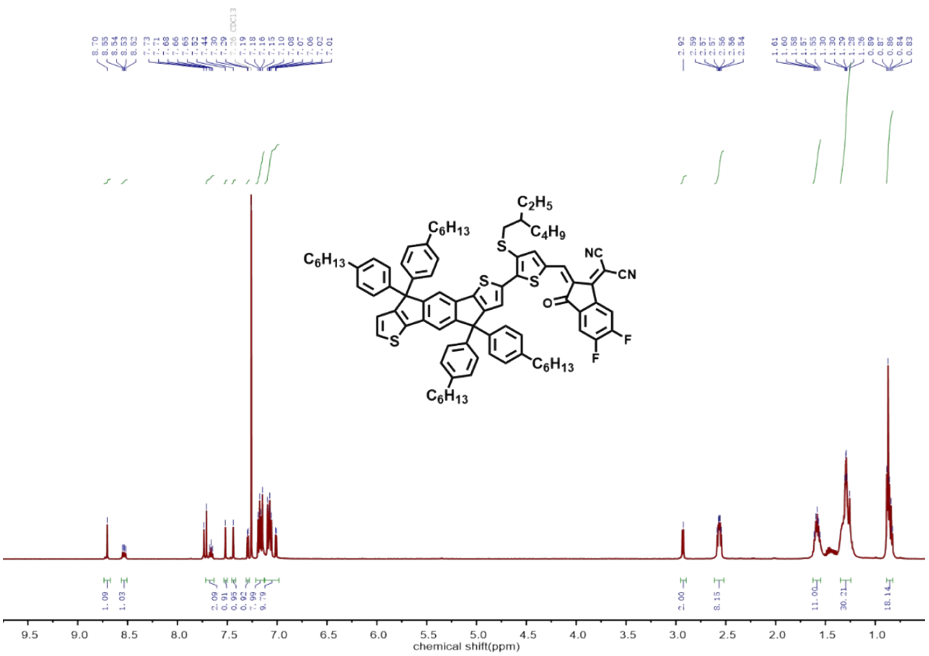


Figure S10. ^{1}H NMR of **IDT-S-2F** in $CDCl_3$.

Figure S11. ^{1}H NMR of **IDT-S-2F-CHO** in $CDCl_3$.

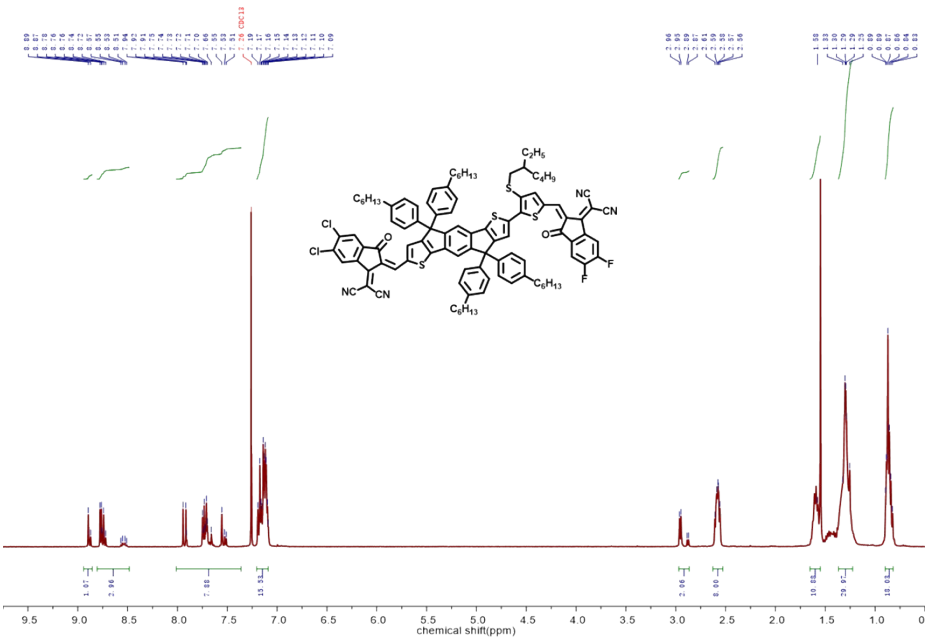


Figure S12. ^{1}H NMR of **IDT-S-2F2Cl** in $CDCl_3$.

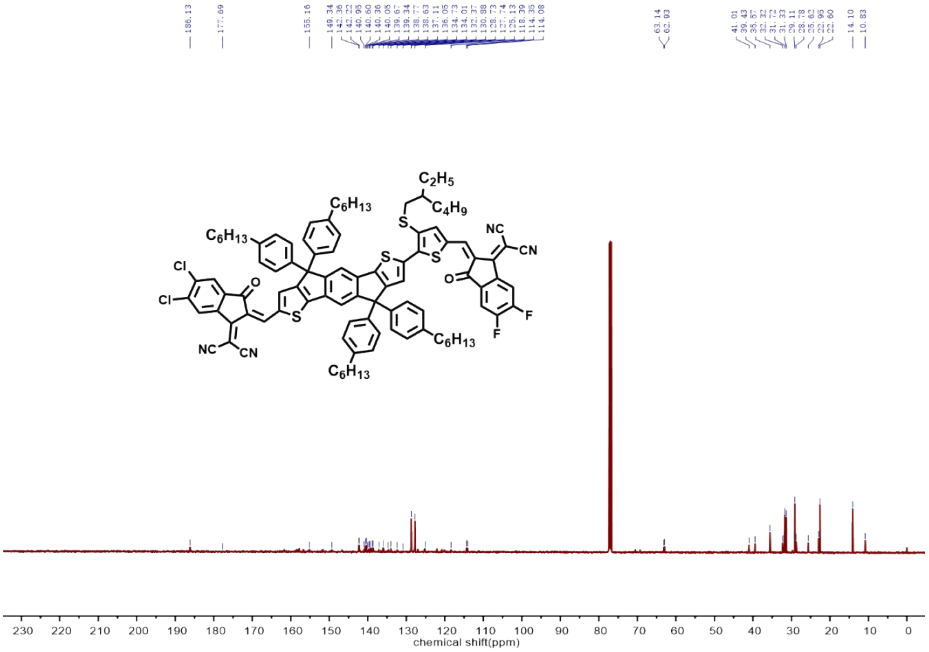


Figure S13. ^{13}C NMR of **IDT-S-2F2Cl** in $CDCl_3$.

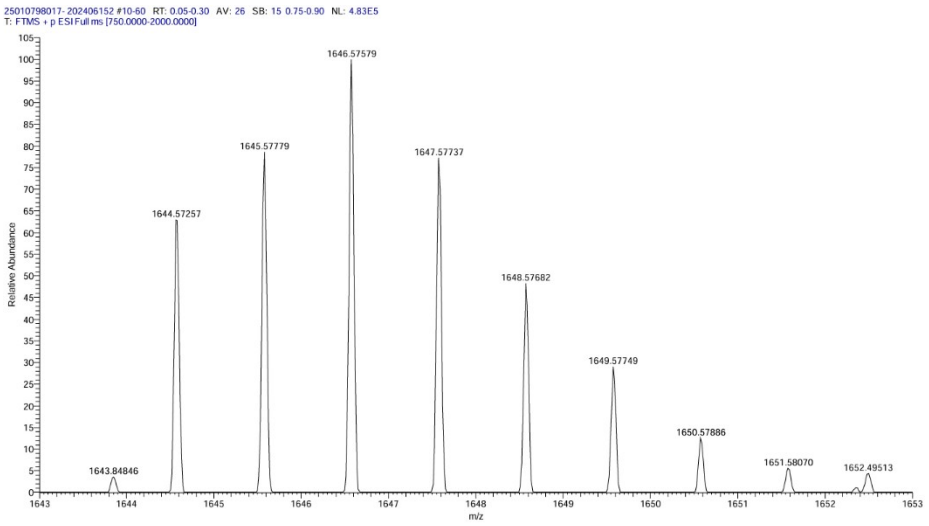


Figure S14. HRMS of **IDT-S-2F2Cl**. MS (HRMS) m/z: Calcd for $C_{102}H_{96}Cl_2F_2N_4O_2S_4$: 1647.05;

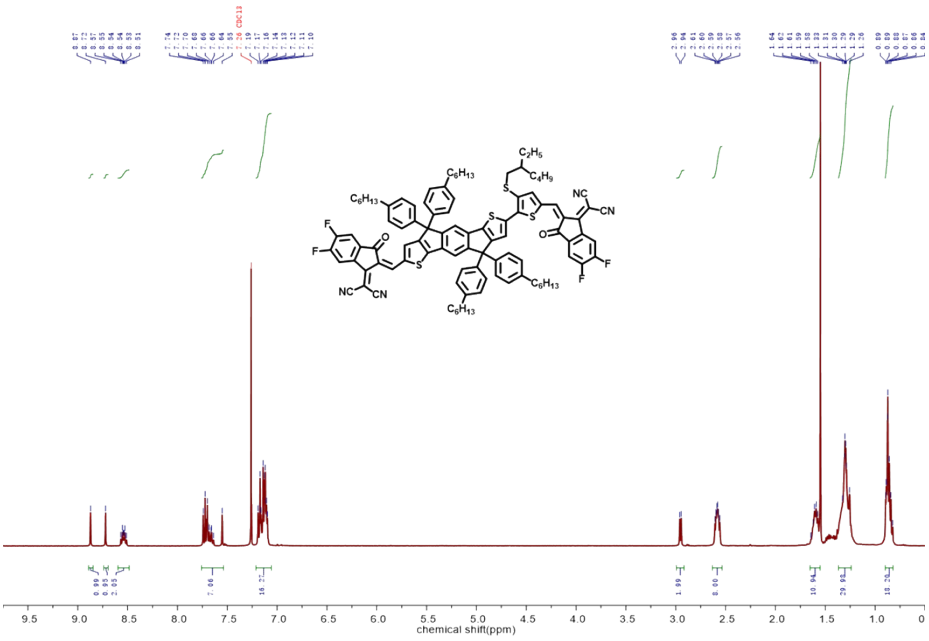


Figure S15. ^{1}H NMR of **IDT-S-4F** in $CDCl_3$.

