Supporting information

Efficient Polymer Solar Cells Enabled by Alkoxy-Phenyl Side-Chain Modified Main-Chain Twisted Small Molecular Acceptor

Baofeng Zhao,[a, †] Weiping Wang, [a, †] Yuan Xie,[b] Heng Zhao,[c] Sha Liu,[b] Jingming Xin, [c] Zhiyuan Cong, [a] Liuchang Wang,[d] Haimei Wu,[a] Quanbin Liang,[b] Wei Ma,[c,] Chao Gao,[a,*] Hongbin Wu, [b,*] Yong Cao [b]*

[a] State Key Laboratory of Fluorine & Nitrogen Chemicals, Xi'an Modern Chemistry Research Institute, Xi'an, Shaanxi, 710065, P. R. China. E-Mail: chaogao1974@hotmail.com (C. Gao).

[b] Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou, 510640, P. R. China. E-Mail: hbwu@scut.edu.cn (H. B. Wu).

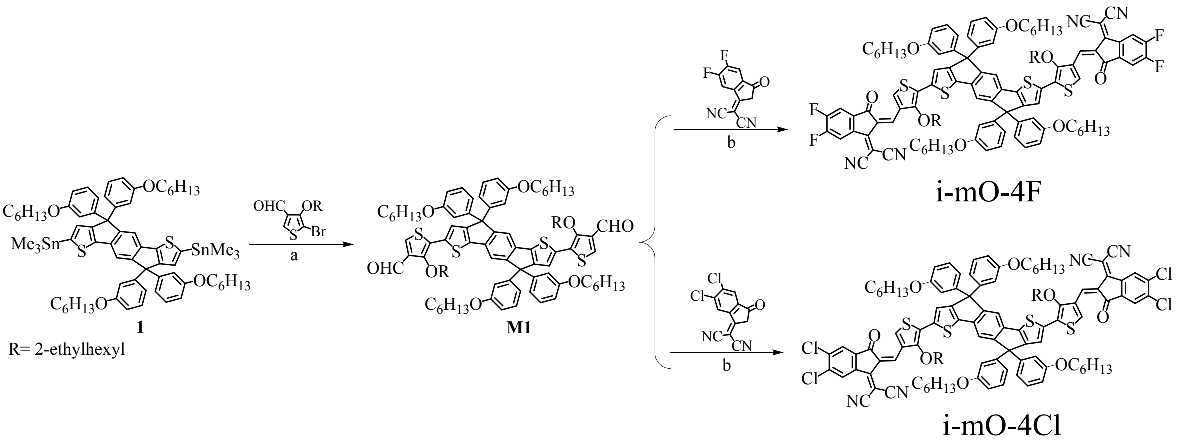
[c] State Key Laboratory for Mechanical Behavior of Materials, Xi'an Jiaotong University, Xi'an 710049, P. R. China. E-Mail: msewma@ xjtu.edu.cn (W. Ma).

[d] School of Chemical Engineering, Xi'an University, No. 168 of South Taibai Road, Xi'an, 710065, China.

[†] B. Zhao and W. Wang contribute equally to this work.

Experimental Methods

PBDB-T was synthesized in our laboratory according to the literature. [1] Using gel permeation chromatography (GPC) method on a PLGPC220 instrument at 150 °C with 1,2,4-trichlorobenzene as eluent and polystyrene as standard, the weight-average molecular weight (M_w) of PBDB-T is measured as 62 kDa with a polydispersity index (PDI) of 2.81. All the other chemicals were purchased as reagent grade from Aladdin, J & K, and Alfa Aesar Chemical Co., and used without further purification unless otherwise noted. The alkoxyl-phenyl modified IDT tin-derivatives (compound **1)** was synthesized according to our previous work. [2] The key intermediate 5-bromo-4-(2-ethylhexyloxy)-thiophene-3-carbaldehyde (compound 2) was synthesized according to the published literature. [3]



Scheme S1. Synthetic route of **i-mO-4F** and **i-mO-4Cl**. Reagents and conditions: a) $Pd(PPh_3)_4$, toluene, reflux; b) pyridine, $CHCl_3$

Synthesis of compound **M1**.

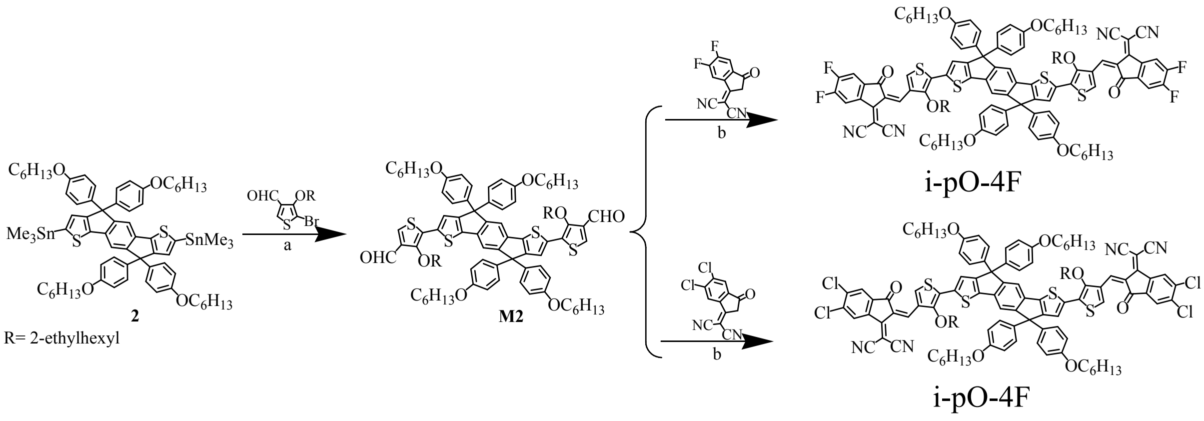
Compound **1** (518 mg) and 5-bromo-4-(2-ethylhexyloxy)-thiophene-3-carbaldehyde (446 mg) were dissolved in a 100 mL dry flask in degassed toluene (26 mL), the mixture was flushed with nitrogen for 30 min, then ($Pd(PPh_3)_4$) (40 mg) was added under nitrogen. After stirring the mixture at 90 °C for 14 hour, the reaction was quenched with 50 mL water and extracted with ethyl acetate. Then, the combined organic solvent was washed with brine and dried over anhydrous magnesium sulfate ($MgSO_4$). After removing the solvent, the compound **M1** was purified with column chromatography on silica-gel using mixture of ethyl acetate (EA) and hexane (1: 20 by volume) as a red solid (420 mg, 72.5%).^{1}H NMR (500 MHz, $CDCl_3$), δ 9.94 (s, 2H), 7.44 (s, 2H), 7.21 (m, 4H), 6.87 (s, 2H), 6.82-6.78 (br, 12H), 4.05 (d, 4H), 3.87 (t, 8H), 1.74 (m, 10H), 1.61-1.30 (m, 40H), 0.97-0.86 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$), δ 180.30, 164.75, 159.18, 156.51, 153.38, 146.56, 145.24, 143.25, 139.22, 135.32, 129.51, 121.75, 120.33, 119.38, 117.85, 115.18, 112.24, 111.30, 74.54, 68.05, 63.64, 39.52, 31.61, 30.41, 29.21, 29.02, 25.73, 23.82, 22.98, 22.59, 14.05, 14.04, 11.14. Anal.Calcd for ($C_{90}H_{110}O_8S_4$): C 74.65, H 7.66, Found: C 74.58, H 7.80.

Synthesis of compound **i-mO-4F**.

To a mixture of compound **M1** (231 mg) and 2-(5,6-difluoro-3-oxo -2,3-dihydro-1H-inden-1-ylidene) malononitrile (2F-INCN, 192 mg) were dissolved in a dry flask in 25 mL chloroform, pyridine (0.8 mL) was added at room temperature. Then the mixture was vigorously stirred at 60 ^{o}C for 12 h. After cooling down, the mixture was extracted with chloroform. Then, the organic layer was dried over anhydrous magnesium sulfate ($MgSO_4$) and concentrated to afford the crude product. The crude product solution was poured into methanol and filtered through a Buchner funnel. Then the solid product of **i-mO-4F** was purified by silica gel by using chloroform as eluent to give a black solid. (200 mg, 66.9%). ^{1}H NMR (500 MHz, $CDCl_3$), δ 9.13 (s, 2H), 8.51 (dd, 2H), 7.60 (t, 2H), 7.53 (d, 4H), 7.23 (t, 4H), 6.92 (s, 2H), 6.85-6.80 (br, 12H), 4.17 (m, 4H), 3.91 (t, 8H), 1.90 (m, 2H), 1.77-1.71 (m, 8H), 1.55-1.28 (m, 40H), 0.97-0.85 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$), δ 188.59, 169.94, 159.24, 158.68, 157.69, 155.04, 154.18, 154.02, 152.98, 146.10, 144.82, 139.41, 135.75, 132.88, 129.68, 123.78, 120.36, 118.28, 117.41, 117.23, 115.26, 115.15, 114.58, 112.22, 109.27, 75.86, 68.09, 67.36, 63.70, 39.30, 31.62, 30.02, 29.22, 28.95, 25.74, 23.45, 23.01, 22.59, 14.11, 14.04, 10.92. Anal.Calcd for ($C_{114}H_{114}F_4N_4O_8S_4$): C 73.13, H 6.14, Found: C 73.25, H 6.31.

Synthesis of compound **i-mO-4Cl**.

To a mixture of **M1** (152mg) and 2-(5,6-dichloro-3-oxo -2,3-dihydro-1H-inden-1-ylidene)malononitrile (2Cl-INCN, 138 mg) were dissolved in a dry flask in 25 mL chloroform, pyridine (0.6 mL) was added at room temperature. Then the mixture was vigorously stirred at 60 ^{o}C for 8 h. After cooling down, the mixture was extracted with chloroform. Then, the organic layer was dried over anhydrous magnesium sulfate ($MgSO_4$) and concentrated to afford the crude product. The crude product solution was poured into methanol and filtered through a Buchner funnel. Then the solid product of **i-mO-4Cl** was purified by silica gel by using chloroform as eluent to give a black solid. (87 mg, 42.8%). ^{1}H NMR (500 MHz, $CDCl_3$), δ 9.15 (s, 2H), 8.71 (s, 2H), 7.84 (s, 2H), 7.54 (d, 4H), 7.23 (t, 4H), 6.92 (s, 2H), 6.85-6.80 (br, 12H), 4.16 (m, 4H), 3.91 (t, 8H), 1.90 (m, 2H), 1.75-1.72 (m, 8H), 1.55-1.28 (m, 40H), 0.97-0.85 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$), δ 186.66, 170.13, 158.82, 158.49, 155.10, 154.52, 145.96, 145.41, 138.85, 135.96, 135.61, 135.20, 128.93, 126.61, 124.58, 123.83, 117.84 115.15, 114.66, 114.57, 109.14, 75.95, 68.06, 67.34, 62.51, 39.28, 31.57, 30.00, 29.24, 28.95, 25.74, 23.44, 23.01, 22.60, 14.12, 14.03, 10.91. Anal.Calcd for ($C_{114}H_{114}Cl_4N_4O_8S_4$): C 70.64, H 5.93, N 2.89 Found: C 68.97, H 5.92. N 2.70.



Scheme S2. Synthetic route of **i-pO-4F** and **i-pO-4Cl**. Reagents and conditions: a) $Pd(PPh_3)_4$, toluene, reflux; b) pyridine, $CHCl_3$

Synthesis of compound **M2**.

Compound 2 (518mg) and 5-bromo-4-(2-ethylhexyloxy)-thiophene-3-carbaldehyde (446 mg) were dissolved in a 100 mL dry flask in degassed toluene (26 mL), the mixture was flushed with nitrogen for 30 min, then ($Pd(PPh_3)_4$) (40 mg) was added under nitrogen. After stirring the mixture at 90 °C for 18 hour, the reaction was quenched with 50 mL water and extracted with ethyl acetate. Then, the combined organic solvent was washed with brine and dried over anhydrous magnesium sulfate ($MgSO_4$). After removing the solvent, the compound 3 was purified with column chromatography on silica-gel using mixture of ethyl acetate (EA) and hexane (1: 50 by volume) as a red solid (460 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$), δ 9.94 (s, 2H), 7.39 (s, 2H), 7.23 (s, 2H), 7.16 (d, 8H), 6.87 (s, 2H), 6.81 (d, 8H), 4.05 (d, 4H), 3.92 (t, 8H), 1.78 (m, 10H), 1.61-1.30 (m, 40H), 0.95-0.88 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$), δ 180.39, 164.89, 158.45, 157.69, 154.39, 146.73, 142.91, 139.34, 135.78, 135.28, 129.06, 121.72, 119.48, 117.70, 114.54, 111.35, 74.66, 68.13, 62.53, 39.64, 31.71, 30.54, 29.38, 29.16, 25.88, 23.95, 23.11, 22.73, 14.19, 14.16, 11.27. Anal.Calcd for ($C_{90}H_{110}O_8S_4$): C 74.65, H 7.66, Found: C 74.49, H 7.82.

Synthesis of compound **i-pO-4F**.

