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Supporting Information For

Halogenation on Benzo[1,2-b:4,5-b]difuran Polymers for Solvent Additive-Free Non-Fullerene Polymer Solar Cells with Efficiency Exceeding 11%

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EXPERIMENTAL SECTION

All reagents from commercial sources were used without further purification. Toluene and tetrahydrofuran (THF) were freshly distilled before use from sodium using benzophenone as indicator. Anhydrous chlorobenzene was purchased from Energy Chemical Company. The electron acceptor *m*-ITIC was purchased from Derthon Optoelectronic Materials Science Technology Co LTD.

Material characterizations

^{1}H NMR spectra were measured on a Bruker-AV 500MHz with d-chloroform as the solvent and trimethylsilane as the internal reference. UV−visible absorption spectra were measured via Beijing Purkinje General-TU-1901 spectrophotometer. Cyclic voltammetry was performed on a CH Instruments CHI660E electrochemical workstation with a three-electrode system in 0.1 M $[Bu_4N]PF_6$ acetonitrile solution at a scan rate of 40 mV s^{-1}. ITO with sample film was used as the working electrode. A Pt wire was used as the counter electrode and Ag/AgCl was used as the reference electrode. Ferrocene/ferrocenium redox couple was used as the external standard and its redox potential is 0.52 V vs. Ag/AgCl. The HOMO and LUMO energy levels were calculated from the onset of the oxidation and reduction potentials using the following equations: $E_{HOMO} = -e(\varphi_{ox} + 4.28)$ (eV); $E_{LUMO} = E_{opt}^{g} + E_{HOMO}$ (eV). Atomic force microscopy (AFM) images were obtained using a NanoMan VS microscope in the tapping mode. Transmission electron microscopy (TEM) images of the polymer:*m*-ITIC blend films were recorded using a JEOL JEM-1400 transmission electron microscope operated at 120 keV.

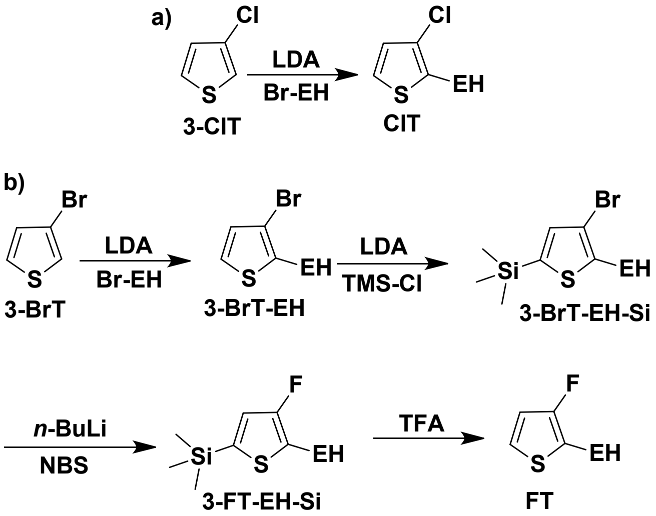
Device fabrication and characterization

The PSCs devices were fabricated with the structure of ITO/ZnO/active layer/ MoO_3/Ag in a N_2-filled glovebox and characterized in the air without encapsulation. The ITO-coated glass substrates were cleaned with isopropyl alcohol, dishwashing liquid, deionized water, ethanol, acetone, and isopropanol for 30 min, respectively. After being dried, the ZnO precursor was spin-coated onto the cleaned ITO glass at 4000 rpm/min for 30s and annealed in the titanium plate under 250 ℃ for 30 mins. The active layer was spin-coated in a N_2-filled glovebox from a solution of Polymer: /m-ITIC with 1: 1.5 weight ratio in chlorobenzene. Subsequently, the active layers were undergone thermal annealing treatment at 130 ℃ for 2 min. Finally, 1 nm MoO_3 and 100 nm Ag were sequentially evaporated on the active layer in the vacuum chamber under a pressure of ca. 2.5×10^{-4} Pa. The effective area of one cell is 4 mm^2. The current-voltage (J-V) characteristics of the devices were measured on a Keithley 2450 Source Measure Unit. The power conversion efficiency (PCE) was measured under an illumination of AM 1.5G (100 mW/cm^2) using a SS-F5-3A (Enli Technology Co. Ltd.) solar simulator (AAA grade, 50 mm x 50 mm photobeam size). The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technololy Co. Ltd.). The light intensity at each wavelength was calibrated with a standard single-crystal Si photovoltaic cell.