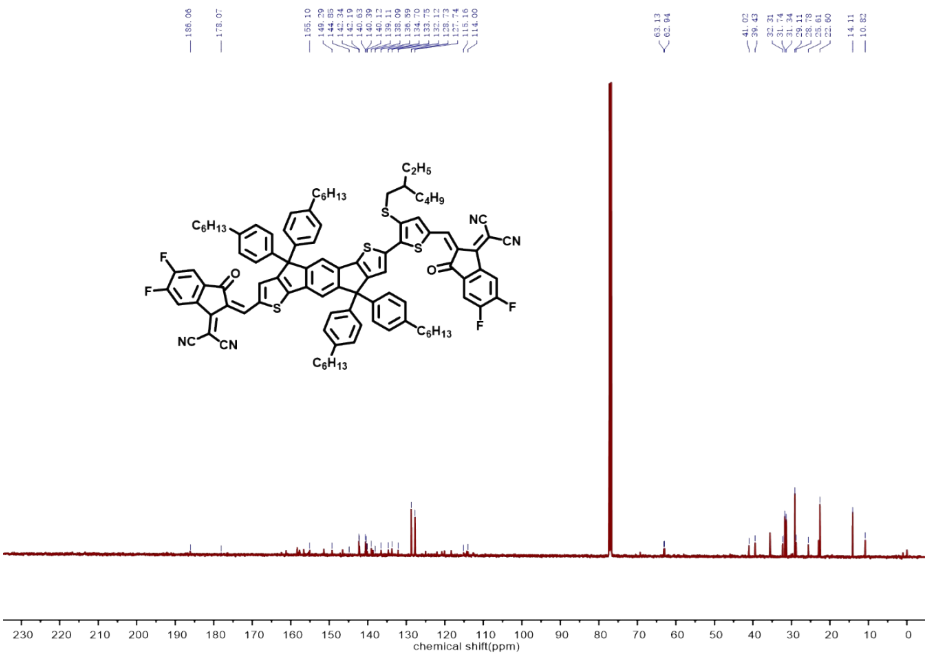


Figure S16. ^{13}C NMR of **IDT-S-4F** in $CDCl_3$.

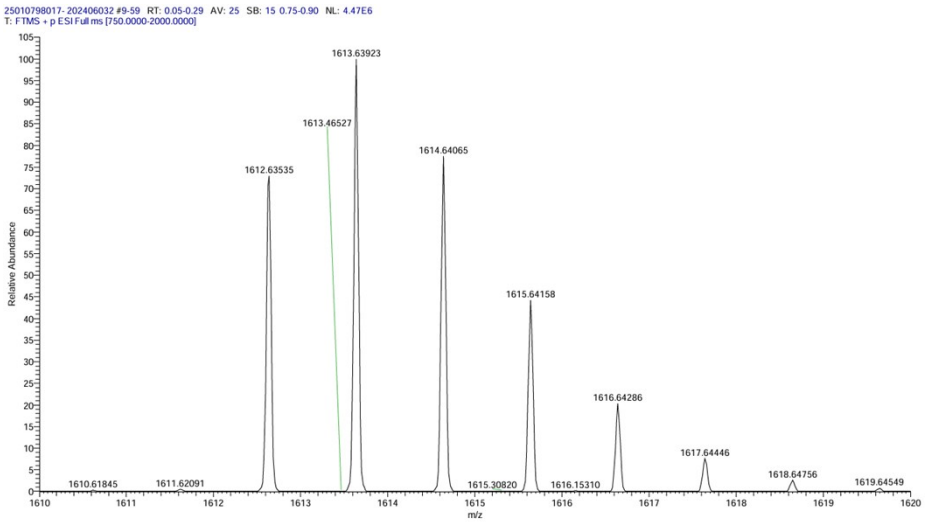


Figure S17. HRMS of **IDT-S-4F**. MS (HRMS) m/z: Calcd for $C_{102}H_{96}F_4N_4O_2S_4$: 1614.15;

2. Device Fabrication Method

The OSC devices were fabricated with the ITO/PEDOT: PSS/PM6: **IDT-2Cl2F** or PM6: **IDT-S-2Cl2F** or PM6: **IDT-S-2F2Cl** or **PM6:IDT-S-4F**/PDINN/Ag (100 nm) structure. Prior to fabrication, the ITO-coated glass substrate was cleaned with deionized water, acetone, and isopropanol. Afterwards, the substrate was treated with

UV-ozone for 30 minutes. The PEDOT: PSS was spin-coated onto the ITO-coated glass surface at a spinning rate of 7000 rpm for 30 seconds. It was then dried at 150°C for 30 minutes and transferred into a nitrogen glove box with less than 5 ppm oxygen and moisture. The active layer was deposited onto the PEDOT: PSS layer by spin-coating a mixed solution of PM6:SMAs (SMAs=**IDT-2Cl2F**, **IDT-S-2Cl2F**, **IDT-S-2F2Cl, IDT-S-4F**) with a blend concentration of 22 mg mL^{-1}. The PDINN solution, with a concentration of 1 mg mL^{-1} in methanol, was spin-coated onto the surface of the ITO-coated active layer at 3400 rpm for 30 seconds. Subsequently, 100 nm of Ag was evaporated onto the active layer in a vacuum chamber under a pressure of approximately 4×10^{-4} Pa.

3.Electron mobility measurements

ITO/ZnO/Active Layer/PDINN/Ag was used to test the electron mobility of these materials. The electron mobilities are calculated according to the space charge limited current (SCLC) method with the equation: $J = 9\mu\varepsilon_r\varepsilon_0 V^2 / 8d^3$, where J is the current density, μ is the hole or electron mobility, V is the internal voltage in the device, ε_r is the relative dielectric constant of active layer material, ε_0 is the permittivity of empty space, and d is the thickness of the active layer.

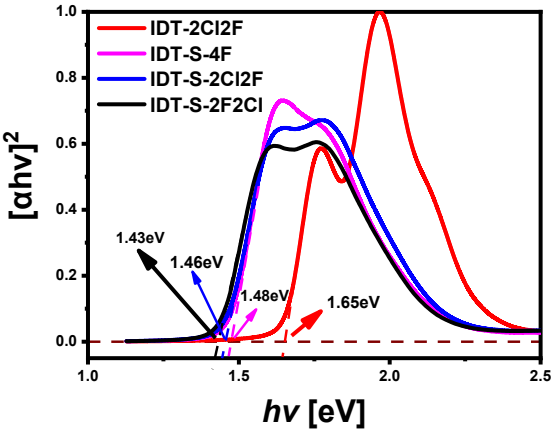


Figure S18. Optical band gaps of **IDT-2Cl2F**, **IDT-S-2Cl2F, IDT-S-2F2Cl** and IDT-S-4F calculated from thin film UV-vis absorption spectra

Table S1. Optical and electrochemical properties of **IDT-2Cl2F**, **IDT-S-2Cl2F**, **IDT-S-2F2Cl** and **IDT-S-4F**.

Material	UV-vis in solid film			CV		
	λ_{max} (nm)	λ_{edge} (nm)	E_g^{opt} (eV)	HOMO (eV)	LUMO (eV)	E_g^{cv} (eV)
IDT-2Cl2F	633	768	1.65	-5.98	-4.01	1.97
IDT-S-2Cl2F	765	881	1.46	-5.64	-4.02	1.62
IDT-S-2F2Cl	774	892	1.43	-5.68	-4.01	1.67
IDT-S-4F	760	872	1.48	-5.68	-4.07	1.61