To a mixture of **M2** (244 mg) and 2-(5,6-difluoro-3-oxo -2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (192 mg) were dissolved in a dry flask in 25 mL chloroform, pyridine (0.8 mL) was added at room temperature. Then the mixture was vigorously stirred at 60 °C for 12 h. After cooling down, the mixture was extracted with chloroform. Then, the organic layer was dried over anhydrous magnesium sulfate ($MgSO_4$) and concentrated to afford the crude product. The crude product solution was poured into methanol and filtered through a Buchner funnel. Then the solid product of compound 4 was purified by silica gel by using chloroform as eluent to give a black solid (213mg, 71%). ^{1}H NMR (500 MHz, $CDCl_3$), δ 9.12 (s, 2H), 8.50 (dd, 2H), 7.60(t, 2H), 7.50 (d, 4H), 7.18 (d, 8H), 6.91 (s, 2H), 6.84 (d, 8H), 4.16 (m, 4H), 3.94 (t, 8H), 1.90(m, 2H), 1.78(m, 8H), 1.62-1.31 (m, 40H), 0.97-0.87

(m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$), δ 186.62, 169.95, 158.74, 158.67, 158.47, 155.04, 154.04, 152.98, 145.72, 139.39, 136.67, 135.58, 135.23, 134.21, 132.82, 128.93, 123.66, 118.03, 117.38, 117.19, 115.05, 114.78, 114.55, 112.14, 111.97, 109.18, 75.87, 68.05, 67.36, 62.50, 39.30, 31.58, 30.01, 29.24, 28.95, 25.76, 23.45, 23.01, 22.61, 14.12, 14.04, 10.92. Anal.Calcd for ($C_{114}H_{114}F_4N_4O_8S_4$): C 73.13, H 6.14, Found: C 73.02, H 6.38.

Synthesis of compound **i-pO-4Cl**.

To a mixture of **M2** (194 mg) and 2-(5,6-dichloro-3-oxo -2,3-dihydro-1*H*-inden-1-ylidene)malononitrile (170 mg) were dissolved in a dry flask in 30 mL chloroform, pyridine (0.8 mL) was added at room temperature. Then the mixture was vigorously stirred at 60 ^{o}C for 10 h. After cooling down, the mixture was extracted with chloroform. Then, the organic layer was dried over anhydrous magnesium sulfate ($MgSO_4$) and concentrated to afford the crude product. The crude product solution was poured into methanol and filtered through a Buchner funnel. Then the solid product **i-pO-4Cl** was purified by silica gel by using chloroform as eluent to give a black solid. (110 mg, 44%). ^{1}H NMR (500 MHz, $CDCl_3$), δ 9.14 (s, 2H), 8.70 (s, 2H), 7.84 (s, 2H), 7.51 (s, 2H), 7.46 (d, 2H), 7.19 (dd, 8H), 6.90 (s, 2H), 6.84 (d, 8H), 4.16 (m, 4H), 3.93 (t, 8H), 1.90 (m, 2H), 1.78-1.73 (m, 8H), 1.55-1.30 (m, 40H), 0.97-0.85 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$), δ 186.67, 170.13, 158.82, 158.49, 155.10, 154.52, 138.85, 138.39, 135.96, 135.61, 135.20, 128.93, 126.61, 124.58, 123.83, 117.84, 115.15, 114.66, 114.57, 109.14, 75.95, 68.06, 67.34, 62.51, 39.28, 31.57, 30.00, 29.24, 28.95, 25.75, 23.44, 23.01, 22.60, 14.12, 14.03, 10.91.

Measurement

All the compounds were characterized by nuclear magnetic resonance spectra (NMR) in chloroform-*d* ($CDCl_3$) using tetramethylsilane (TMS) as the internal reference recorded on a Bruker AV 500 spectrometer at room temperature. The absorption spectra of the materials were measured by a PerkinElmer Lambda 750 UV/Vis/NIR spectrometer. Thermal stabilities of the acceptors were investigated on a Universal V2.6D TA instruments. The electrochemical cyclic voltammetry of the materials was conducted on a CHI 660D Electrochemical Workstation in a 0.1mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution, using glassy carbon, platinum wire, and Ag/Ag^+ electrode as working electrode, the counter electrode, and the reference electrode, respectively. Atomic force microscopy (AFM) images were collected under ambient conditions in air on a MultiMode scanning probe microscope (AFM, Veeco Multi Mode V).

Fabrication and characterization of the photovoltaic cells

The device structure was ITO/ZnO/PBDB-T:acceptors/MoO_3/Al. The carefully cleaned ITO glass was treated with ultraviolet-ozone for 20 min. Zinc acetate dihydrate dissolved in 2-methoxyethanol and a small amount of ethanolamine was spin-cast on ITO glass, and then baked at 170 ^{o}C for 10 min in air to form a 40 nm ZnO layer.

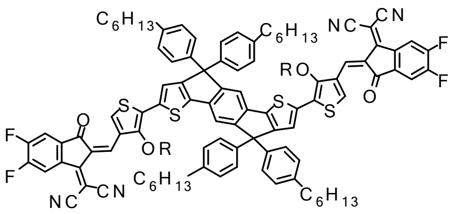
The photoactive layer (80-90 nm) was prepared by spin-coating from the chlorobenzene (CB) solution of the NF acceptor and PBDB-T on the top of ITO/ZnO substrate in a glove box. Then a 10 nm MoO_3 layer and 120 nm Al layer were deposited subsequently in a vacuum evaporator. As determined by the shadow mask used during deposition of Al cathode, the effective area of the device was 0.16 cm^2. PCE values were determined on a Keithley 2400 source meter from current density (*J*)-voltage *(V)* curve measurements under 1 sun, AM 1.5G spectrum from a monocrystal silicon cell (VLSI Standards Inc.) calibrated solar simulator (Newport model 94021A, 100 mW cm^{-2}). EQE was obtained by Solar Cell Spectral Response Measurement System QE-R3018 (Enli Technology Co., Ltd.) and standard Si photovoltaic cell was employed to calibrate the light intensity.

Carrier mobility measurement.

To measure the hole and electron mobility, space-charge limited current (SCLC) method was used in a devices structure of ITO/PEDOT:PSS (40nm)/Active layer/MoO_3(10 nm)/Ag(100 nm) and ITO/ZnO(40nm) /Active layer/Ca (10 nm)/Al (100 nm) with the effective area of 0.16 cm^2, respectively, by taking the dark current density and fitting the results to a space charge limited form. [4] SCLC is described by the equation: $J= 9\varepsilon_0\varepsilon_r\mu_0V^2/8L^3$, where J is the current density, ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), ε_r is the relative dielectric constant of the transport medium, μ_0 is the hole or electron mobility, V (= V_{appl}- V_{bi}) is the internal voltage in the device, where V_{appl} is the applied voltage to the device and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes, L is the film thickness of the active layer.

GIWAXS and RSoXS Characterization

GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source. Samples were prepared on Si substrates using identical blend solutions as those used in devices. The 10 keV X-ray beam was incident at a grazing angle of 0.12°-0.16°, selected to maximize the scattering intensity from the samples. The scattered x-rays were detected using a Dectris Pilatus 2M photon counting detector. RSoXS transmission measurements were performed at beamline 11.0.1.2 at the Advanced Light Source with an X-ray energy of 284.2 eV. Thin films were flowed and transferred onto Si_3N_4 substrate and experiment was done in transition mode.



i-IEICO-4F

Figure S1. Chemical structure of i-IEICO-4F.

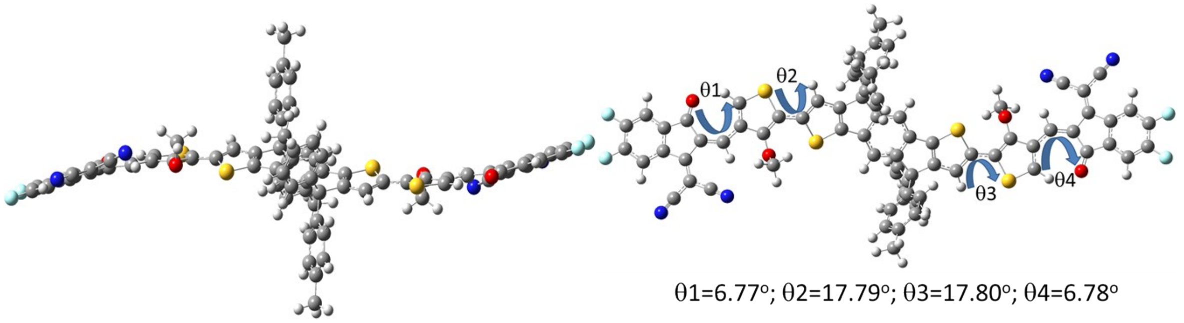


Figure S2. Side-veiw and top-view of i-IEICO-4F.

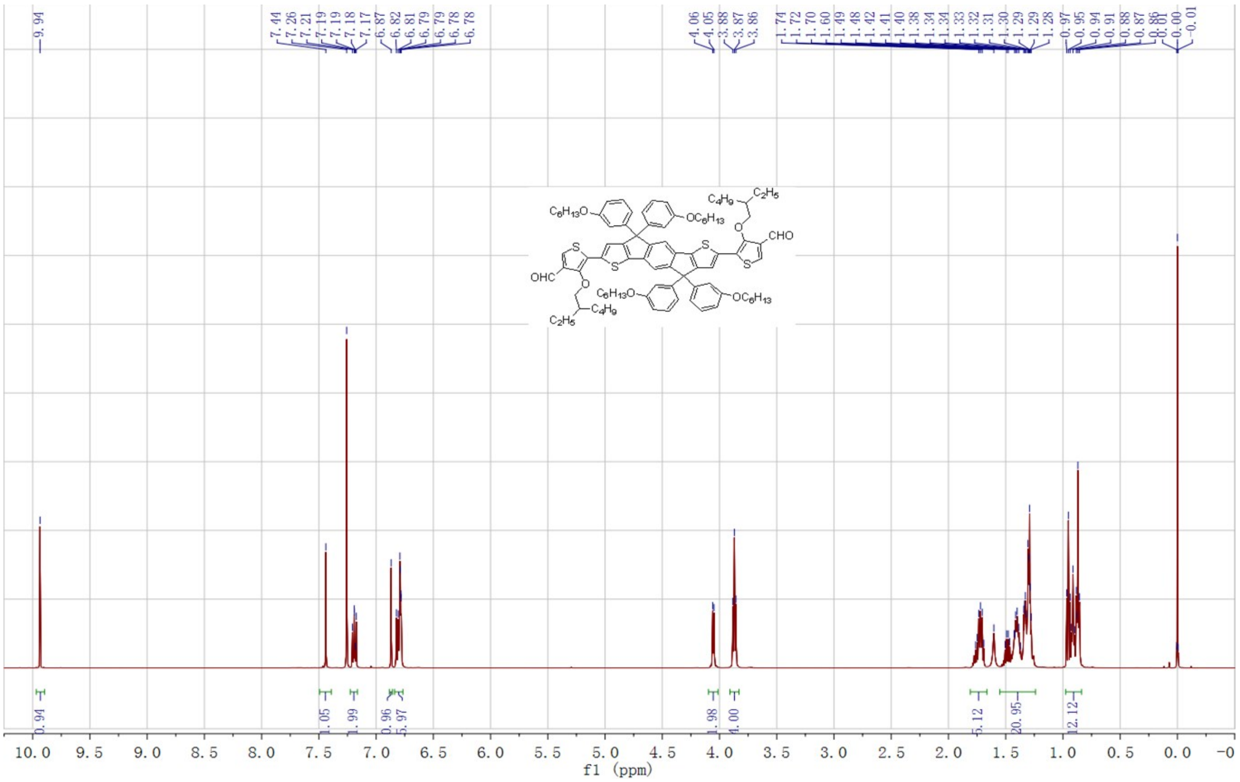


Figure S3. ^{1}H NMR spectrum of compound **M1**.

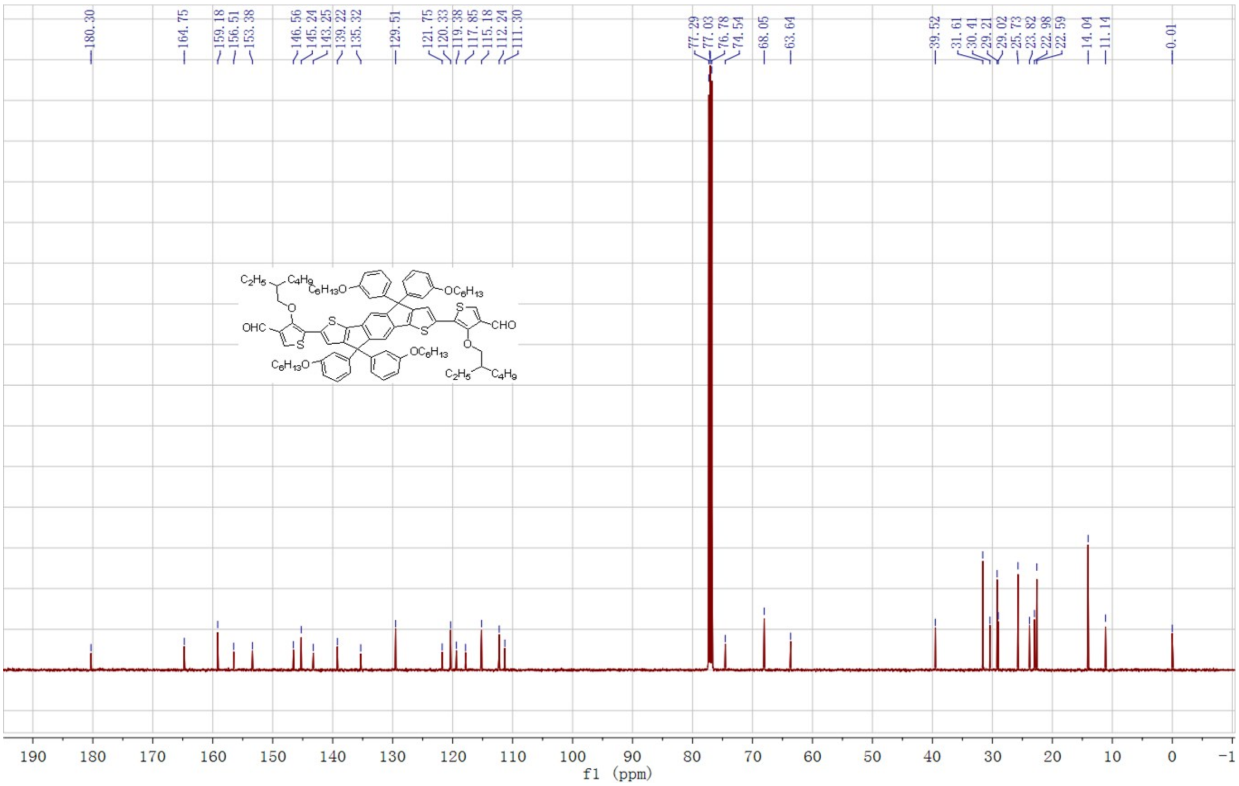


Figure S4. ^{13}C NMR spectrum of compound **M1**.