The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by the equation:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_h\frac{V^2}{d^3}$$

Where J is the current, μ_h is the zero-field mobility, ε_0 is the permittivity of free soace, ε_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage.



Scheme S1. The synthetic routes toward ClT and FT.

3-Chloro-2-(2-ethylhexyl)thiophene (ClT)

Under argon protection, 3-chlorothiophene (5 g, 0.042 mol) was added into a 250 mL of two-neck-round-bottom flask containing 80 mL of tetrahydrofuran (THF) and the solution was cooled to -78 °C. Lithium diisopropylamide (LDA) (2M, 22 mL) was then added by dropwise. Subsequently, 2-ethylhexyl bromide (8.55 g, 0.044 mol) was added into the flask. The reaction was further stirred at room temperature overnight. The product of 2.5 g was obtained by reduced pressure distillation.^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 7.10 (d, 2H), 6.85 (d, 2H), 2.73–2.71 (d, 2H), 1.63 (m, 1H),1.30 (m, 8H), 0.89 (m, 6H).

3-bromo-2-(2-ethylhexyl)thiophene (3-BrT-EH)

The synthesis procedure and equivalent ratio are the same with compound ClT.

(5-(2-ethylhexyl)-4-bromothiophen-2-yl)trimethylsilane (3-BrT-EH-Si)

Compound 3BrT-EH (12g, 0.044 mol) resolves in 100 mL of dry THF with argon protection in a 500 mL flask. The solution was then cooled to -78 ℃ and LDA (2M, 28.2 mL) was added by dropwise. The mixture was further stirred at -78 ℃ for 1 h, and trimethyl chlorosilane (14.14g, 0.13 mol) was added in one portion. The reaction system was stirred at room temperature overnight. The target compound was obtained by reduced pressure distillation and used without further purification.

(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)trimethylsilane (3-FT-EH-Si)

3-BrT-EH-Si (5.22g, 0.03 mol) was dissolved into 80 mL of dry THF under argon protection and then the solution was cooled to -78 ℃. n-Butyllithium (0.033 mol) was then added dropwise. The mixture was stirred at -78 ℃ for 1 h and then the solution of NFSI (28.32 g, 0.08mol) in THF (100 mL) was added by dropwise. The reation was stirred at room temperature overnight and then poured into 100 mL of water. The organic phase was extracted with petroleum ether and concentrated with rotary evaporator, and the target compound was purified with chromatographic column by using petroleum ether as the eluent and used without further purification. **2-(2-ethylhexyl)-3-fluorothiophene (FT)**

3-FT-EH-Si (0.016 mmol) was dissolved into 20 mL of dichloromethane, and then 3 mL of trifluoroacetic acid (TFA) was mixed into the solution. The mixture was stirred at room temperature for 0.5-1 h until the raw material reacted completely. The product was then poured into water and extracted with petroleum ether. The organic phase was combined and washed with water, dried by anhydrous sodium sulfate and filtered. After concentrating by rotary evaporator, the product 2.6 g was obtained through chromatographic column by using petroleum ether as the eluent. ^{1}H NMR (400 MHz, $CDCl_3$), δ(ppm): 6.97 (s, 1H), 6.75 (d, ^{1}H), 2.67 (d, 2H), 1.56 (m, 1H), 1.33 (m, 8H), 0.90 (m, 6H).