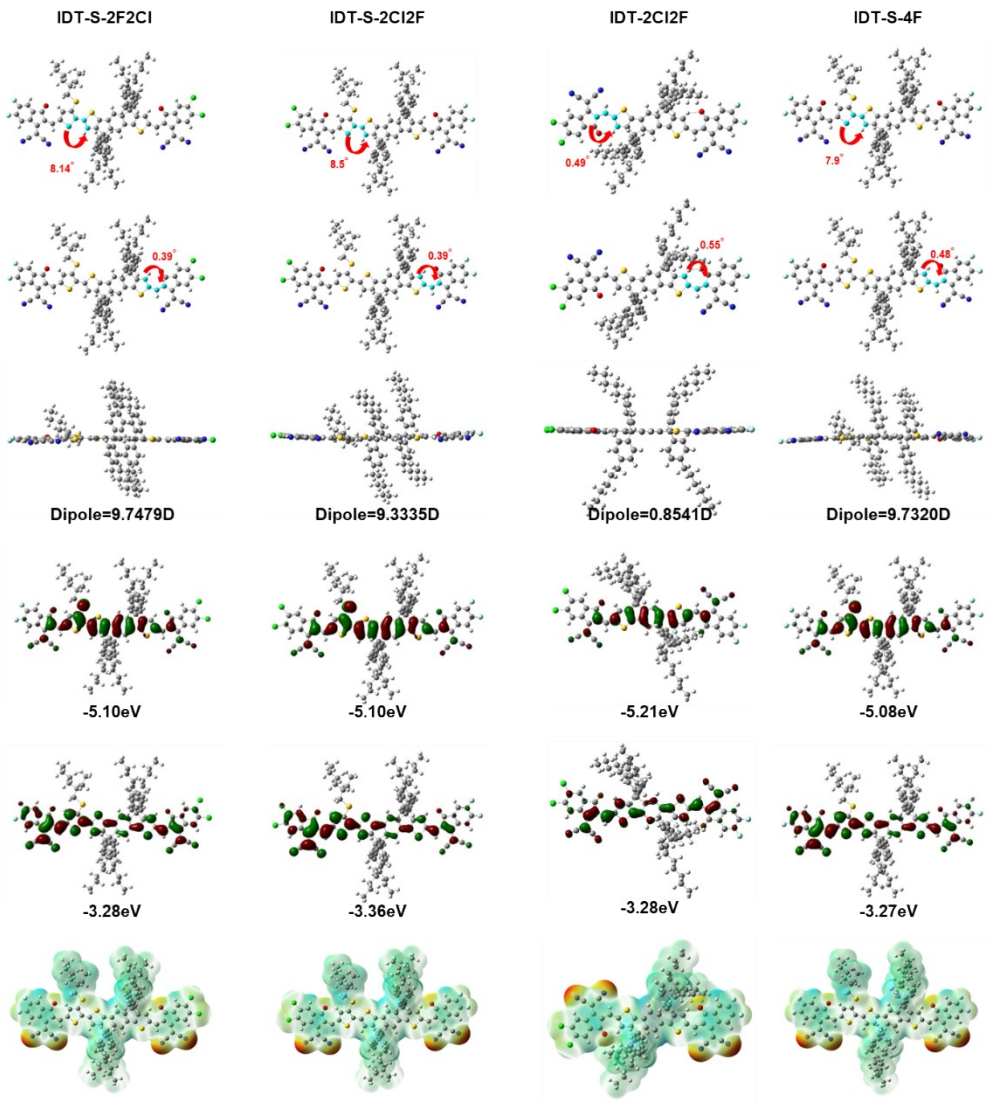


Figure S19. The chemical structures of **IDT-2Cl2F**, **IDT-S-2Cl2F**, **IDT-S-2F2Cl**, and **IDT-S-4F**, along with their corresponding molecular conformations, electron cloud distributions of the frontier molecular orbitals, and electrostatic potential (ESP) maps, were determined based on DFT theoretical calculations at the B3LYP/6-31G(d,p) level.

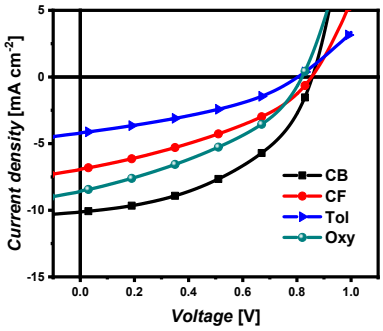


Figure S20. *J-V* plots of PM6: **IDT-2Cl2F**-based OSCs with different solvents under the illumination of AM 1.5G, 100 mW cm^{-2},

Table S2. Photovoltaic parameters of PM6: **IDT-2Cl2F**-based OSCs with different solvents under the illumination of AM 1.5G, 100 mW cm^{-2}

Solvent	V_{oc} (V)	J_{sc} mA cm^{-2})	FF (%)	PCE (%)
CB	0.857	10.13	46.07	4.00
CF	0.854	6.93	36.95	2.18
Tol	0.804	4.20	36.54	1.23
Oxy	0.819	8.58	38.29	2.69

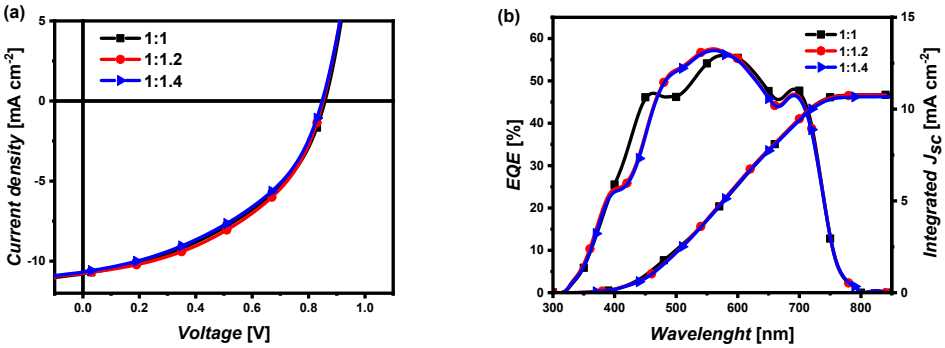


Figure S21. (a) *J-V* plots of PM6: **IDT-2Cl2F**-based OSCs with different D/A under the illumination of AM 1.5G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S3. Photovoltaic parameters of PM6: **IDT-2Cl2F**-based OSCs with different D/A under the illumination of AM 1.5G, 100 mW cm^{-2}

PM6: IDT-2Cl2F	V_{oc} (V)	J_{sc} mA cm^{-2})	Cal. J_{sc} [a] (mA cm^{-2})	FF (%)	PCE (%)
1:1	0.858	11.10	10.78	43.97	4.18
1:1.2	0.852	11.08	10.76	45.94	4.34
1:1.4	0.848	10.99	10.67	43.91	4.09

[a] Integral J_{sc} from EQE curves.

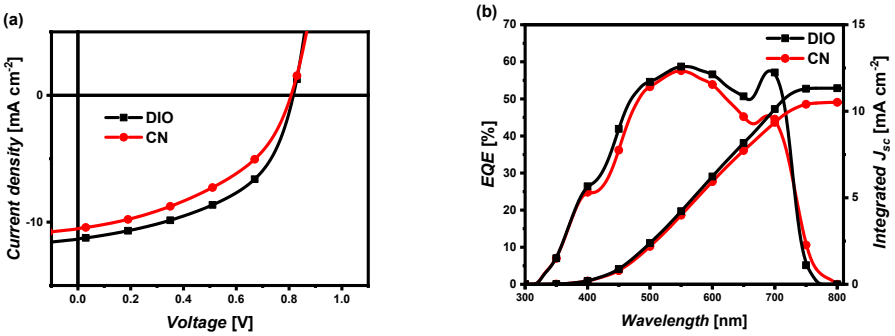


Figure S22. (a) *J-V* plots of PM6: **IDT-2Cl2F**-based OSCs (1:1.2, w/w) with different additive under the illumination of AM 1.5 G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S4. Photovoltaic parameters of PM6: **IDT-2Cl2F**-based OSCs (1:1.2, w/w) with different additive under the illumination of AM 1.5 G, 100 mW cm^{-2}

Additive	V_{oc} (V)	J_{sc} mA cm^{-2})	Cal. J_{sc} [a] (mA cm^{-2})	FF (%)	PCE (%)
CN [b]	0.808	10.83	10.52	44.09	3.85
DIO [c]	0.817	11.67	11.33	49.87	4.75

[a] Integral J_{sc} from EQE curves, [b] CN is an abbreviation of 1-Chloronaphthalene; [c] DIO is an abbreviation of 1,8-Diiodooctane.

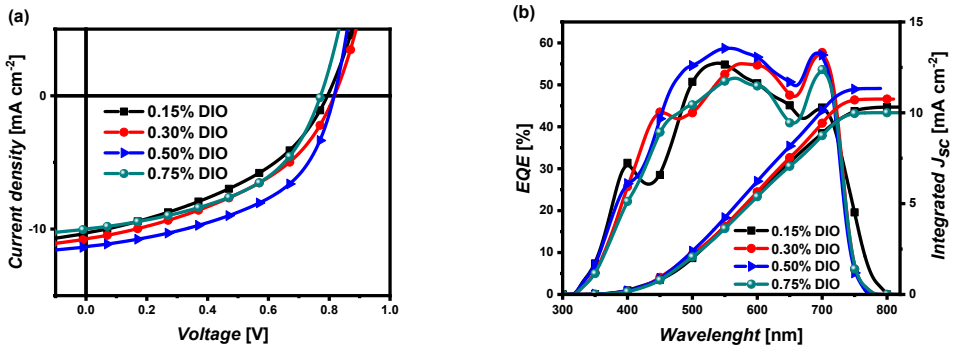


Figure S23. (a) *J-V* plots of PM6: **IDT-2Cl2F**-based OSCs (1:1.2, w/w) with different DIO contents under the illumination of AM 1.5 G, 100 mW cm^{-2}, (b) The corresponding EQE curves of the OSCs.