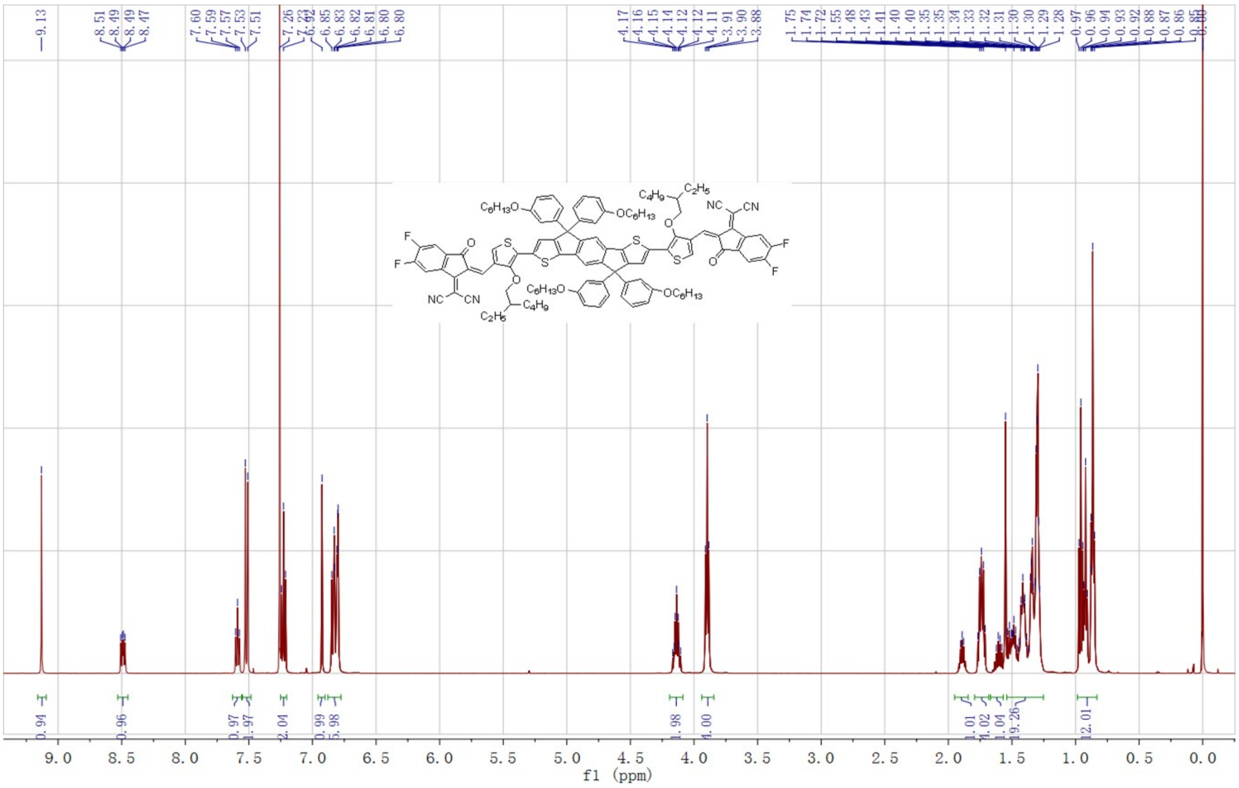


Figure S5. ^{1}H NMR spectrum of **i-mO-4F**.

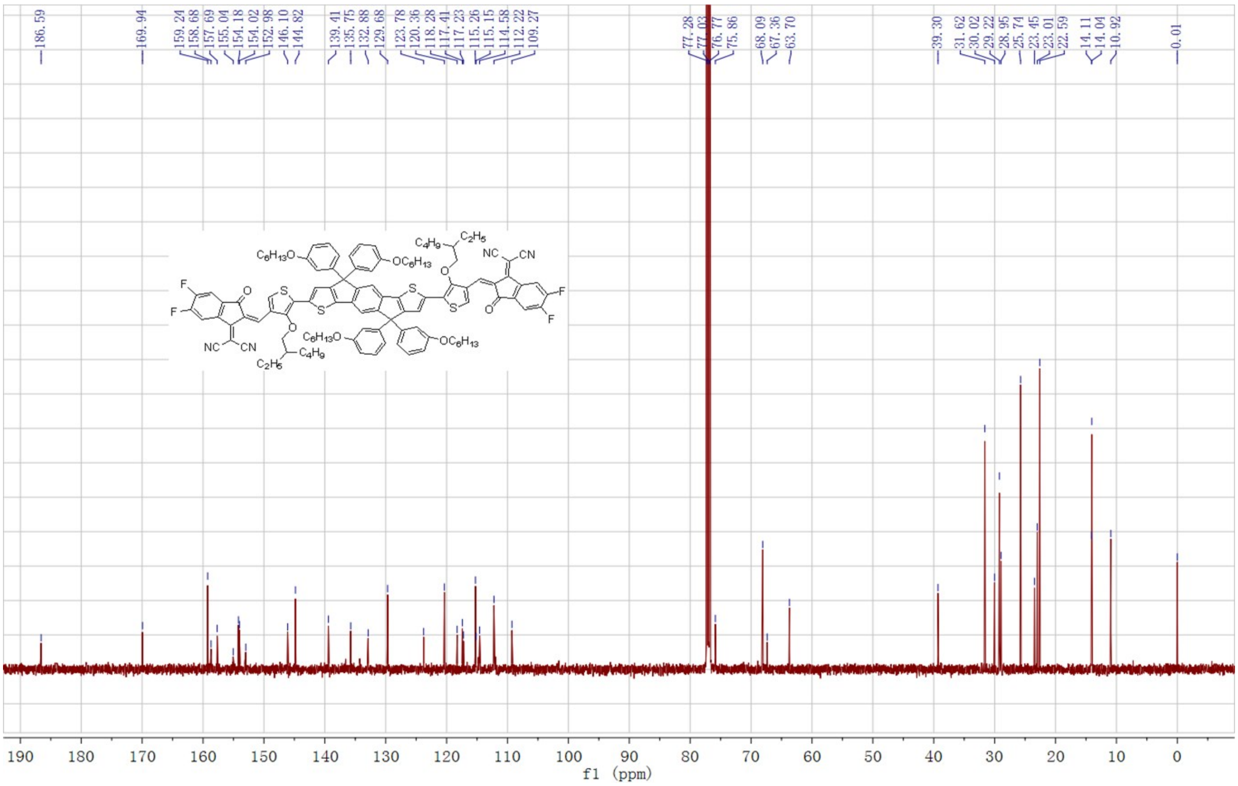


Figure S6. ^{13}C NMR spectrum of **i-mO-4F**.

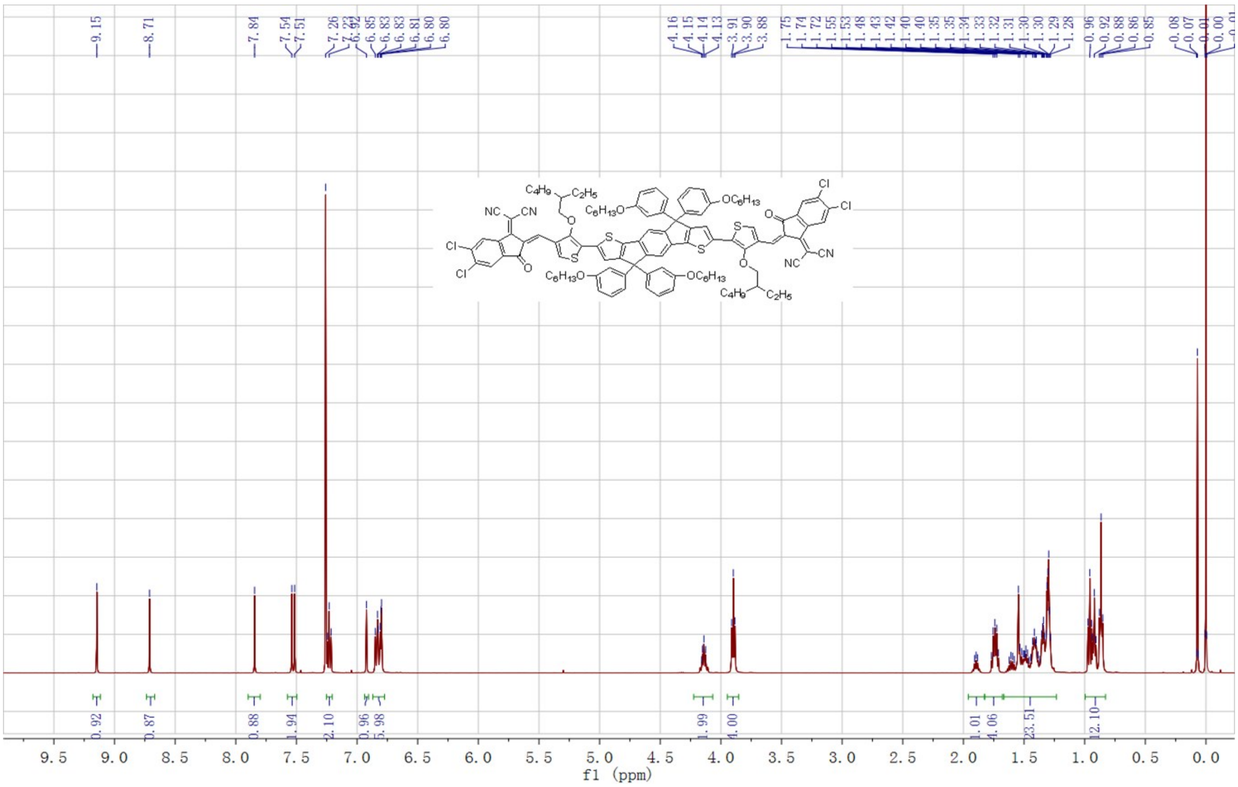


Figure S7. ^{1}H NMR of **i-mO-4Cl**.

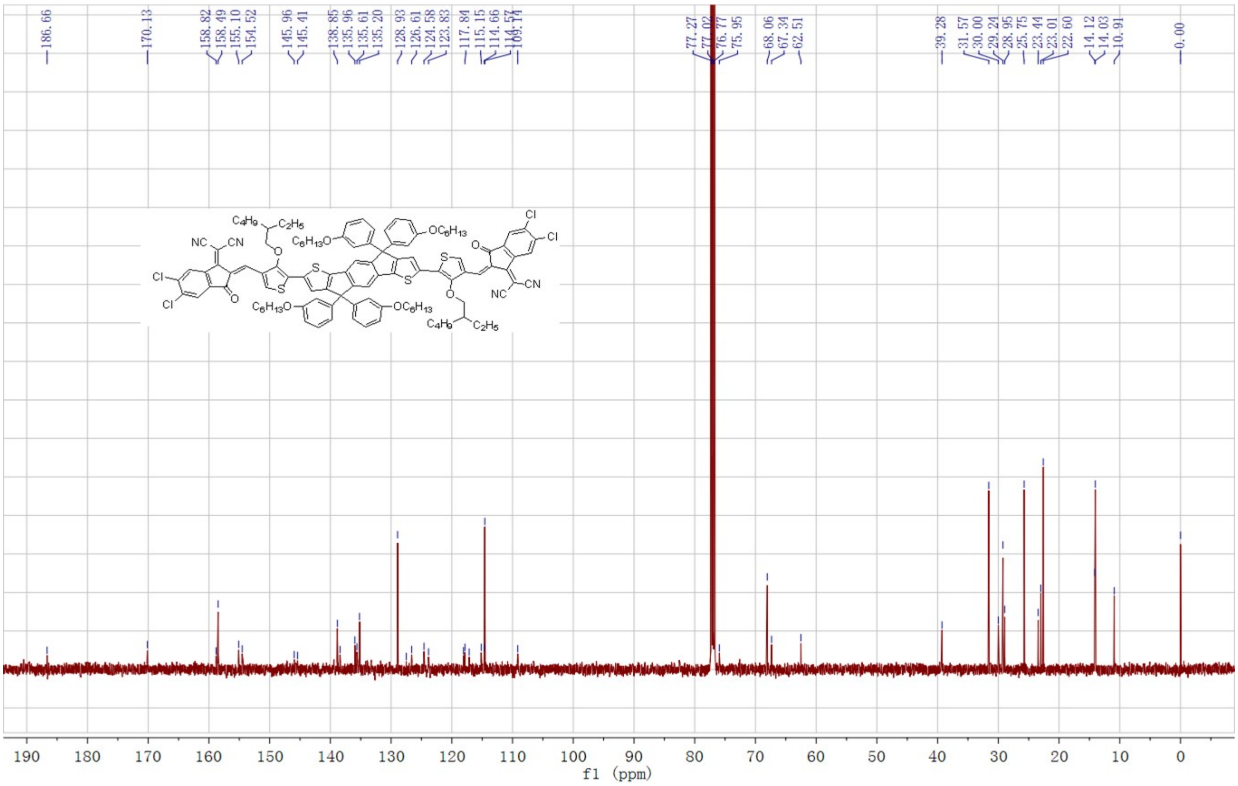


Figure S8.^{13}C NMR of **i-mO-4Cl**.