Synthesis of FT-BDF

The solution of 2-(2-ethylhexyl)-3-fluorothiophene (FT) (2.5g, 11.69 mmol) in dry THF (40 mL) with argon protection was cooled to -78℃. Then *n*-BuLi (11.69 mmol, 4.67 mL, 2.5 M in hexane) was slowly added and stirred for 1 h at -78℃ and stirred for another 0.5 h at room temperature after the cooler removing. Subsequently benzo[1,2-b:4,5-b′]-difuran-4,8-dione (0.89 g, 4.68 mmol) was added into the flask in one portion and then stirred at room temperature for 3 h. A mixture of $SnCl_2 \cdot 2H_2O$ (9g, 40 mmol) in 10% HCl (15 mL) was added into the mixture at 0℃ and stirred over night at room temperature. Then the mixture was poured slowly into ice water and extracted with diethyl ether, and the combined organic phases were concentrated to obtain the crude product which was then further purified by column chromatography on silica gel using petroleum ether as the eluent to obtain 2.10 g pale yellow solid with a yield of 77.2%. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm): 7.78 (d, 2H), 7.53(s, 2H), 7.35(d, 2H), 2.76 (d, 4H), 170-1.64 (m, 2H), 1.45-1.28 (m, 16H), 0.92-0.88 (m, 12H).

Synthesis of ClT-BDF

The solution of 2-(2-ethylhexyl)-3-chloro-thiophene (ClT) (2.4 g,10.4 mmol) in dry THF (40 mL) with argon protection was cooled to -78℃. Then *n*-BuLi (10.4 mmol, 4.16 mL, 2.5 M in hexane) was slowly added and stirred for 1 h at -78℃ and stirred for another 0.5 h at room temperature after the cooler removing. Subsequently benzo[1,2-

b:4,5-b′]-difuran-4,8-dione (0.79 g, 4.16 mmol) was added into the flask in one portion and then stirred at room temperature for 3 h. A mixture of $SnCl_2 \cdot 2H_2O$ (9g, 40 mmol) in 10% HCl (15 mL) was added into the mixture at 0℃ and stirred over night at room temperature. Then the mixture was poured slowly into ice water and extracted with diethyl ether, and the combined organic phases were concentrated to obtain the crude product which was then further purified by column chromatography on silica gel using petroleum ether as the eluent to obtain 2.0 g pale yellow solid with a yield of 78.1%.^{1}H NMR (500 MHz, $CDCl_3$ δ ppm): 7.78 (d, 2H), 7.62(s, 2H), 7.32(d, 2H), 2.81 (d, 4H), 1.78-1.70 (m,2H), 1.48-1.30 (m, 16H), 0.97-0.89 (m, 12H).

Synthesis of FT-BDF-Tin (M1)

In a 250 mL flask with argon protection, a solution of **FT-BDF** (3.6 mmol) in 40 mL of THF was cooled to -78 ℃ by using liquid nitrogen-ethanol bath. *n*-Butyllithium (2.5 M, 3.43 mL) was added into the flask dropwise and then the mixture was stirred for 0.5 h at -78℃ and 0.5 h below -78℃. Subsequently, chlorotrimethylstannane (1.0 M, 11.5 mL) was added into the flask dropwise, and the reaction was stirred for overnight at room temperature. The mixture solution was poured into water and extracted by diethyl ether, the crude product was concentrated and purified by recrystallization from ethanol. The product was obtained as 2.0 g pale yellow crystalline solid with a yield of 61.1%.^{1}H NMR (500 MHz, $CDCl_3$ δ ppm):7.54 (s, 2H), 7.46 (t, 2H), 2.78 (d, 4H), 1.72-1.64 (m, 2H), 1.48-1.30 (m, 16H), 0.98-0.88 (m, 12H), 0.62-0.34 (m, 18H)

Synthesis of ClT-BDF-Tin (M2)