Table S5. Photovoltaic parameters of PM6: **IDT-2Cl2F**-based OSCs (1:1.2, w/w) with different DIO contents under the illumination of AM 1.5 G, 100 mW cm^{-2}

PM6: IDT-2Cl2F	**V_{oc} (V)**	**J_{sc} mA cm^{-2})**	**Cal. J_{sc} [a] ($mA\ cm^{-2}$)**	**FF (%)**	**PCE (%)**
0.15% DIO	0.794	10.63	10.32	40.76	3.44
0.30% DIO	0.817	11.07	10.75	42.47	3.86
0.50% DIO	0.817	11.67	11.33	49.87	4.75
0.75% DIO	0.772	10.31	10.01	48.34	3.58

[a] Integral J_{sc} from EQE curves.

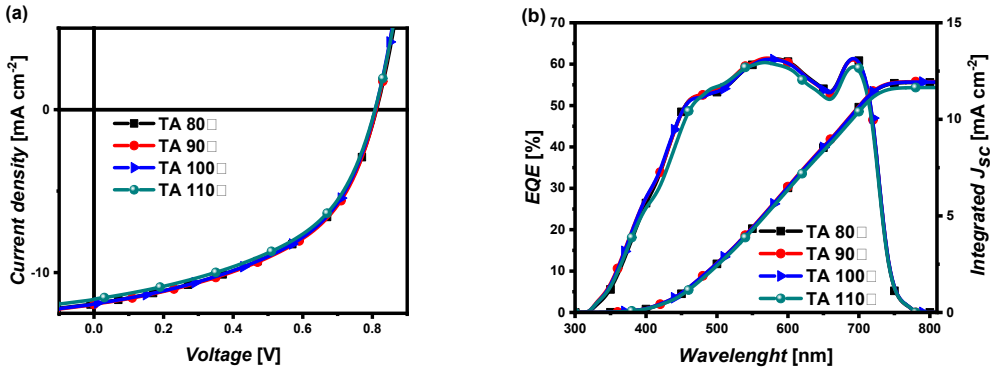


Figure S24. (a) *J-V* plots of PM6: **IDT-2Cl2F**-based OSCs (1:1.2, w/w) with different TA temperature for 5 min, 0.50% DIO as additive under the illumination of AM 1.5 G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S6. Photovoltaic parameters of PM6: **IDT-2Cl2F**-based OSCs (1:1.2, w/w) with different TA temperature for 5 min, 0.50% DIO as additive under the illumination of AM 1.5 G, 100 mW cm^{-2}

PM6: IDT-2Cl2F		V_{oc} (V)	J_{sc} mA cm^{-2})	Cal. J_{sc} [a] (mA cm^{-2})	FF (%)	PCE (%)
0.50% DIO TA 5min	TA 80℃	0.812	12.27	11.91	48.74	4.85
	TA 90℃	0.812	12.31	11.95	49.01	4.90
	TA 100℃	0.808	12.29	11.93	48.82	4.85
	TA 110℃	0.807	11.99	11.64	48.78	4.58

[a] Integral J_{sc} from EQE curves.

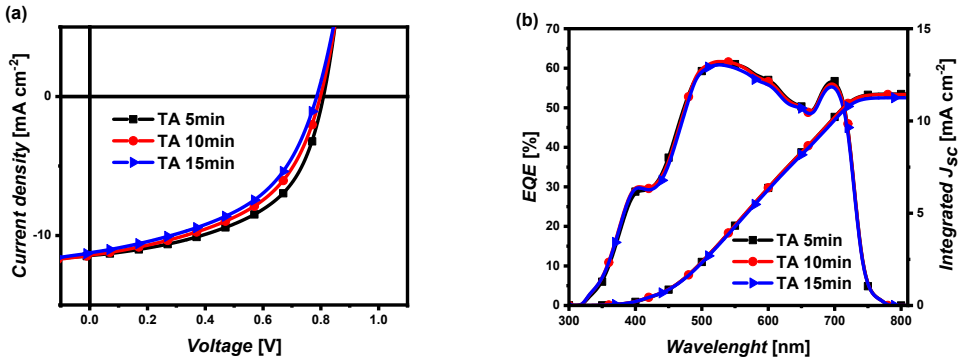


Figure S25. (a) *J-V* plots of PM6: **IDT-2Cl2F**-based OSCs (1:1.2, w/w) with different TA time, 0.50% DIO as additive and TA treatment at 90°C under the illumination of AM 1.5 G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S7. Photovoltaic parameters of PM6: **IDT-2Cl2F**-based OSCs (1:1.2, w/w) with different TA time, 0.50% DIO as additive and TA treatment at 90°C under the illumination of AM 1.5 G, 100 mW cm^{-2}

PM6: IDT-2Cl2F		V_{oc} (V)	J_{sc} mA cm^{-2})	Cal. J_{sc} [a] (mA cm^{-2})	FF (%)	PCE (%)
0.50% DIO TA 90°C	TA 5min	0.810	11.80	11.46	52.49	5.01
	TA 10min	0.798	11.77	11.43	49.27	4.63
	TA 15min	0.786	11.60	11.26	48.03	4.38

[a] Integral J_{sc} from EQE curves.

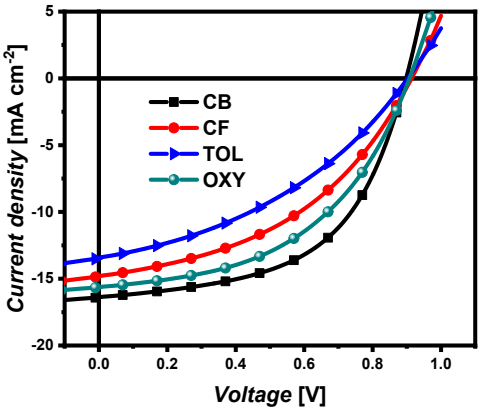


Figure S26. *J-V* plots of PM6: **IDT-S-2Cl2F**-based OSCs with different solvents under the illumination of AM 1.5G, 100 mW cm^{-2},

Table S8. Photovoltaic parameters of PM6: **IDT-S-2Cl2F**-based OSCs with different solvents under the illumination of AM 1.5G, 100 mW cm^{-2}

Solvent	V_{oc} (V)	J_{sc} mA cm^{-2})	FF (%)	PCE (%)
CB	0.898	16.38	54.57	8.03
CF	0.914	14.82	43.35	5.87
Tol	0.903	13.45	38.55	4.68
Oxy	0.908	15.63	48.47	6.88

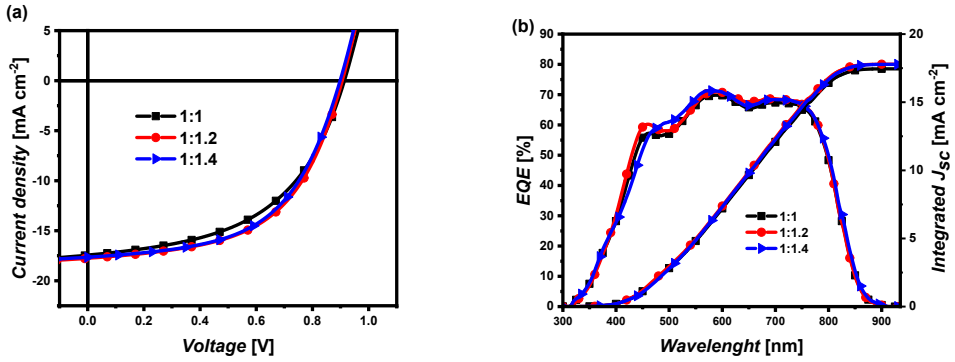


Figure S27. (a) *J-V* plots of PM6: **IDT-S-2Cl2F**-based OSCs with different D/A under the illumination of AM 1.5G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S19. Photovoltaic parameters of PM6: **IDT-S-2Cl2F**-based OSCs with different D/A under the illumination of AM 1.5G, 100 mW cm^{-2}

PM6: IDT-S-2Cl2F	V_{oc} (V)	J_{sc} mA cm^{-2})	Cal. J_{sc} [a)] (mA cm^{-2})	FF (%)	PCE (%)
1:1	0.914	17.99	17.47	50.86	8.36
1:1.2	0.906	18.32	17.79	54.84	9.10
1:1.4	0.898	18.31	17.78	54.72	8.99

[a)] Integral J_{sc} from EQE curves.

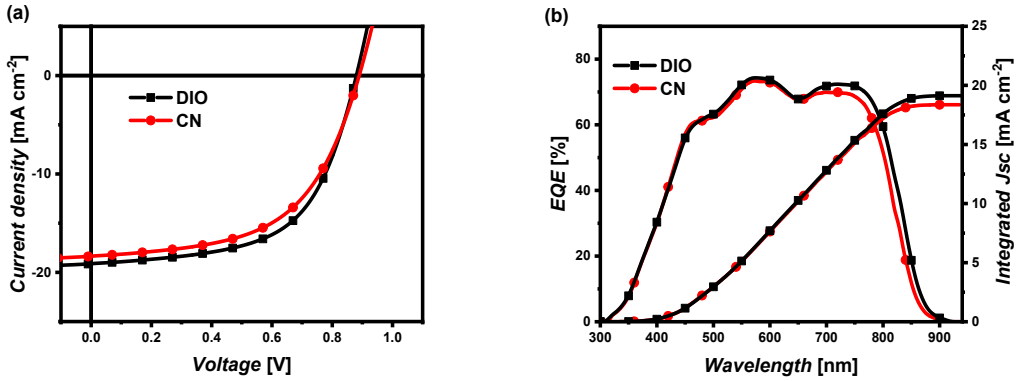


Figure S28. (a) *J-V* plots of PM6: **IDT-S-2Cl2F**-based OSCs (1:1.2, w/w) with different additive under the illumination of AM 1.5 G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S10. Photovoltaic parameters of PM6: **IDT-S-2Cl2F**-based OSCs (1:1.2, w/w) with different additive under the illumination of AM 1.5 G, 100 mW cm^{-2}

Additive	V_{oc} (V)	J_{sc} mA cm^{-2})	Cal. J_{sc} [a)] (mA cm^{-2})	FF (%)	PCE (%)
CN [b)]	0.890	18.91	18.36	55.50	9.34
DIO [c)]	0.880	19.69	19.12	58.84	10.2

[a)] Integral J_{sc} from EQE curves, [b)] CN is an abbreviation of 1-Chloronaphthalene; [c)] DIO is an abbreviation of 1,8-Diiodooctane.