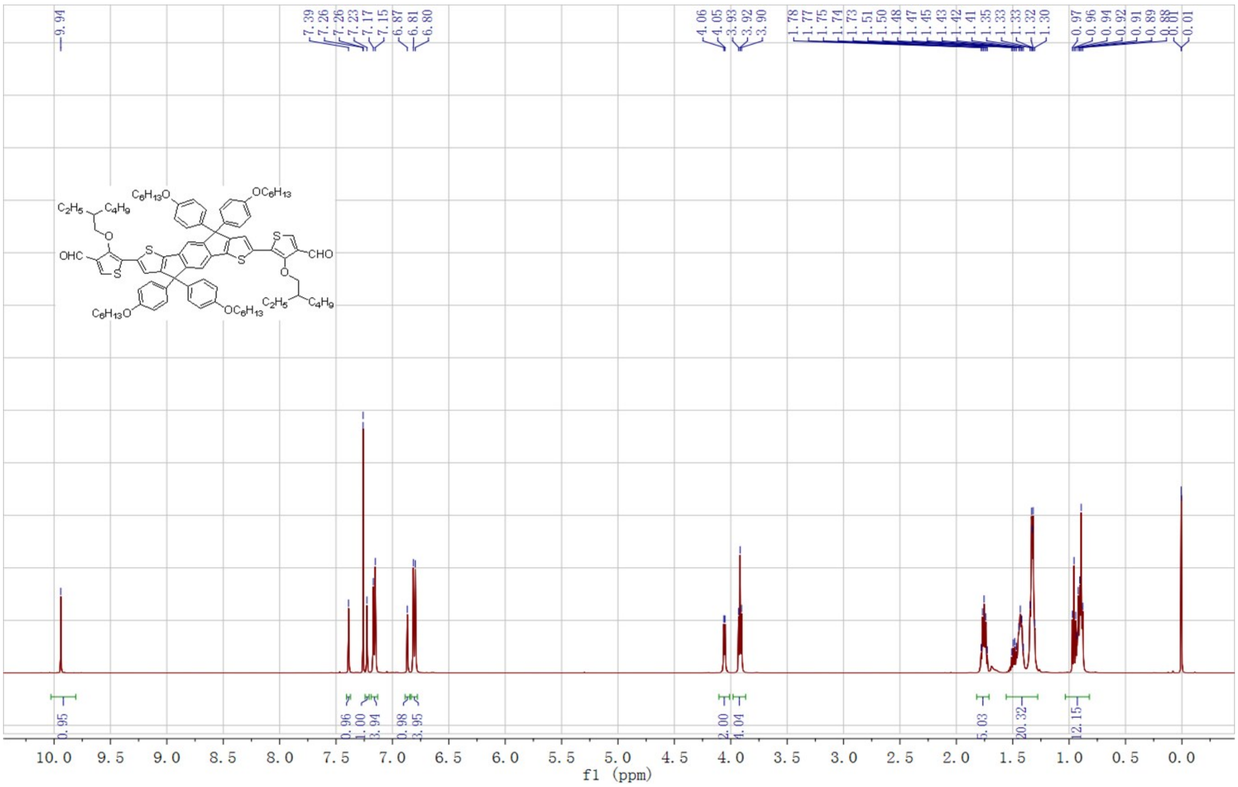


Figure S9. ^{1}H NMR spectrum of compound **M2**.

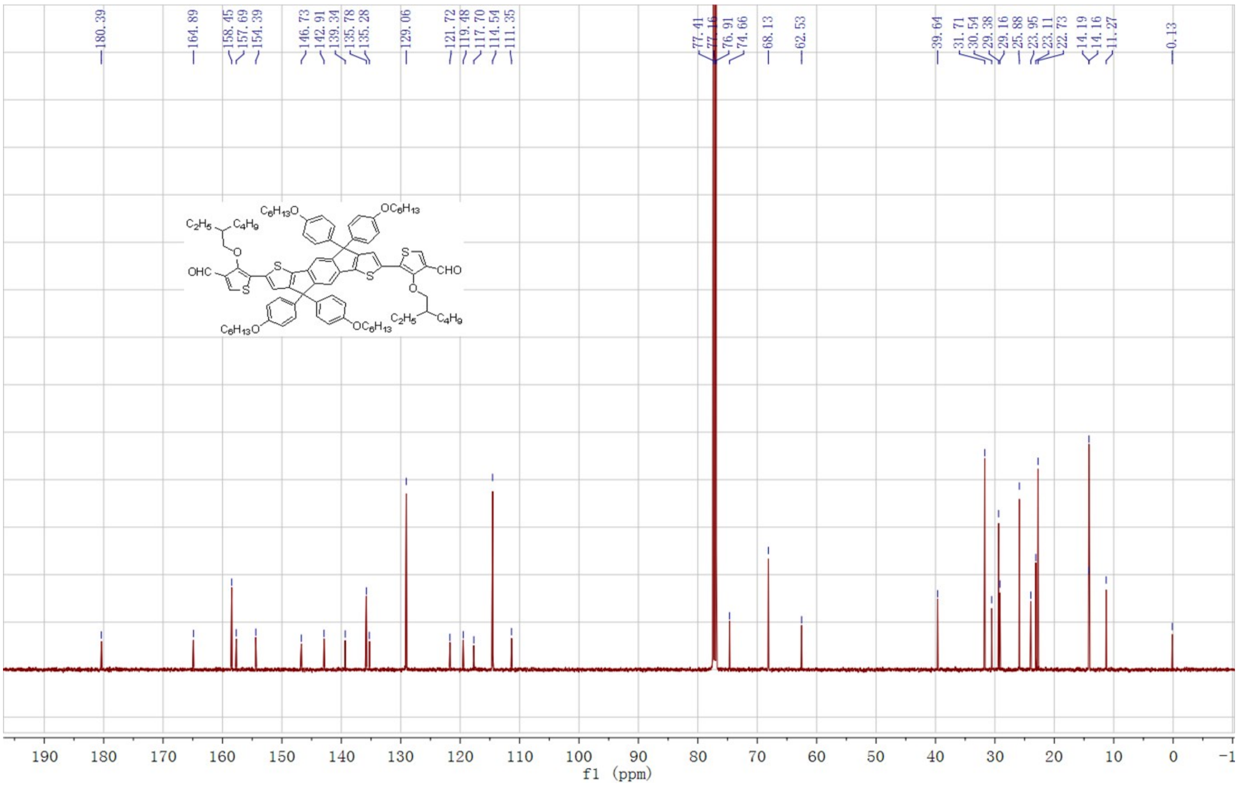


Figure S10. ^{13}C NMR spectrum of compound **M2**.

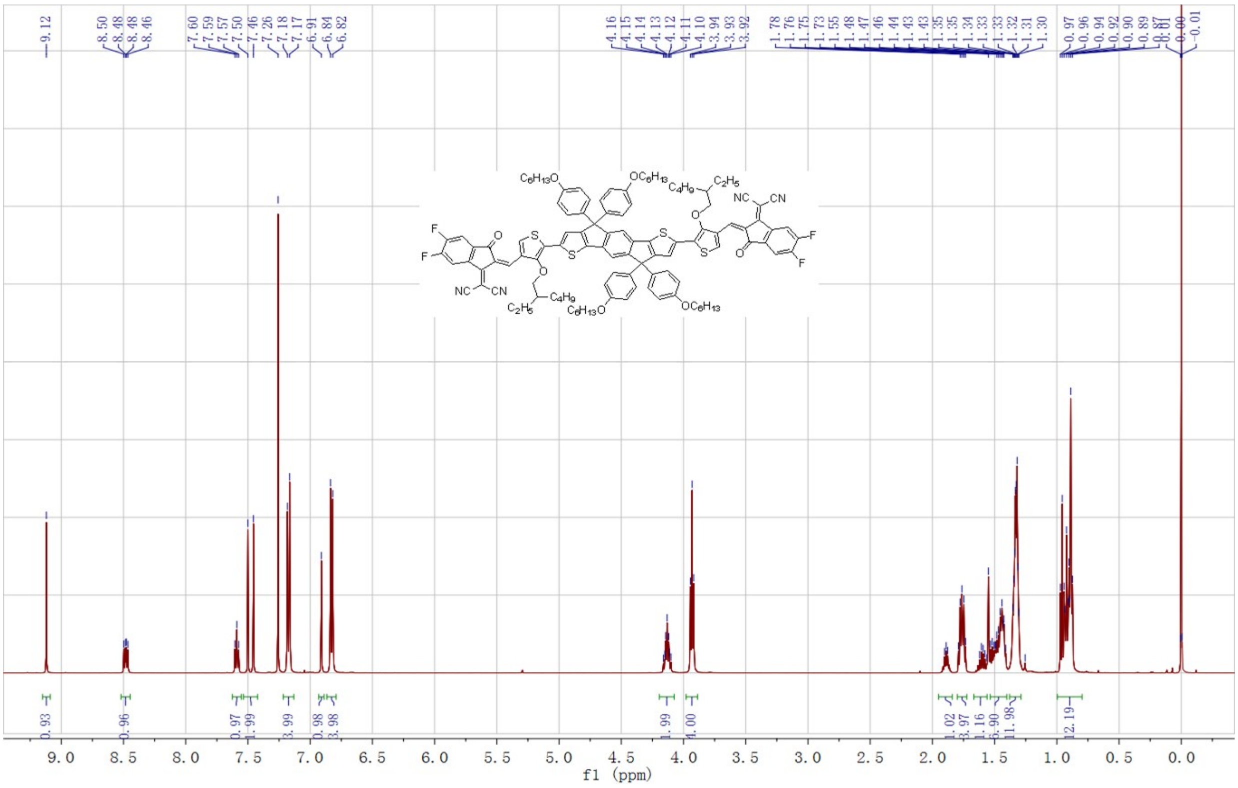


Figure S11. ^{1}H NMR spectrum of compound **i-pO-4F**.

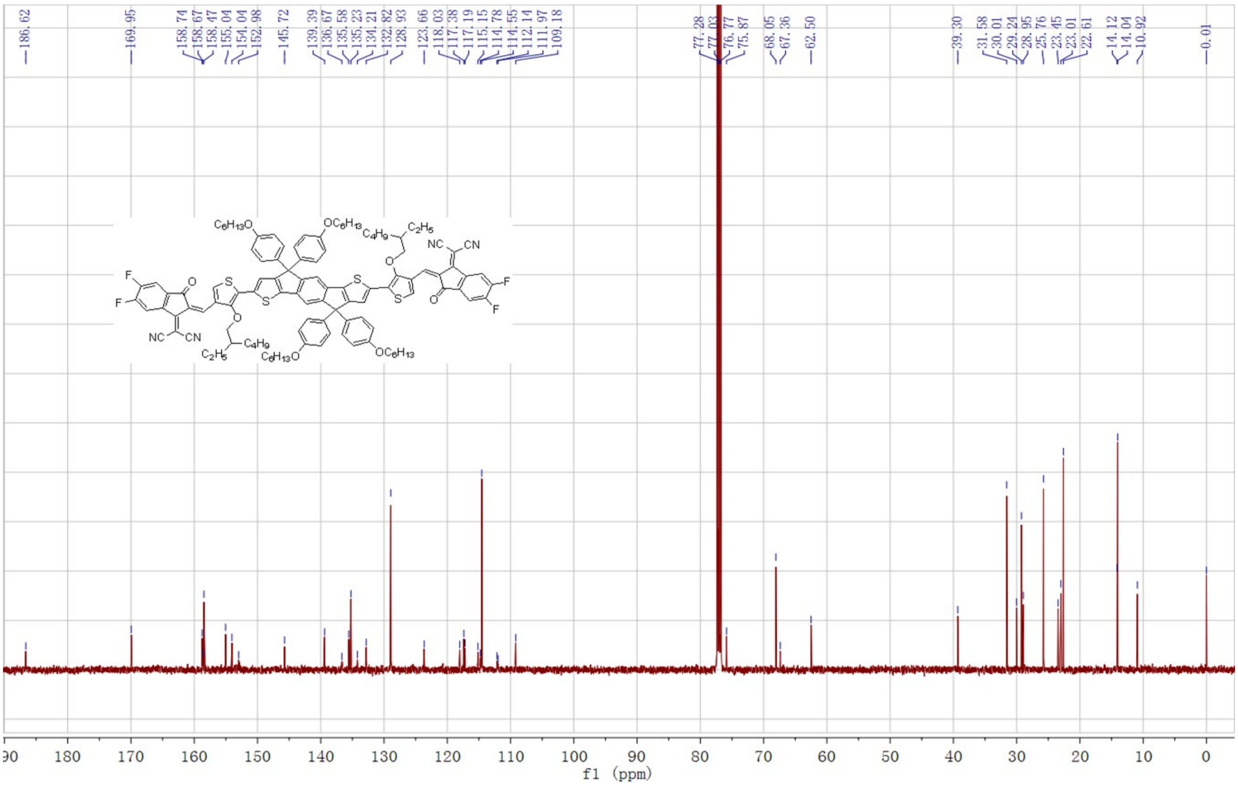


Figure S12. ^{13}C NMR spectrum of compound **i-pO-4F**.