In a 250 mL flask with argon protection, a solution of **ClT-BDF** (3.41mmol) in 40 mL of THF was cooled to -78 ℃ by using liquid nitrogen-ethanol bath. *n*-Butyllithium (2.5 M, 3.1 mL) was added into the flask dropwise and then the mixture was stirred for 0.5 h at -78℃ and 0.5 h below -78℃. Subsequently, chlorotrimethylstannane (1.0 M, 10.3 mL) was added into the flask dropwise, and the reaction was stirred for overnight at room temperature. The mixture solution was poured into water and extracted by diethyl ether, the crude product was concentrated and purified by recrystallization from ethanol. The product was obtained as 1.7 g pale yellow crystalline solid with a yield of 53.0%. ^{1}H NMR (500 MHz, $CDCl_3$, δ ppm):7.62 (s, 2H), 7.44 (t, 2H), 2.86 (d, 4H), 1.79-1.72 (m, 2H), 1.50-1.25 (m, 16H), 0.98-0.86 (m, 12H), 0.62-0.35 (m, 18H)

Polymerization (F10 and F11):

The **FT-BDF-Tin/ClT-BDF-Tin** monomer (0.2 mmol) and BTA-Br monomer (compound 9, 0.2 mmol) was mixed in 5 mL of dry toluene, and then the solution was purged with argon for 10 min. The catalyst, $Pd(PPh_3)_4$ (8 mg), was added in one portion, and the mixture was purged with argon for another 20 min. The reaction was then stirred at 110 °C for 24 h under argon protection. The polymer solution was cooled to room temperature and precipitated from 50 mL of methanol. The crude polymer was collected by filtration and purified by Soxhlet extraction with methanol, acetone, petroleum ether and chloroform in order. The polymer was precipitated from methanol again and flited to dry under vacuum at 50 °C overnight and collected as dark purple solid with the yield of 41.2% for PFTBDF-TBz (F10) and the yield of 42.0 % for PClTBDF-TBz (F11).

PFTBDF-TBz (F10): M_n= 9.67 kDa; M_w= 41.33 kDa; PDI = 4.27; ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): 8.00-7.62 (m, 4H), 7.40-7.18 (m, 2H), 7.13-6.78 (m, 2H), 4.74 (m, 2H), 2.80–2.31 (m, 5H), 1.69-1.30 (br, 42H), 0.91–0.76 (br, 18H).

PClTBDF-TBz (F11): M_n= 8.48 kDa; M_w= 38.68 kDa; PDI = 4.56; ^{1}H-NMR (400 MHz, $CDCl_3$, δ, ppm): 8.01-7.70 (m, 4H), 7.39-7.20 (m, 2H), 7.14-6.80 (m, 2H), 4.73 (m, 2H), 2.80-2.32 (m, 5H), 1.69-1.310 (br, 42H), 0.92-0.76 (br, 18H).