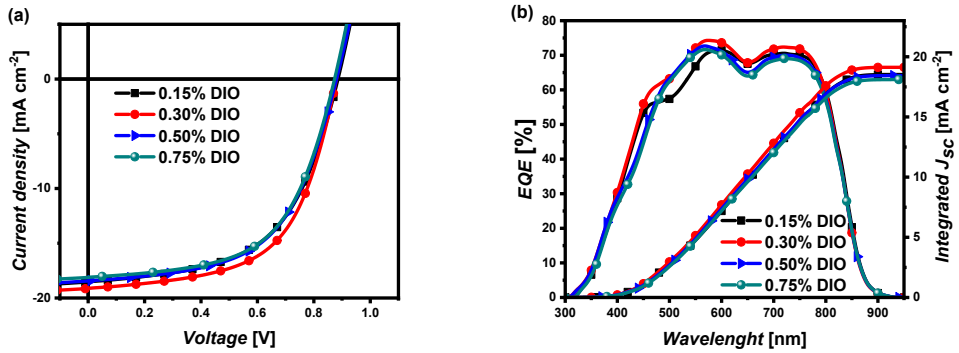


Figure S29. (a) *J-V* plots of PM6: **IDT-S-2Cl2F**-based OSCs (1:1.2, w/w) with different DIO contents under the illumination of AM 1.5 G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S11. Photovoltaic parameters of PM6: **IDT-S-2Cl2F**-based OSCs (1:1.2, w/w) with different DIO contents under the illumination of AM 1.5 G, 100 mW cm^{-2}

PM6: IDT-S-2Cl2F	**V_{oc} (V)**	**J_{sc} mA cm^{-2})**	**Cal. J_{sc} [a] (mA cm^{-2})**	**FF (%)**	**PCE (%)**
0.15% DIO	0.886	19.09	18.53	55.77	9.43
0.30% DIO	0.880	19.69	19.12	58.84	10.2
0.50% DIO	0.880	18.99	18.44	56.72	9.48
0.75% DIO	0.873	18.65	18.11	57.78	9.41

[a] Integral J_{sc} from EQE curves.

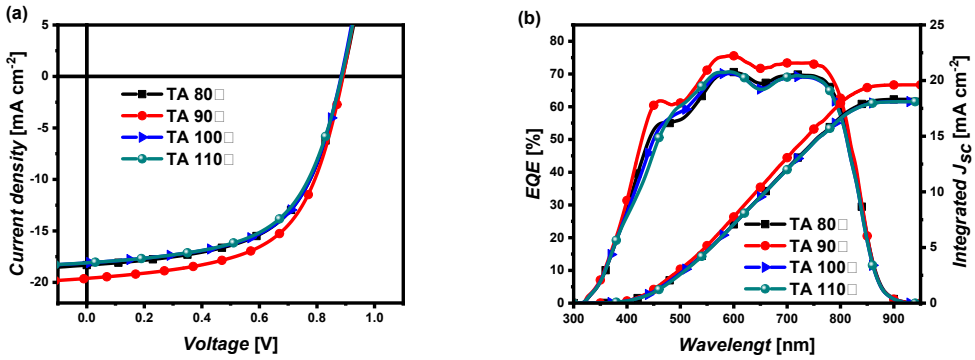


Figure S30. (a) *J-V* plots of PM6: **IDT-S-2Cl2F**-based OSCs (1:1.2, w/w) with different TA temperature for 5 min, 0.30% DIO as additive under the illumination of AM 1.5 G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S12. Photovoltaic parameters of PM6: **IDT-S-2Cl2F**-based OSCs (1:1.2, w/w) with different TA temperature for 5 min, 0.30% DIO as additive under the illumination of AM 1.5 G, 100 mW cm^{-2}

PM6: IDT-S-2Cl2F		V_{oc} (V)	J_{sc} mA cm^{-2})	Cal. J_{sc} [a] (mA cm^{-2})	FF (%)	PCE (%)
0.30% DIO TA 5min	TA 80°C	0.890	18.87	18.32	57.87	9.72
	TA 90°C	0.891	20.21	19.62	58.51	10.53
	TA 100°C	0.884	18.65	18.11	58.81	9.70
	TA 110°C	0.886	18.64	18.10	57.89	9.56

[a] Integral J_{sc} from EQE curves.

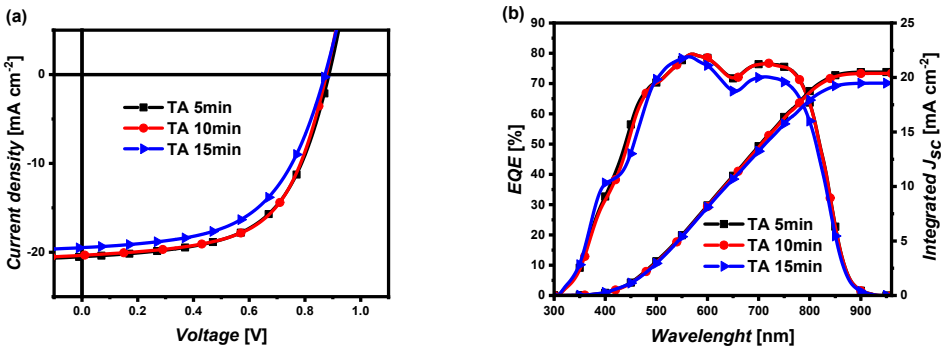


Figure S31. (a) *J-V* plots of PM6: **IDT-S-2Cl2F**-based OSCs (1:1.2, w/w) with different TA time, 0.30% DIO as additive and TA treatment at 90°C under the illumination of AM 1.5 G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S13. Photovoltaic parameters of PM6: **IDT-S-2Cl2F**-based OSCs (1:1.2, w/w) with different TA time, 0.30% DIO as additive and TA treatment at 90°C under the illumination of AM 1.5 G, 100 mW cm^{-2}

PM6: IDT-S-2Cl2F		V_{oc} (V)	J_{sc} mA cm^{-2})	Cal. J_{sc} [a] (mA cm^{-2})	FF (%)	PCE (%)
0.30% DIO TA 90°C	TA 5 min	0.887	21.12	20.5	58.13	10.89
	TA 10 min	0.877	20.96	20.35	59.61	10.95
	TA 15 min	0.872	20.06	19.48	55.71	9.74

[a] Integral J_{sc} from EQE curves.

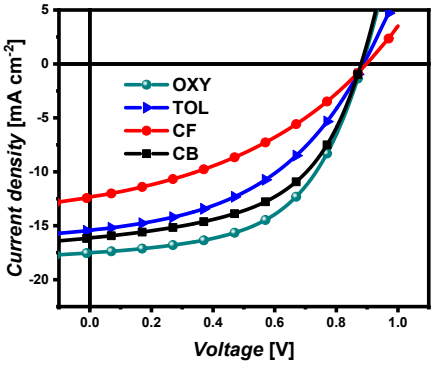


Figure S32. *J-V* plots of PM6: **IDT-S-2F2Cl**-based OSCs with different solvents under the illumination of AM 1.5G, 100 mW cm^{-2},

Table S14. Photovoltaic parameters of PM6: **IDT-S-2F2Cl**-based OSCs with different solvents under the illumination of AM 1.5G, 100 mW cm^{-2}

Solvent	V_{oc} (V)	J_{sc} mA cm^{-2})	FF (%)	PCE (%)
CB	0.880	16.14	52.28	7.42
CF	0.897	12.84	38.38	4.42
Tol	0.888	15.43	44.67	6.12
Oxy	0.885	17.51	54.24	8.41

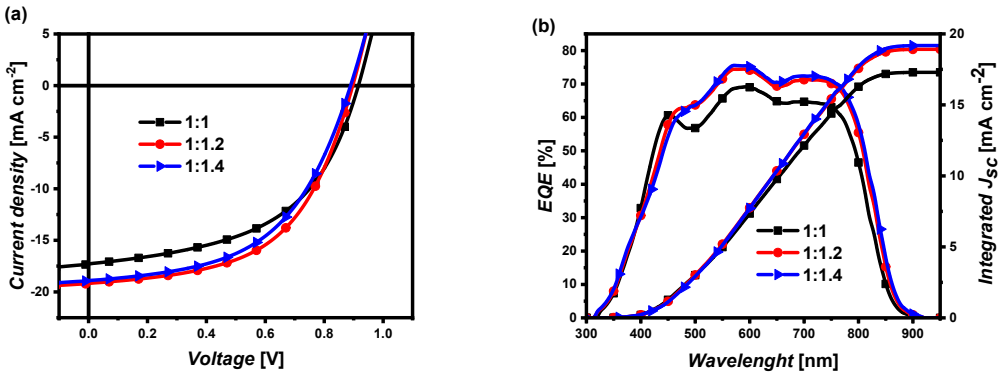


Figure S33. (a) *J-V* plots of PM6: **IDT-S-2F2Cl**-based OSCs with different D/A under the illumination of AM 1.5G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S15. Photovoltaic parameters of PM6: **IDT-S-2F2Cl**-based OSCs with different D/A under the illumination of AM 1.5G, 100 mW cm^{-2}

PM6: IDT-S-2F2Cl	V_{oc} (V)	J_{sc} mA cm^{-2})	Cal. J_{sc} [a)] (mA cm^{-2})	FF (%)	PCE (%)
1:1	0.916	17.82	17.30	51.54	8.41
1:1.2	0.897	19.76	19.18	54.30	9.34
1:1.4	0.890	19.48	18.91	52.11	8.77

[a)] Integral J_{sc} from EQE curves.