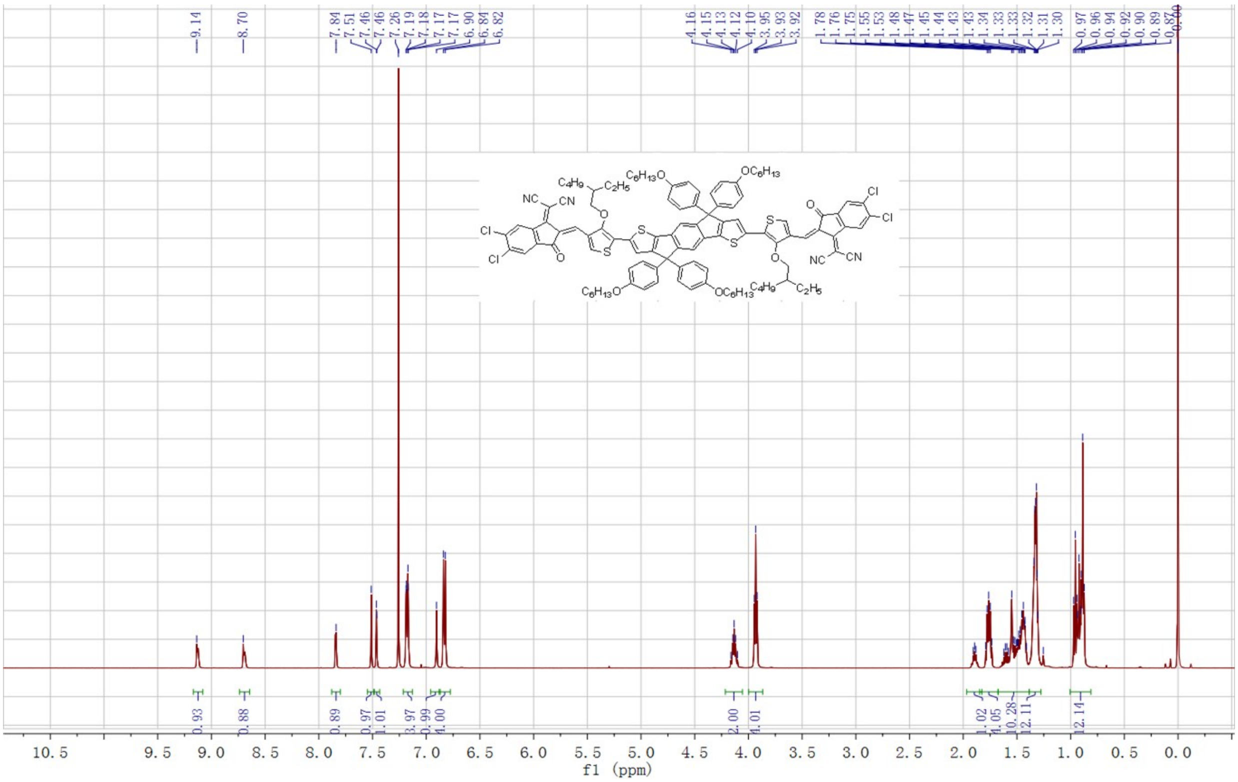


Figure S13. ^1H NMR spectrum of compound **i-pO-4Cl**.

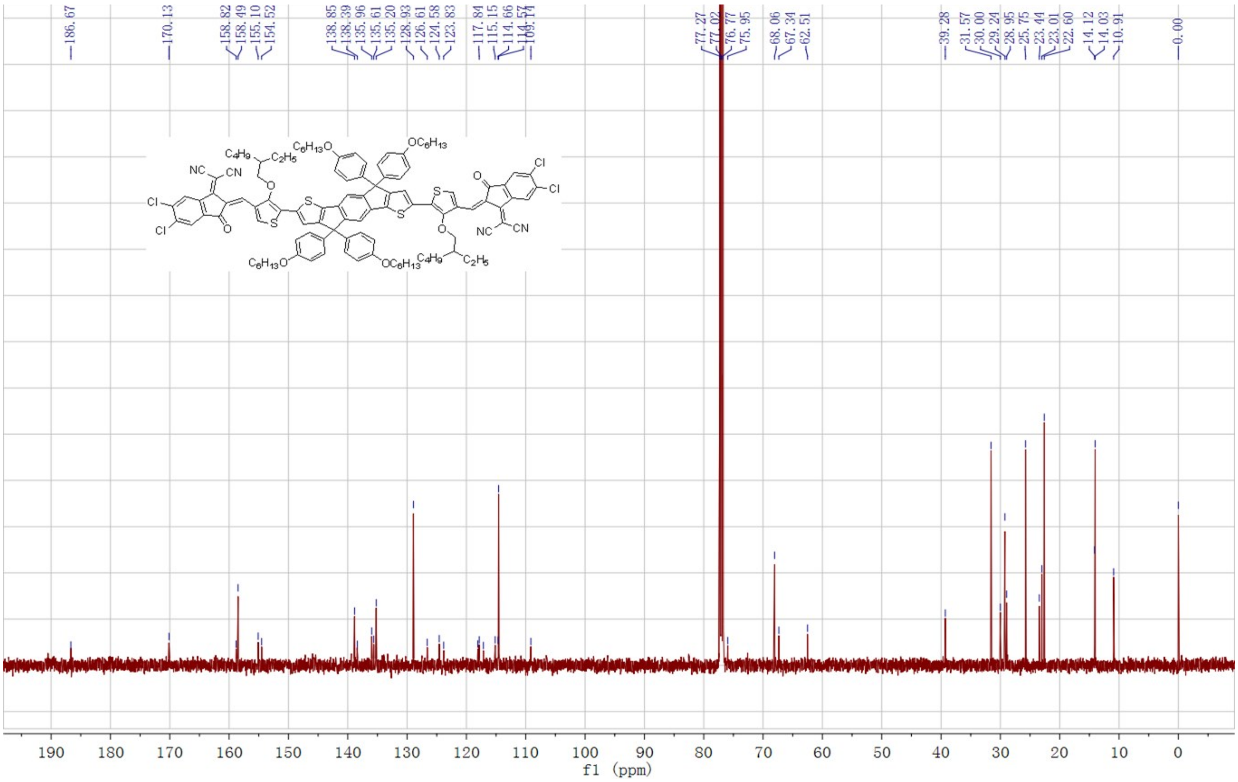


Figure S14. ^{13}C NMR spectrum of compound **i-pO-4Cl**.

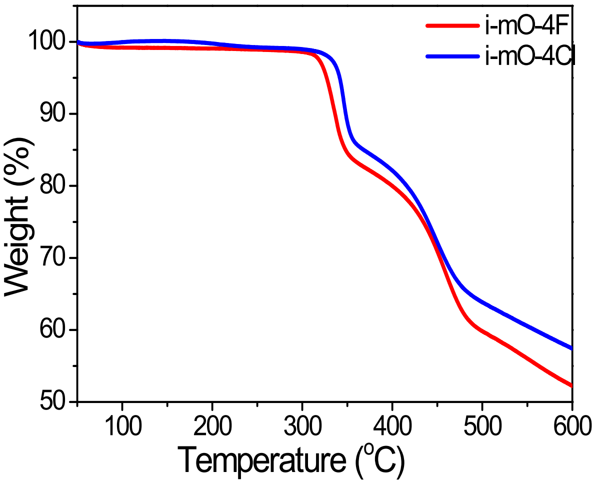


Figure S15.TGA plots of **i-mO-4F** and **i-mO-4Cl**.

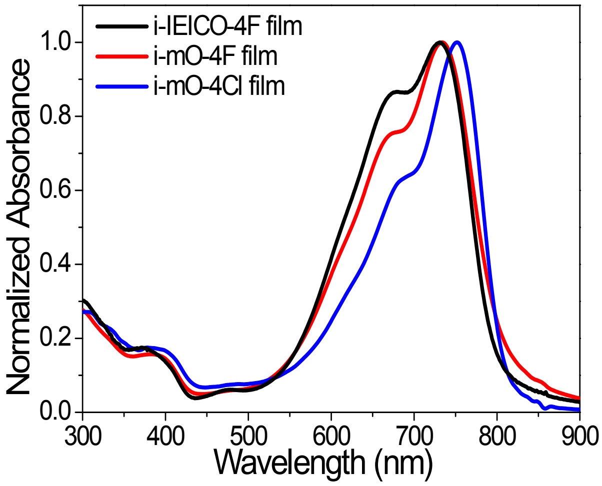


Figure S16. Normalized absorption spectra of **i-IEICO-4F**, **i-mO-4F** and **i-mO-4Cl** films.

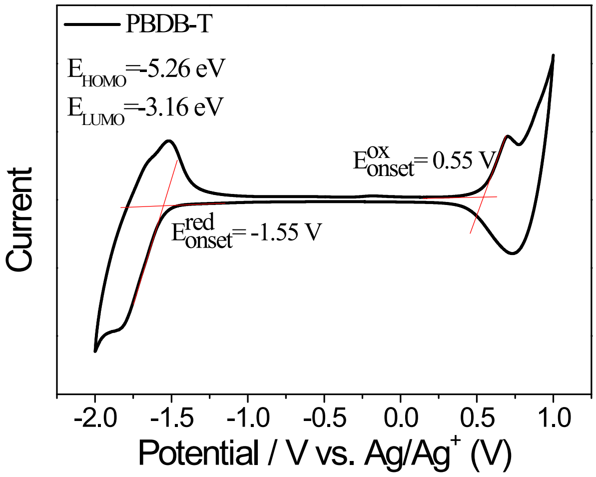


Figure S17. CV plot of PBDB-T film.

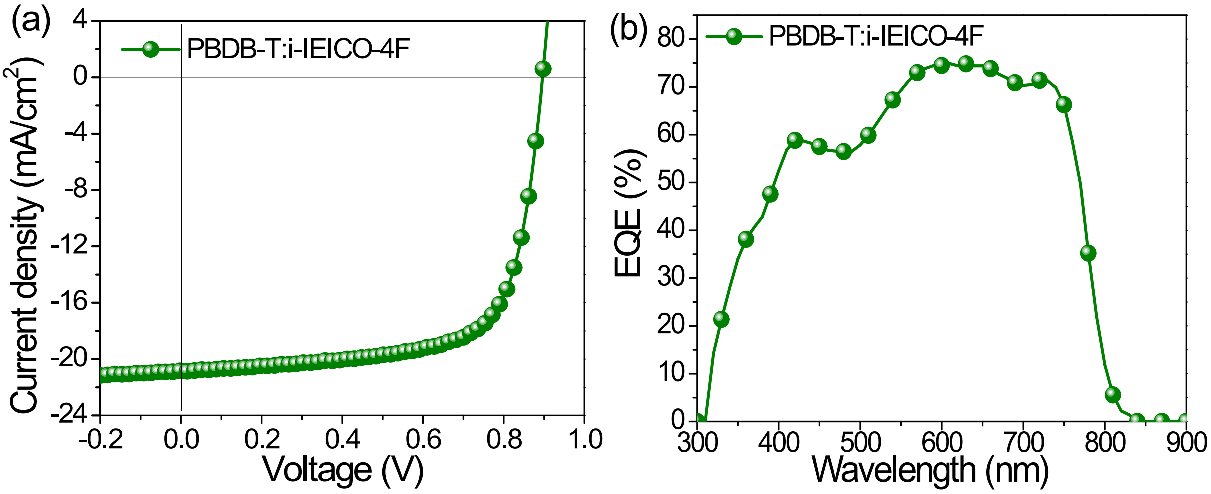


Figure S18. (a). J-V plots of PBDB-T:**i-IEICO-4F** (1:1) device with 150 °C TA treatment;(b) The corresponding EQE curve.