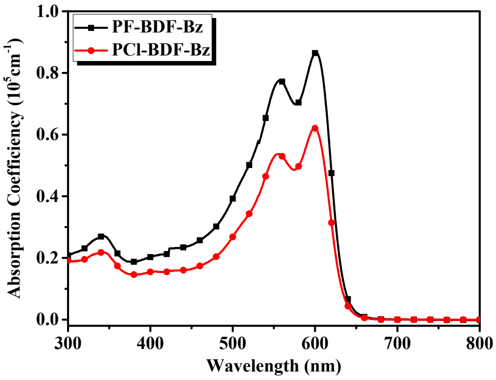


Fig. S1. The UV-Vis absorption of F10 and F11 in chloroform solutions

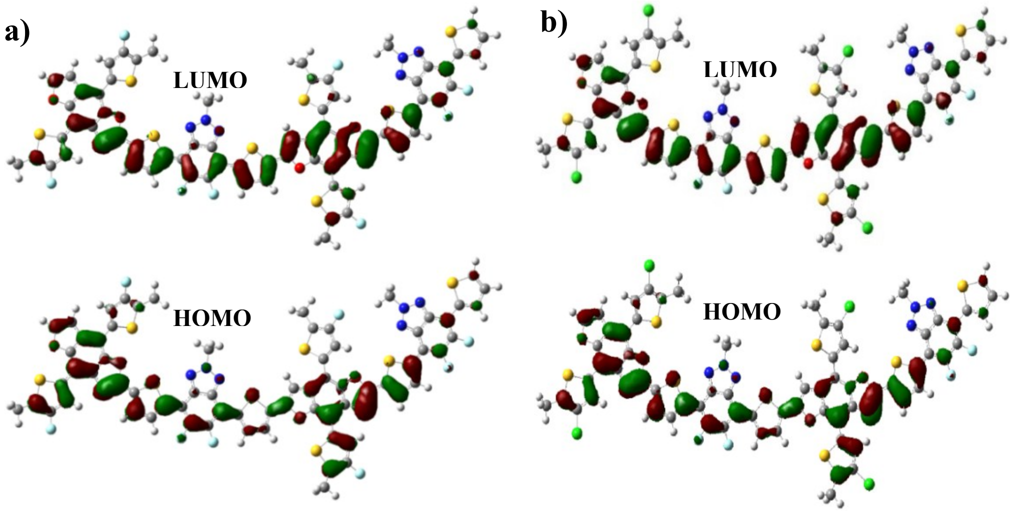


Fig. S2. HOMO and LUMO electron density distributions of F10 (c) and F11 (d) by density functional theory with the B3LYP/6-31G (d,p) basis set. The S atoms are marked in yellow, O atoms are marked in red, N atoms are shown in blue, F atoms are marked in sky blue, Cl atoms are marked in green, C atoms are shown in gray, and H atoms are marked in white.

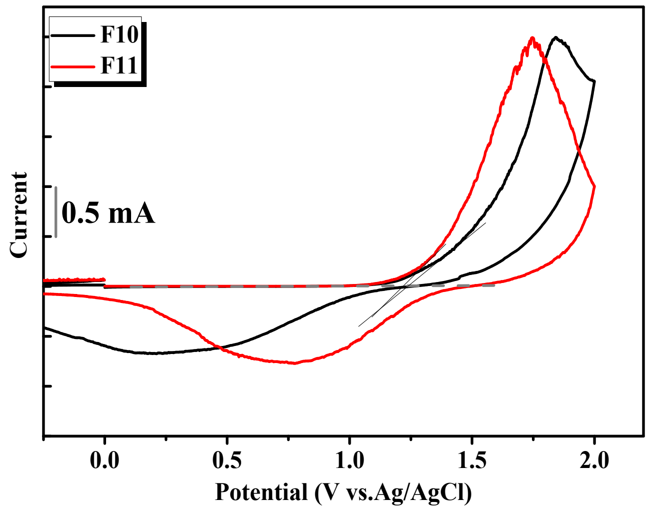


Fig. S3. Cyclic voltammograms of the F10 and F11 films on glassy carbon electrodes in 0.1 mol L^{-1} Bu_4NPF_6 in acetonitrile at a scan rate of 40 mV s^{-1}.