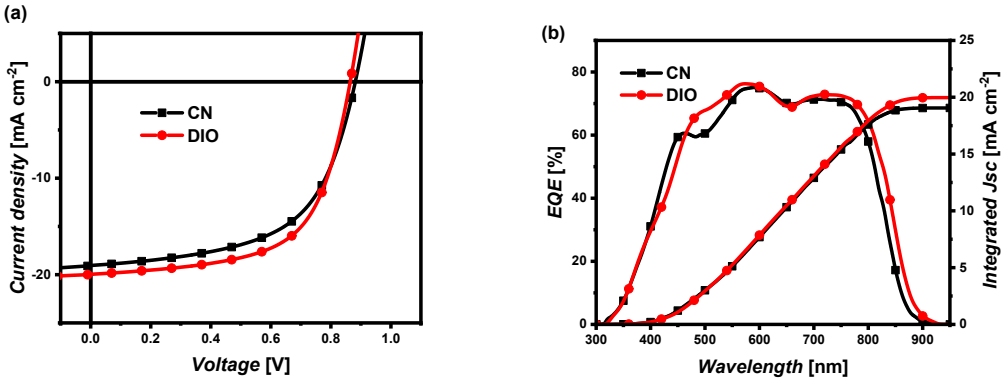


Figure S34. (a) *J-V* plots of PM6: **IDT-S-2F2Cl**-based OSCs (1:1.2, w/w) with different additive under the illumination of AM 1.5 G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S16. Photovoltaic parameters of PM6: **IDT-S-2F2Cl**-based OSCs (1:1.2, w/w) with different additive under the illumination of AM 1.5 G, 100 mW cm^{-2}

Additive	V_{oc} (V)	J_{sc} mA cm^{-2})	Cal. J_{sc} [a)] (mA cm^{-2})	FF (%)	PCE (%)
CN [b)]	0.882	19.63	19.06	57.71	9.99
DIO [c)]	0.864	20.57	19.97	61.96	11.01

[a)] Integral J_{sc} from EQE curves, [b)] CN is an abbreviation of 1-Chloronaphthalene; [c)] DIO is an abbreviation of 1,8-Diiodooctane.

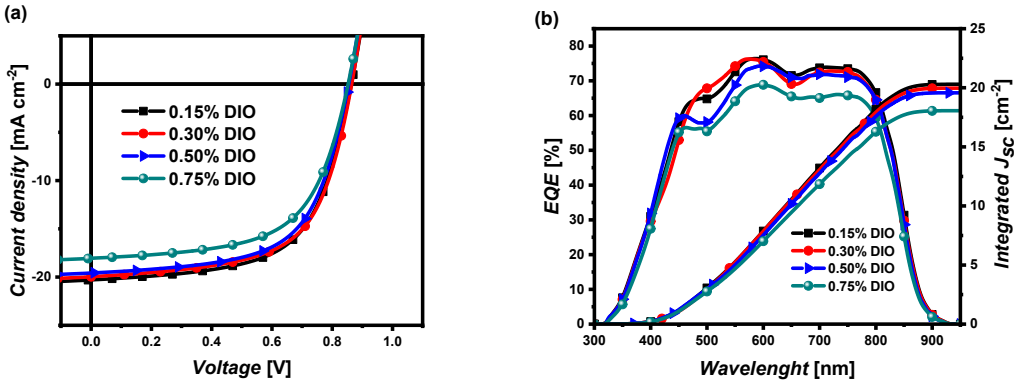


Figure S35. (a) *J-V* plots of PM6: **IDT-S-2F2Cl**-based OSCs (1:1.2, w/w) with different DIO contents under the illumination of AM 1.5 G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S17. Photovoltaic parameters of PM6: **IDT-S-2F2Cl**-based OSCs (1:1.2, w/w) with different DIO contents under the illumination of AM 1.5 G, 100 mW cm^{-2}

PM6: IDT-S-2F2Cl	**V_{oc} (V)**	**J_{sc} mA cm^{-2})**	**Cal. J_{sc} [a)] (mA cm^{-2})**	**FF (%)**	**PCE (%)**
0.15% DIO	0.864	20.91	20.30	61.69	11.14
0.30% DIO	0.864	20.57	19.97	61.96	11.01
0.50% DIO	0.855	20.16	19.58	61.84	10.66
0.75% DIO	0.853	18.60	18.06	60.77	9.64

[a)] Integral J_{sc} from EQE curves.

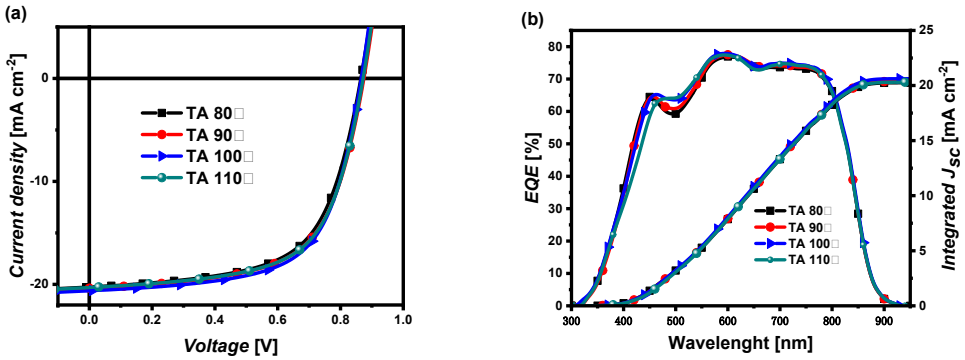


Figure S36. (a) *J-V* plots of PM6: **IDT-S-2F2Cl**-based OSCs (1:1.2, w/w) with different TA temperature for 5 min, 0.15% DIO as additive under the illumination of AM 1.5 G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S18. Photovoltaic parameters of PM6: **IDT-S-2F2Cl**-based OSCs (1:1.2, w/w) with different TA temperature for 5 min, 0.15% DIO as additive under the illumination of AM 1.5 G, 100 mW cm^{-2}

PM6: IDT-S-2F2Cl		V_{oc} (V)	J_{sc} mA cm^{-2})	Cal. J_{sc} [a] (mA cm^{-2})	FF (%)	PCE (%)
0.15% DIO TA 5min	TA 80°C	0.864	20.85	20.25	62.22	10.88
	TA 90°C	0.875	20.98	20.37	62.44	11.13
	TA 100°C	0.866	21.03	20.62	63.82	11.39
	TA 110°C	0.872	20.91	20.30	62.96	11.15

[a] Integral J_{sc} from EQE curves.

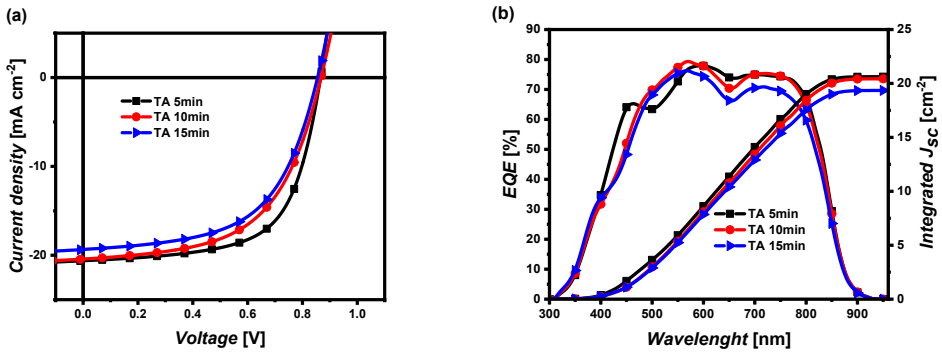


Figure S37. (a) *J-V* plots of PM6: **IDT-S-2F2Cl**-based OSCs (1:1.2, w/w) with different TA time, 0.15% DIO as additive and TA treatment at 100°C under the illumination of AM 1.5 G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S19. Photovoltaic parameters of PM6: **IDT-S-2F2Cl**-based OSCs (1:1.2, w/w) with different TA time, 0.15% DIO as additive and TA treatment at 100°C under the illumination of AM 1.5 G, 100 mW cm^{-2}

PM6: IDT-S-2F2Cl		V_{oc} (V)	J_{sc} mA cm^{-2})	Cal. J_{sc} [a] (mA cm^{-2})	FF (%)	PCE (%)
0.15% DIO TA 100°C	TA 5min	0.866	21.03	20.62	63.82	11.39
	TA 10min	0.868	21.01	20.43	56.20	10.24
	TA 15min	0.855	19.93	19.35	56.87	9.41

[a] Integral J_{sc} from EQE curves.