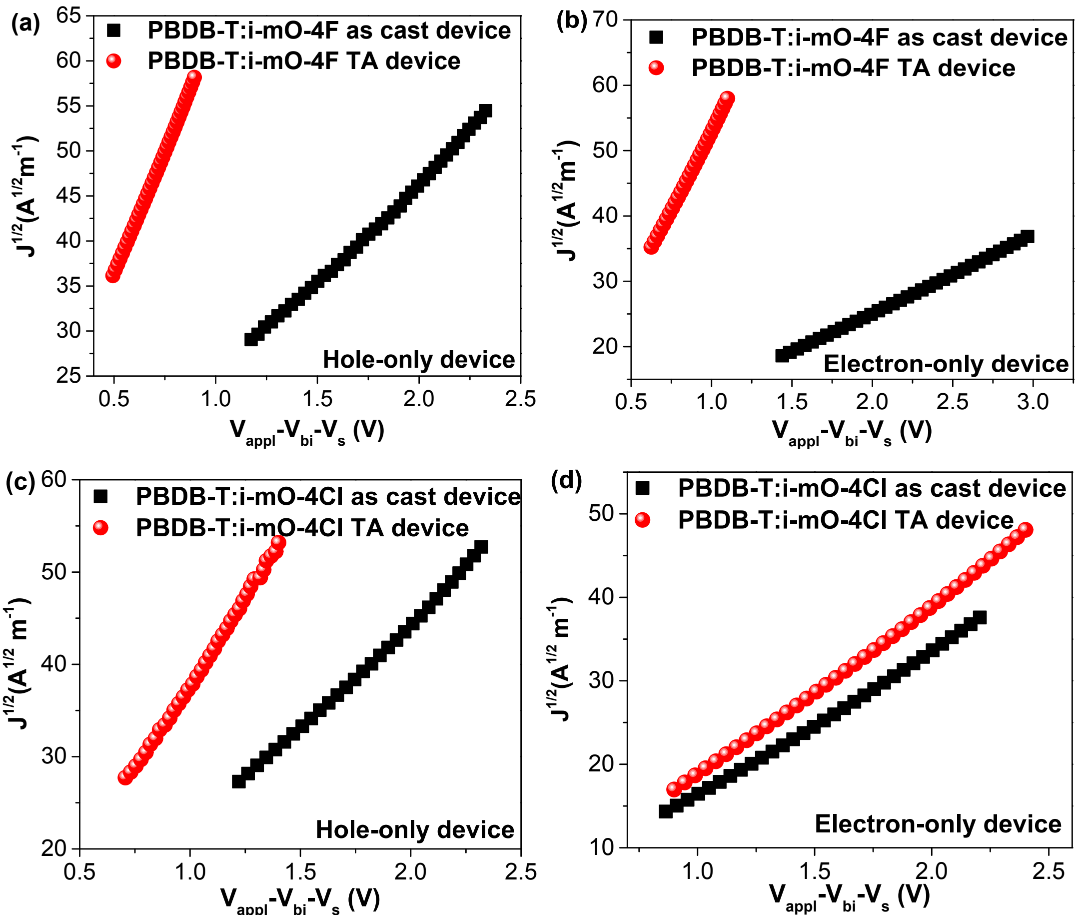


Figure S19. $J^{1/2}$ vs V plots: PBDB-T:**i-mO-4F** and PBDB-T:**i-mO-4Cl** hole-only diode (a) and (c) and electron-only diode (b) and (d).

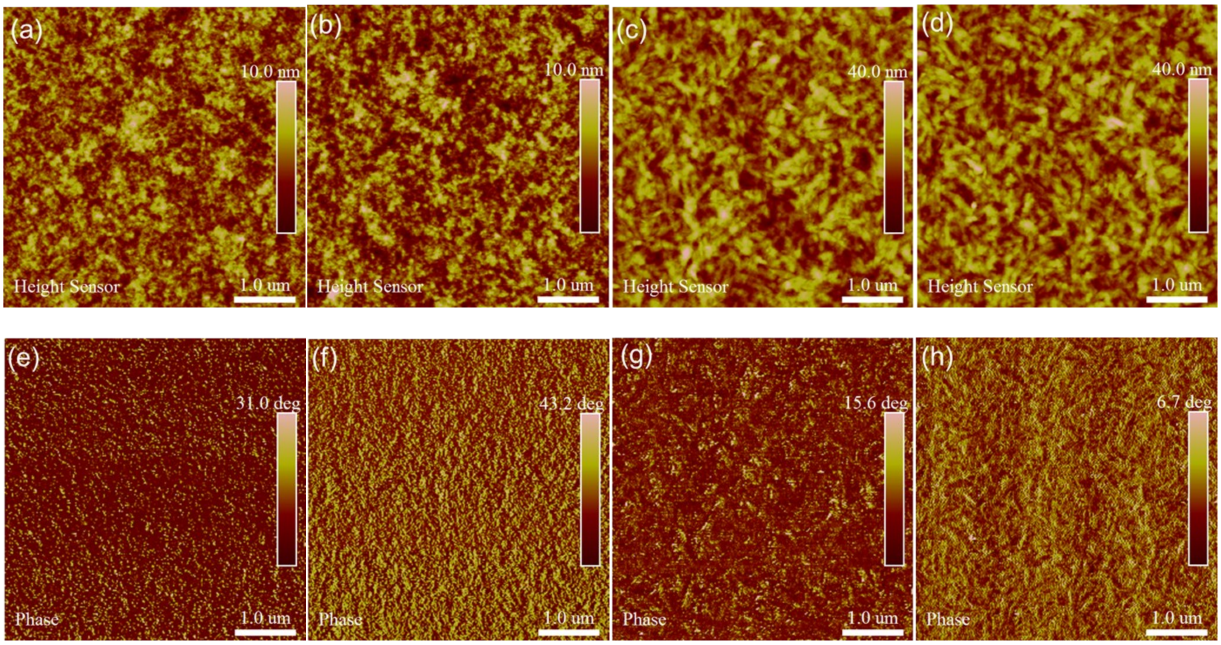


Figure S20. AFM height imagines of (a) PBDB-T:**i-mO-4F** as cast film (RMS=1.36 nm); (b) PBDB-T:**i-mO-4F** TA film (RMS=RMS=1.53 nm);(c)PBDB-T:**i-mO-4Cl** as cast film (RMS=5.14 nm);(d) PBDB-T:**i-mO-4Cl** as cast film (RMS=5.05 nm); AFM phase imagines. (e) PBDB-T**:i-mO-4F** as cast film; (f) PBDB-T:**i-mO-4F** TA film; (g) PBDB-T:**i-mO-4Cl** as cast film; (h) PBDB-T:**i-mO-4Cl** TA film.

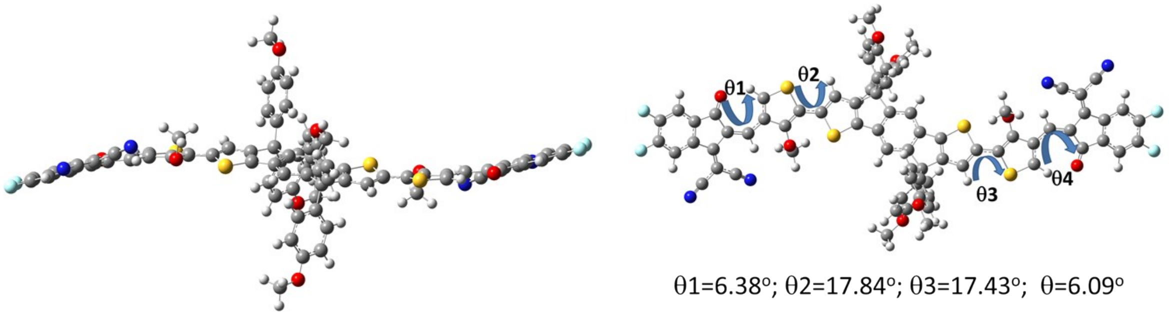


Figure S21. Side-view and top-view of **i-pO-4F**.

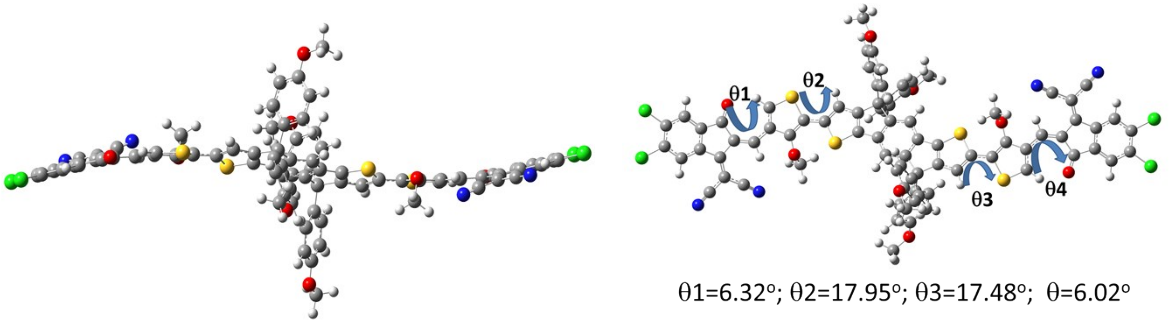


Figure S22. Side-view and top-view of **i-pO-4Cl**.

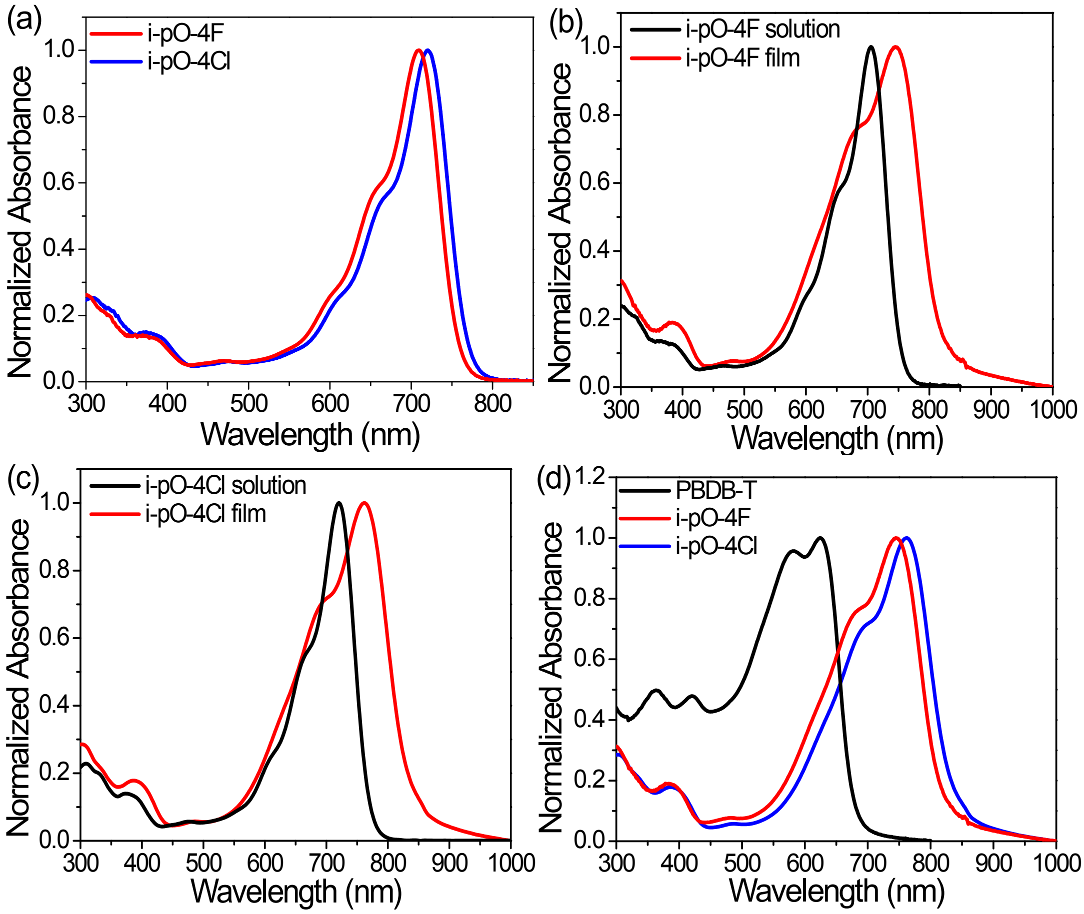


Figure S23. (a) Normalized absorption spectra of **i-pO-4F** and **i-pO-4Cl** in chloroform solutions; (b)

Normalized absorption spectra of **i-pO-4F** in solution and in films; (c) Normalized absorption spectra of **i-pO-4Cl** in solution and in films; (d) Normalized absorption spectra of PBDB-T, **i-pO-4F**, and **i-pO-4Cl** films.

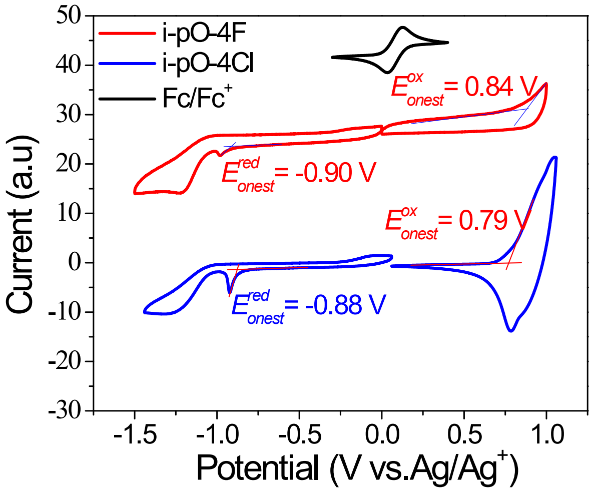


Figure S24. CV plots of **i-pO-4F** (a), and **i-pO-4Cl** (b) films.