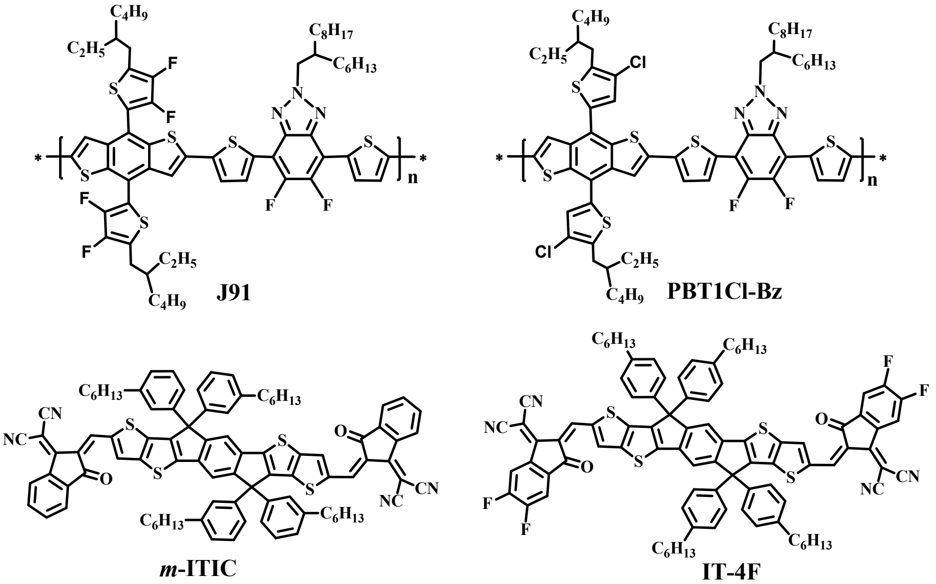


Fig. S4. The chemical structures of J91, PBT1Cl-Bz, m-ITIC and IT-4F.

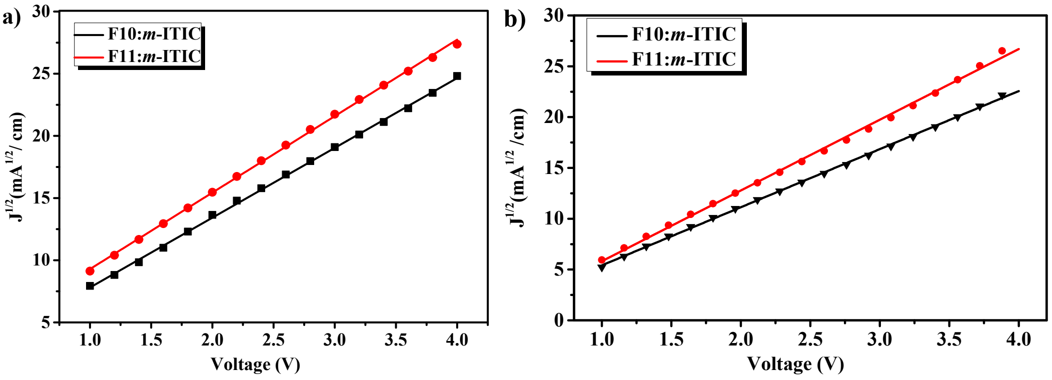


Fig. S5. J-V plots of the hole only devices (a) and electron-only devices (b) for F10 and F11.Solid lines are the fitting lines of the data

Table S1. The molecular weight, optical and electrochemical properties of polymer F10, F11, J91 and PBT1Cl-Bz.

Polymer	**M_n (kDa)**	**M_w (kDa)**	**PDI**	**λ_{onset} (nm)**	**E_{opt} (eV)**	**E_{HOMO} (eV)**	**E_{LUMO} (eV)**
F10	9.67	41.33	4.27	642	1.93	-5.48	-3.48
F11	8.48	38.68	4.56	645	1.92	-5.50	-3.55
J91	6.97	13.40	1.92	620	2.00	-5.50	-3.02
PBT1Cl-Bz	26.06	45.87	1.76	633	1.96	-5.47	-3.58

Table S2. Hole and electron mobilities of the blend films of F10:*m*-ITIC and F11:*m*-ITIC.

Active layer	Ratio	μ_h[cm^2 V^{-1} s^{-1}]	μ_e [cm^2 V^{-1} s^{-1}]	$\mu_{e/}\mu_h$
F10:*m*-ITIC	1:1.5	1.27×10^{-4}	1.08×10^{-4}	0.85
F11:*m*-ITIC	1:1.5	1.57×10^{-4}	1.49×10^{-4}	0.95