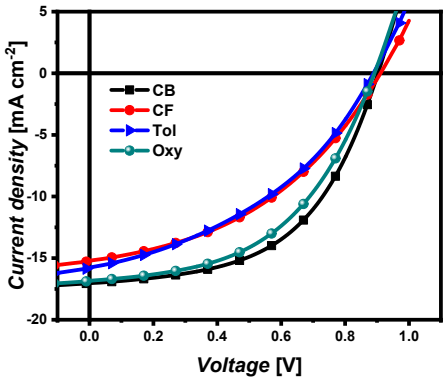


Figure S38. *J-V* plots of PM6: **IDT-S-4F**-based OSCs with different solvents under the illumination of AM 1.5G, 100 mW cm^{-2},

Table S20. Photovoltaic parameters of PM6: **IDT-S-4F**-based OSCs with different solvents under the illumination of AM 1.5G, 100 mW cm^{-2}

Solvent	V_{oc} (V)	J_{sc} mA cm^{-2})	FF (%)	PCE (%)
CB	0.903	17.04	52.73	8.35
CF	0.911	15.23	41.44	5.92
Tol	0.889	15.79	39.82	5.76
Oxy	0.892	16.85	49.47	7.66

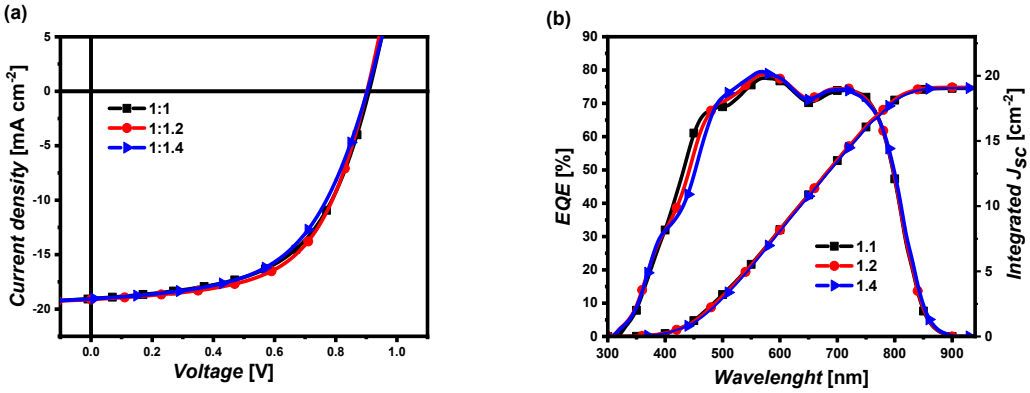


Figure S39. (a) *J-V* plots of PM6: **IDT-S-4F**-based OSCs with different D/A under the illumination of AM 1.5G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S21. Photovoltaic parameters of PM6: **IDT-S-4F**-based OSCs with different D/A under the illumination of AM 1.5G, 100 mW cm^{-2}

PM6: IDT-S-4F	V_{oc} (V)	J_{sc} mA cm^{-2})	Cal. J_{sc} [a)] (mA cm^{-2})	FF (%)	PCE (%)
1:1	0.909	19.62	19.05	56.18	10.02
1:1.2	0.901	19.68	19.11	58.32	10.34
1:1.4	0.903	19.63	19.06	55.18	9.78

[a)] Integral J_{sc} from EQE curves.

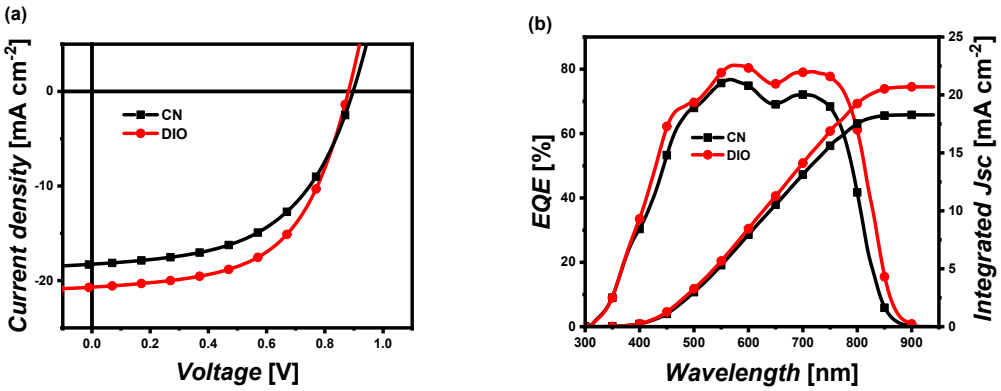


Figure S40. (a) *J-V* plots of PM6: **IDT-S-4F**-based OSCs (1:1.2, w/w) with different additive under the illumination of AM 1.5 G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S22. Photovoltaic parameters of PM6: **IDT-S-4F**-based OSCs (1:1.2, w/w) with different additive under the illumination of AM 1.5 G, 100 mW cm^{-2}

Additive	V_{oc} (V)	J_{sc} mA cm^{-2})	Cal. J_{sc} [a)] (mA cm^{-2})	FF (%)	PCE (%)
CN [b)]	0.897	18.83	18.28	52.78	8.91
DIO [c)]	0.881	21.32	20.70	56.26	10.57

[a)] Integral J_{sc} from EQE curves, [b)] CN is an abbreviation of 1-Chloronaphthalene; [c)] DIO is an abbreviation of 1,8-Diiodooctane.

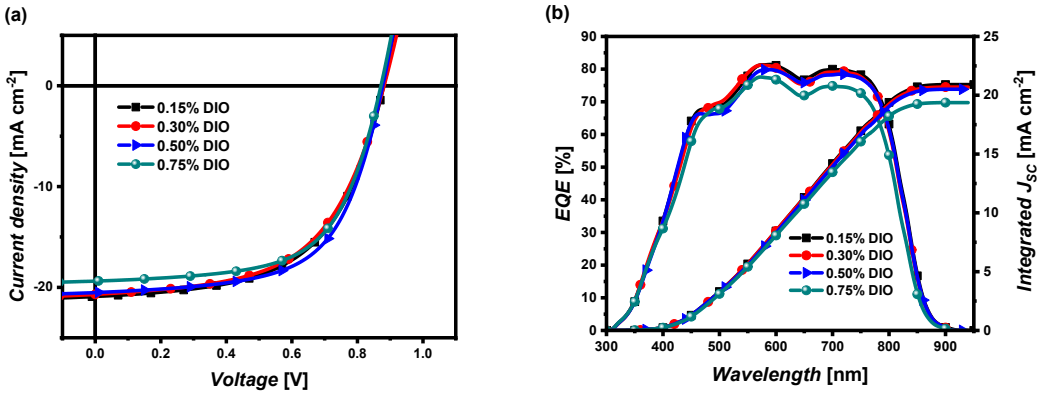


Figure S41. (a) *J-V* plots of PM6: **IDT-S-4F**-based OSCs (1:1.2, w/w) with different DIO contents under the illumination of AM 1.5 G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S23. Photovoltaic parameters of PM6: **IDT-S-4F**-based OSCs (1:1.2, w/w) with different DIO contents under the illumination of AM 1.5 G, 100 mW cm^{-2}

PM6: IDT-S-4F	V_{oc} (V)	J_{sc} mA cm^{-2})	Cal. J_{sc} [a] (mA cm^{-2})	FF (%)	PCE (%)
0.15% DIO	0.880	21.54	20.91	56.94	10.79
0.30% DIO	0.881	21.32	20.70	56.26	10.57
0.50% DIO	0.877	21.14	20.52	61.43	11.39
0.75% DIO	0.872	19.96	19.38	61.60	10.72

[a] Integral J_{sc} from *EQE* curves.

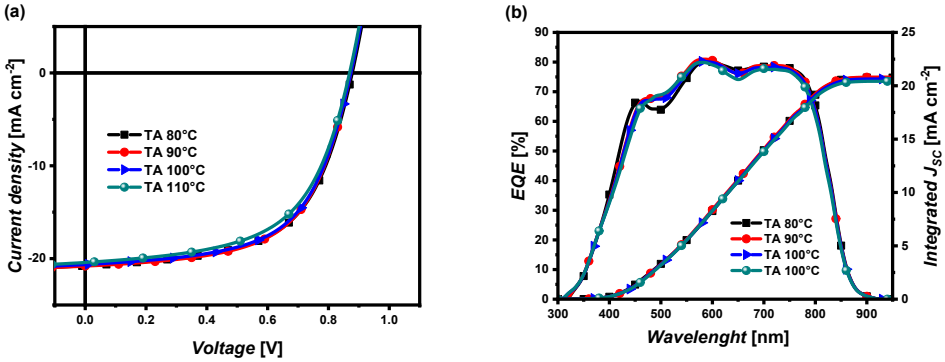


Figure S42. (a) *J-V* plots of PM6: **IDT-S-4F**-based OSCs (1:1.2, w/w) with different TA temperature for 5 min, 0.50% DIO as additive under the illumination of AM 1.5 G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S24. Photovoltaic parameters of PM6: **IDT-S-2F2Cl**-based OSCs (1:1.2, w/w) with different TA temperature for 5 min, 0.50% DIO as additive under the illumination of AM 1.5 G, 100 mW cm^{-2}

PM6: IDT-S-4F		V_{oc} (V)	J_{sc} mA cm^{-2})	Cal. J_{sc} [a] (mA cm^{-2})	FF (%)	PCE (%)
0.50% DIO TA 5min	TA 80°C	0.878	21.39	20.77	59.34	11.14
	TA 90°C	0.874	21.43	20.81	59.69	11.18
	TA 100°C	0.874	21.26	20.64	59.44	11.04
	TA 110°C	0.870	21.03	20.42	57.70	10.25

[a] Integral J_{sc} from EQE curves.