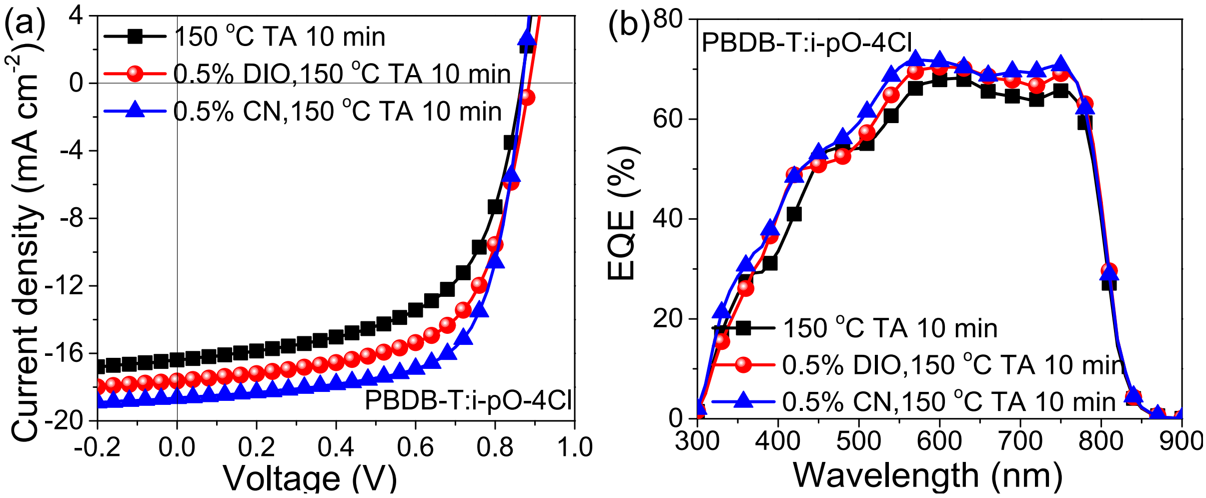
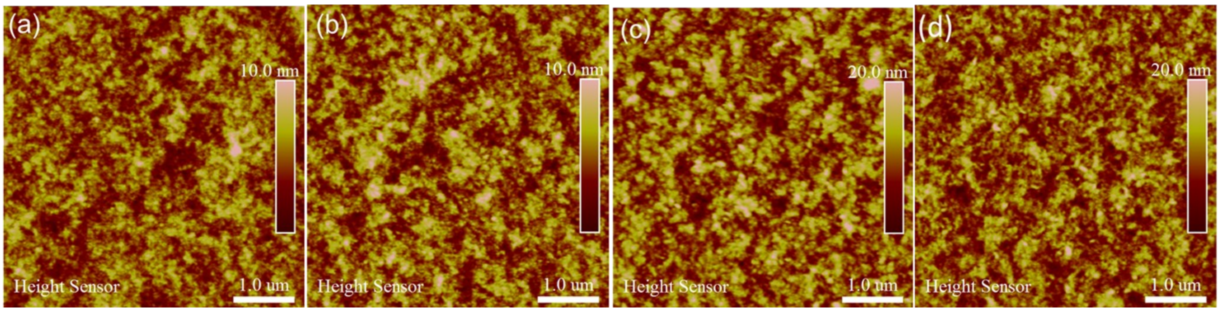


Figure 25. (a) J-V plots of PBDB-T:**i-pO-4Cl** devices with various additive; (b) EQE plots.



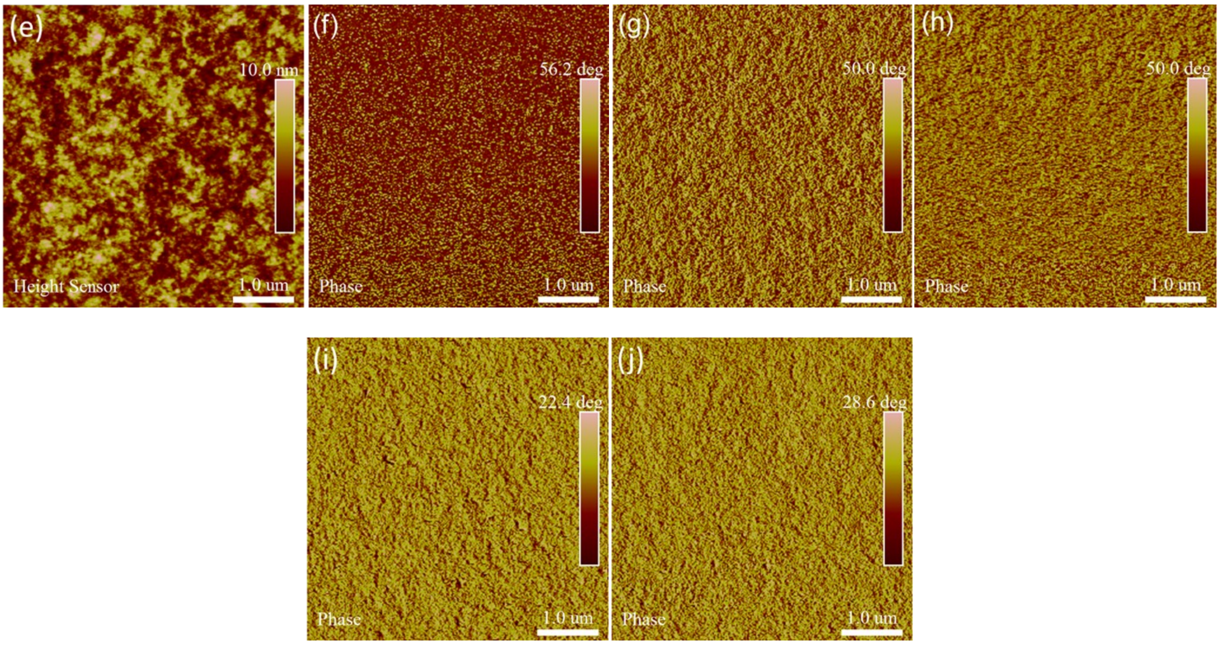
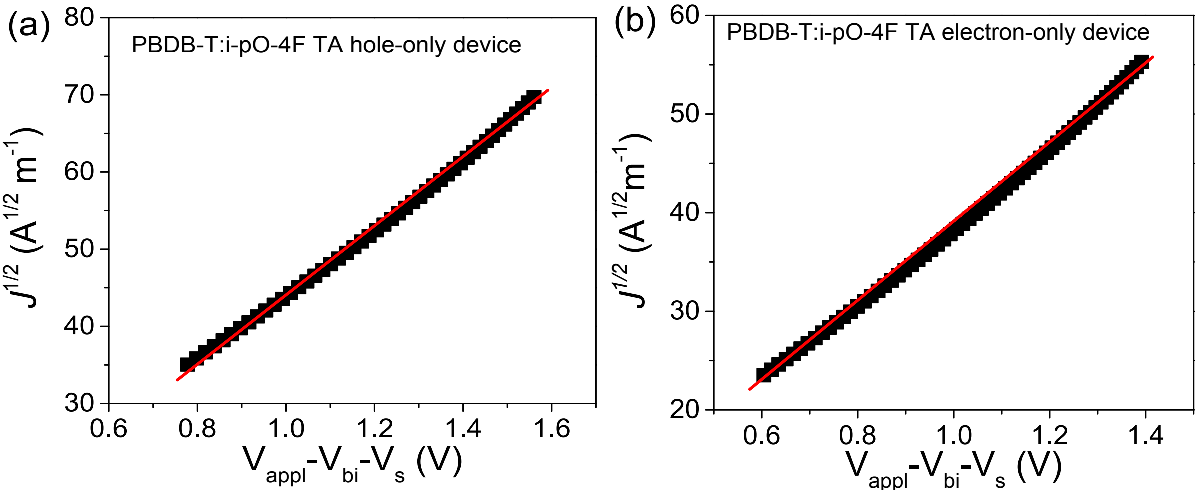


Figure S26. AFM height imagines of (a) PBDB-T:**i-pO-4F** as cast film (RMS roughness 1.40 nm); (b) PBDB-T:**i-pO-4F** TA film (RMS roughness 1.56 nm);(c)PBDB-T:**i-pO-4Cl** as cast film (RMS roughness 3.16 nm);(d) PBDB-T:**i-pO-4Cl** TA film (RMS roughness 2.93 nm); (e) PBDB-T:**i-pO-4Cl** with 0.5% CN TA film (RMS roughness 1.75 nm); AFM phase imagines. (f) PBDB-T:**i-pO-4F** as cast film; (g) PBDB-T:**i-pO-4F** TA film; (h) PBDB-T:**i-pO-4Cl** as cast film; (i) PBDB-T:**i-pO-4Cl** TA film; (j) PBDB-T:**i-pO-4Cl** with 0.5% CN TA film.



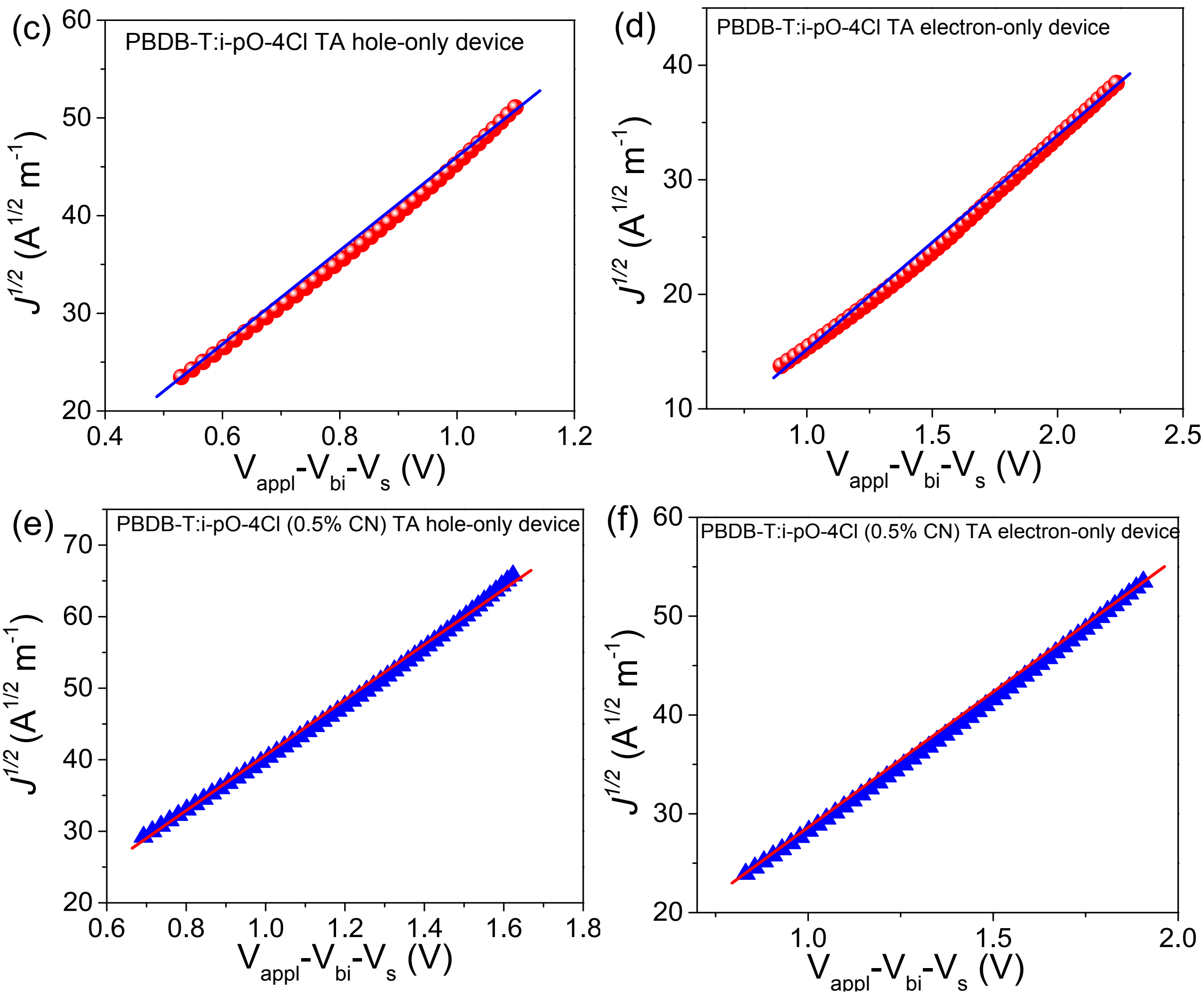
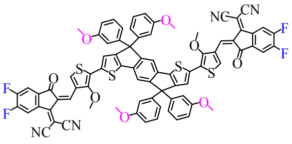
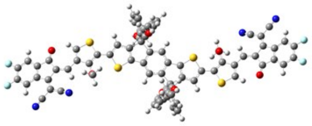
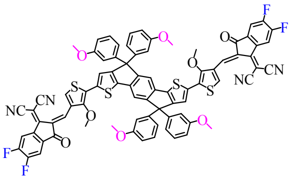
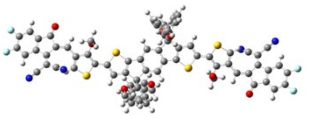
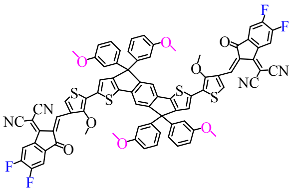
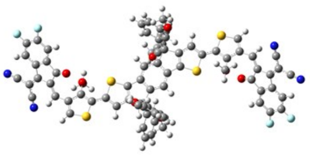
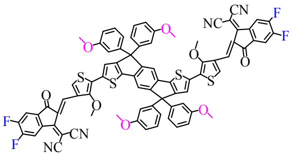
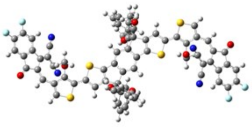
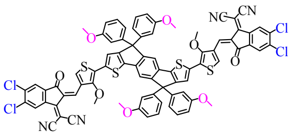
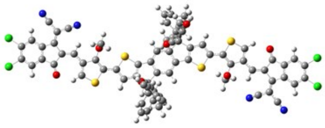
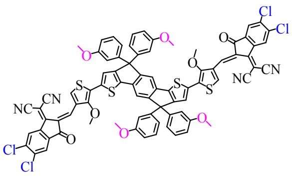
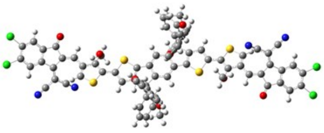
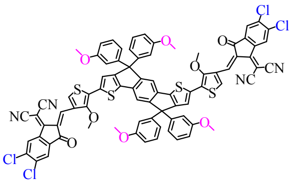
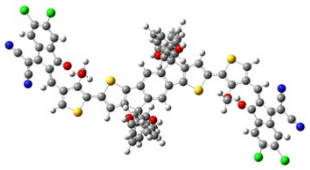
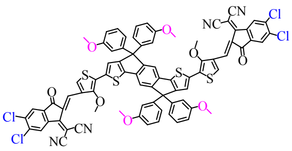
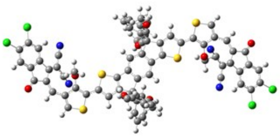


Figure S27. $J^{1/2}$ *vs* V plots of PBDB-T:**i-pO-4F** TA hole-only diode (a) TA electron-only diode (b); $J^{1/2}$ *vs* V plots of PBDB-T:**i-pO-4Cl** TA hole-only diode (c) TA electron-only diode (d); $J^{1/2}$ *vs* V plots of PBDB-T:**i-pO-4Cl** (0.5% CN) TA hole-only diode (e) (0.5% CN) TA electron-only diode (f).

Table S1. Calculations of total energy and their geometries of the four isomers of **i-mO-F**, **i-mO-4Cl** and **i-IEICO-4F**.

Molecule	Isomers	Total energy (a.u)	Calculations of the geometries of the isomers
i-mO-4F		-5888.9679	
		-5888.9488	
		-5888.9467	
		-5888.9453	
i-mO-4Cl		-7330.4175	
		-7330.3985	
		-7330.3962	
		-7330.3952	

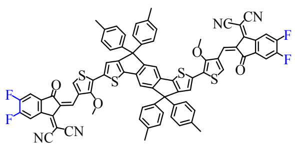
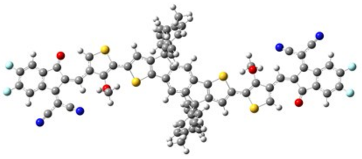
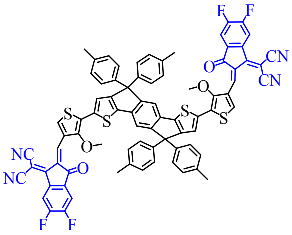
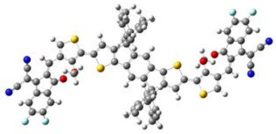
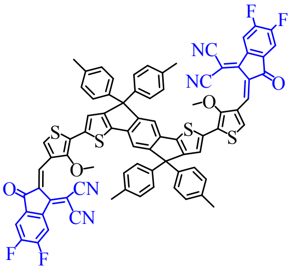
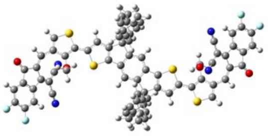
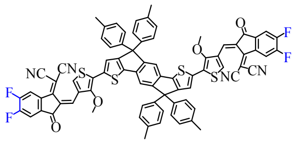
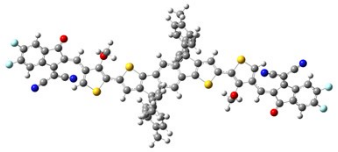
i-IEICO-4F		-5588.1504	
		-5588.1294	
		-5588.1275	
		-5588.1264	

Table S2. Calculated molecular energy levels of **i-IEICO-4F**, **i-mO-4F** and **i-mO-4Cl** at their optimized geometry from the DFT at B3LYP/6-31G(d) level.

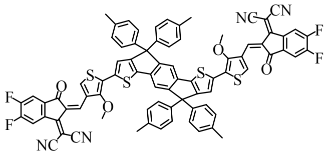
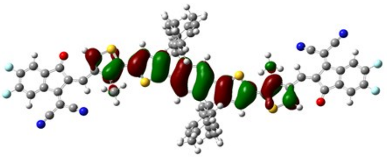
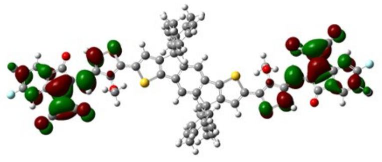
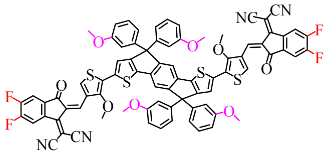
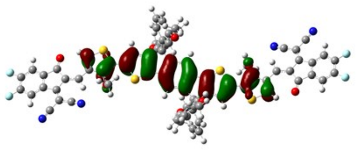
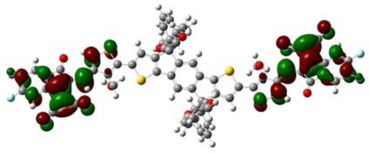
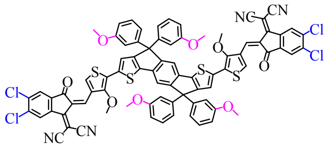
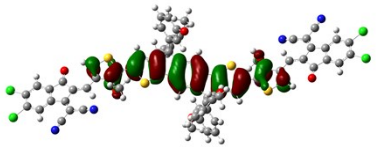
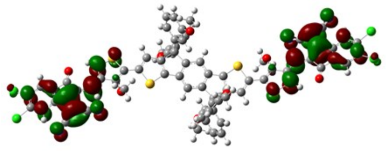
Molecules	HOMO	LUMO
 i-IEICO-4F	 HOMO= -5.05 eV	 LUMO= -3.34 eV
 i-mO-4F	 HOMO= -4.97 eV	 LUMO= -3.30 eV
 i-mO-4Cl	 HOMO= -5.01 eV	 LUMO= -3.39 eV

Table S3. Photovoltaic parameters of PBDB-T:**i-mO-4F** (1:1) devices upon different TA treatments.

TA condition	V_{OC} [V]	J_{SC} [mA/cm^{2}]	FF [%]	PCE [%]
As cast	0.92±0.00	18.78±0.16	62.5±0.7	10.80±0.08
	0.92	19.10	63.2	11.10
110 ^{o}C	0.90±0.01	19.28±0.57	66.2±0.5	11.40±0.17
	0.90	19.22	66.8	11.56
130 ^{o}C	0.90±0.01	19.90±0.25	66.7±0.7	11.90±0.13
	0.90	19.84	67.4	12.03
150 ^{o}C	0.91±0.01	20.82±0.06	71.1±0.5	13.46±0.15
	0.92	20.86	70.7	13.57
170 ^{o}C	0.88±0.00	19.59±0.06	66.7±1.4	11.50±0.21
	0.88	19.58	67.6	11.65

Table S4. Photovoltaic parameters of the best PBDB-T:**i-IEICO-4F** device.

Active Layer	V_{OC} [V]	J_{SC} [mA/cm^{2}]	FF [%]	PCE [%]
PBDB-T:**i-IEICO-4F**=1:1	0.898±0.005	20.68±0.18	70.4±0.2	13.08±0.09
	0.898	20.84	70.37	13.17

Table S5. Measurement of the hole and electron mobilities.

Active layer	Post-treatment	Thickness (nm)	μ_h (cm^{2} V^{-1} s^{-1})	μ_e (cm^{2} V^{-1} s^{-1})	μ_h/μ_e
PBDB-T:**i-mO-4F**	As cast	66	4.62×10^{-5}	1.37×10^{-5}	3.37
	150 ^{o}C TA 10min	66	2.87×10^{-4}	2.21×10^{-4}	1.23
PBDB-T:**i-mO-4Cl**	As cast	71	6.23×10^{-5}	3.59×10^{-5}	1.74
	150 ^{o}C TA 10min	71	1.66×10^{-4}	5.08×10^{-5}	3.27

Table S6. Calculations of the lowest energy and their geometries of **i-pO-4F** and **i-pO-4Cl**.

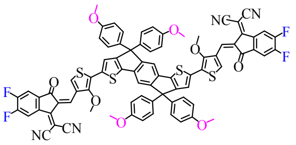
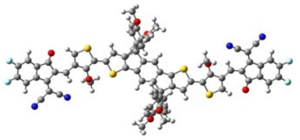
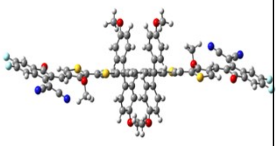
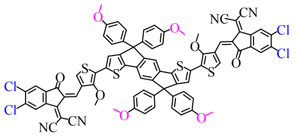
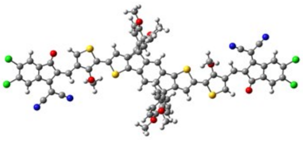
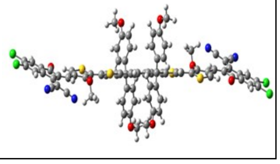
Molecule	Structure	Total energy (a.u)	Top-view	Side-view
i-pO-4F		-5888.9673		
i-pO-4Cl		-7330.4169		

Table S7. Calculated energy levels of **i-pO-4F** and **i-pO-4Cl**.

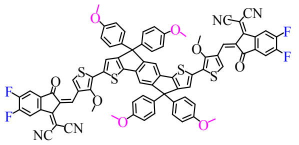
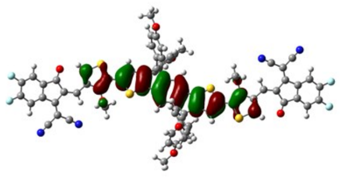
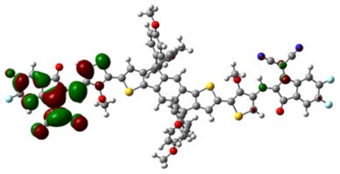
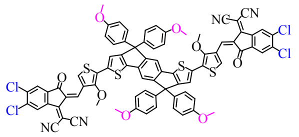
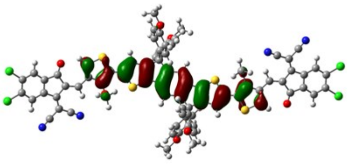
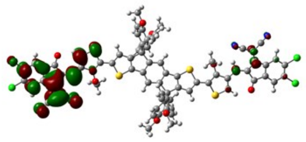
Molecule	HOMO	LUMO
 i-pO-4F	 HOMO= -4.99 eV	 LUMO= -3.33 eV
 i-pO-4Cl	 HOMO= -5.03 eV	 LUMO= -3.42 eV

Table S8. Photophysical and electrochemical properties of **i-pO-4F**, **i-pO-4Cl**.

Acceptor	λ_{max}(sol) [nm]	λ_{max}(film) [nm]	λ_{edge}(film) [nm]	E_{HOMO} $^{a)}$ [eV]	E_{LUMO} $^{a)}$ [eV]	$E_g^{opt\ b)}$ [eV]	E_{HOMO} $^{c)}$ [eV]	E_{HOMO} $^{c)}$ [eV]
i-pO-4F	709	745	818	-5.47	-3.73	1.52	-4.99	-3.33
i-pO-4Cl	720	762	836	-5.41	-3.75	1.48	-5.03	-3.42

$^{a)}$ Obtained by CV plots; $^{b)}$ Obtained from film absorption spectra; $^{c)}$ Data from the DFT calculation.

Table S9. Photovoltaic parameters of PBDB-T:**i-pO-4Cl** devices with various additive.

Blend	Post-treatment	V_{OC}a),b) [V]	J_{SC} a),b) [mA/cm2]	FF a),b) [%]	PCE a),b) [%]
PBDB-T:**i-pO-4Cl**	150 °C TA 10 min	0.874±0.002 (0.872)	14.93±0.16 (15.08)	56.2±0.2 (56.4)	7.33±0.08 (7.41)
	0.5% DIO,150 °C TA 10 min	0.890±0.004 (0.886)	17.58±0.07 (17.64)	62.5±0.2 (62.71)	9.78±0.03 (9.80)
	0.5% CN,150 °C TA 10 min	0.868±0.006 (0.869)	18.54±0.16 (18.65)	66.5±1.6 (67.71)	10.70±0.40 (10.98)

Table S10. Measurement of the hole and electron mobilities.

Active layer	Post-treatment	Thickness (nm)	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	μ_h/μ_e
PBDB-T:**i-pO-4F**	150 °C TA 10min	75	2.73×10^{-4}	2.27×10^{-4}	1.20
PBDB-T:**i-pO-4Cl**	150 °C TA 10min	66	2.24×10^{-4}	3.37×10^{-5}	6.65
	With 0.5% CN, 150 °C TA 10min	75	1.45×10^{-4}	1.06×10^{-4}	1.37

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