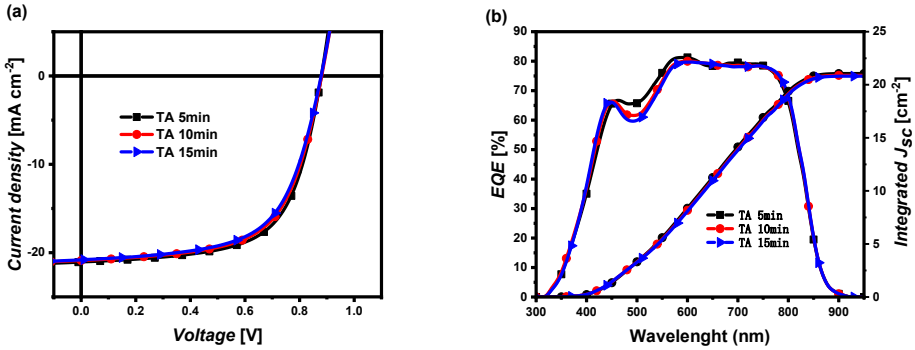


Figure S43. (a) *J-V* plots of PM6: **IDT-S-4F**-based OSCs (1:1.2, w/w) with different TA time, 0.50% DIO as additive and TA treatment at 90°C under the illumination of AM 1.5 G, 100 mW cm^{-2}; (b) The corresponding EQE curves of the OSCs.

Table S25. Photovoltaic parameters of PM6: **IDT-S-4F**-based OSCs (1:1.2, w/w) with different TA time, 0.50% DIO as additive and TA treatment at 90°C under the illumination of AM 1.5 G, 100 mW cm^{-2}

PM6: IDT-S-4F		V_{oc} (V)	J_{sc} mA cm^{-2})	Cal. J_{sc} [a] (mA cm^{-2})	FF (%)	PCE (%)
0.50% DIO TA 90°C	TA 5min	0.880	21.68	21.06	63.86	12.18
	TA 10min	0.881	21.52	20.89	62.46	11.84
	TA 15min	0.879	21.43	20.81	61.64	11.61

[a)] Integral J_{sc} from EQE curves.

Table S26. Parameters extracted from photo-CELIV plots.

Active Layer	*A* (V ms^{-1})	t_{max} (μs)	*Δj* (mA)	*j(0)* (mA)	*Δj/ j(0)*	*d* (nm)	*μ*[a)] (cm^2 V^{-1}s^{-1})
PM6: **IDT-2Cl2F**	72.5	3.270	5.75	1.85	3.108	100	4.04×10^{-5}
PM6: **IDT-S-2Cl2F**	72.5	2.369	4.39	2.61	1.680	100	1.02×10^{-4}
PM6: **IDT-S-2F2Cl**	72.5	2.273	3.00	1.18	2.540	100	9.29×10^{-5}
PM6: **IDT-S-4F**	72.5	2.037	2.88	1.55	1.858	100	1.32×10^{-4}

[a)] Calculated from the formula, $\mu = 2d^2/[3At^2_{max}(1+0.36\Delta j/j(0))]$, where d is the active layer thickness, A is the voltage ramp, t_{max} is the maximum current time, Δj is the peak transient current, and $j(0)$ is the displacement current.

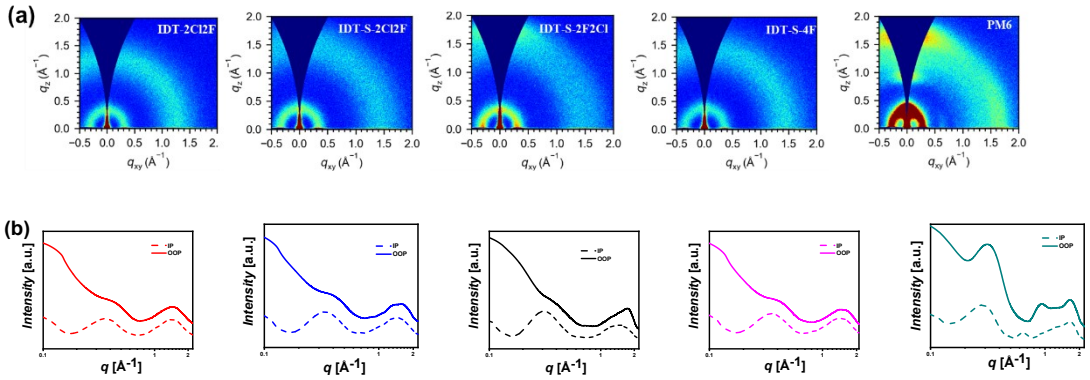


Figure S44. (a) GIWAXS patterns; (b) 1D GIWAXS profiles of the **IDT-2Cl2F**, **IDT-S-2Cl2F**, **IDT-S-2F2Cl, IDT-S-4F,** PM6-based neat films.

Table S27. GIWAXS parameters of the PM6, **IDT-S-2Cl2F**, **IDT-S-2F2Cl**, **IDT-2Cl2F** and **IDT-S-4F** films.

Active layer	In plane (100)			Out of plane (010)		
	Location ($Å^{-1}$)	*d*-spacing (Å)	CCL (Å)	Location ($Å^{-1}$)	*d*-spacing (Å)	CCL (Å)
PM6	0.28	22.44	38.80	1.66	3.79	7.54
IDT-2Cl2F	0.36	17.45	26.67	1.46	4.30	7.50
IDT-S-2Cl2F	0.33	19.04	28.55	1.59	3.95	7.67
IDT-S-2F2Cl	0.30	20.94	35.33	1.73	3.63	8.43
IDT-S-4F	0.35	17.95	28.63	1.49	4.22	7.28

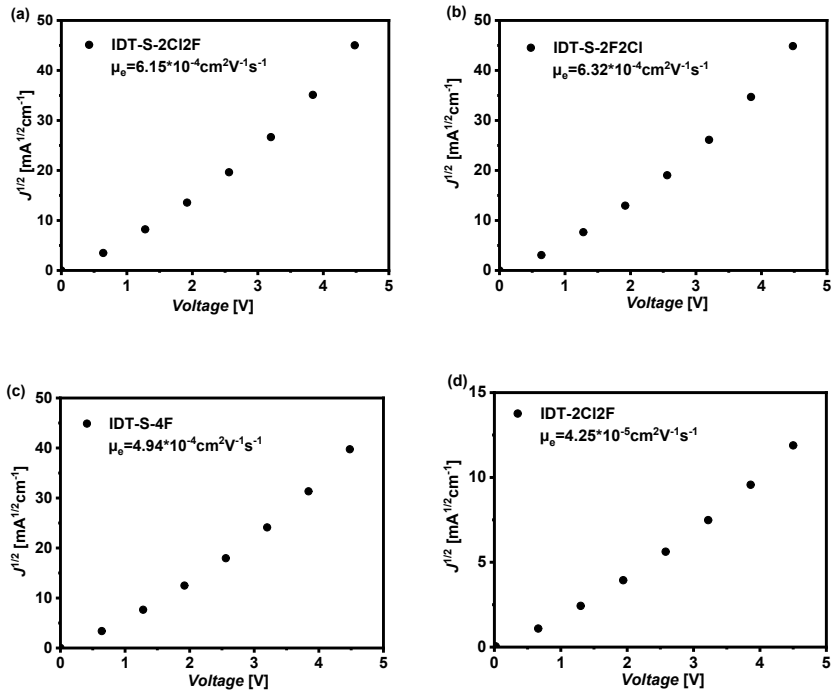


Figure S45 $J^{1/2}$~V characteristics of the charge carrier mobility measurements of the blend films in the dark.

Table S28. GIWAXS parameters of the PM6:**IDT-2Cl2F**, PM6:**IDT-S-2Cl2F**, PM6:**IDT-S-2F2Cl** and PM6:**IDT-S-4F** films.

Active layer	In plane (100)			Out of plane (010)		
	Location ($Å^{-1}$)	*d*-spacing (Å)	CCL (Å)	Location ($Å^{-1}$)	*d*-spacing (Å)	CCL (Å)
PM6:**IDT-2Cl2F**	0.29	21.67	46.15	1.68	3.74	13.58
Pm6:**IDT-S-2Cl2F**	0.30	20.94	47.33	1.72	3.65	13.06
PM6:**IDT-S-2F2Cl**	0.30	20.94	46.12	1.72	3.65	13.83
PM6:**IDT-S-4F**	0.30	20.94	48.15	1.72	3.65	17.62