

Electronic Supplementary Information

Quantifying Alkyl Pendants of Acceptors Induced V_{oc} Loss in Organic Solar Cells

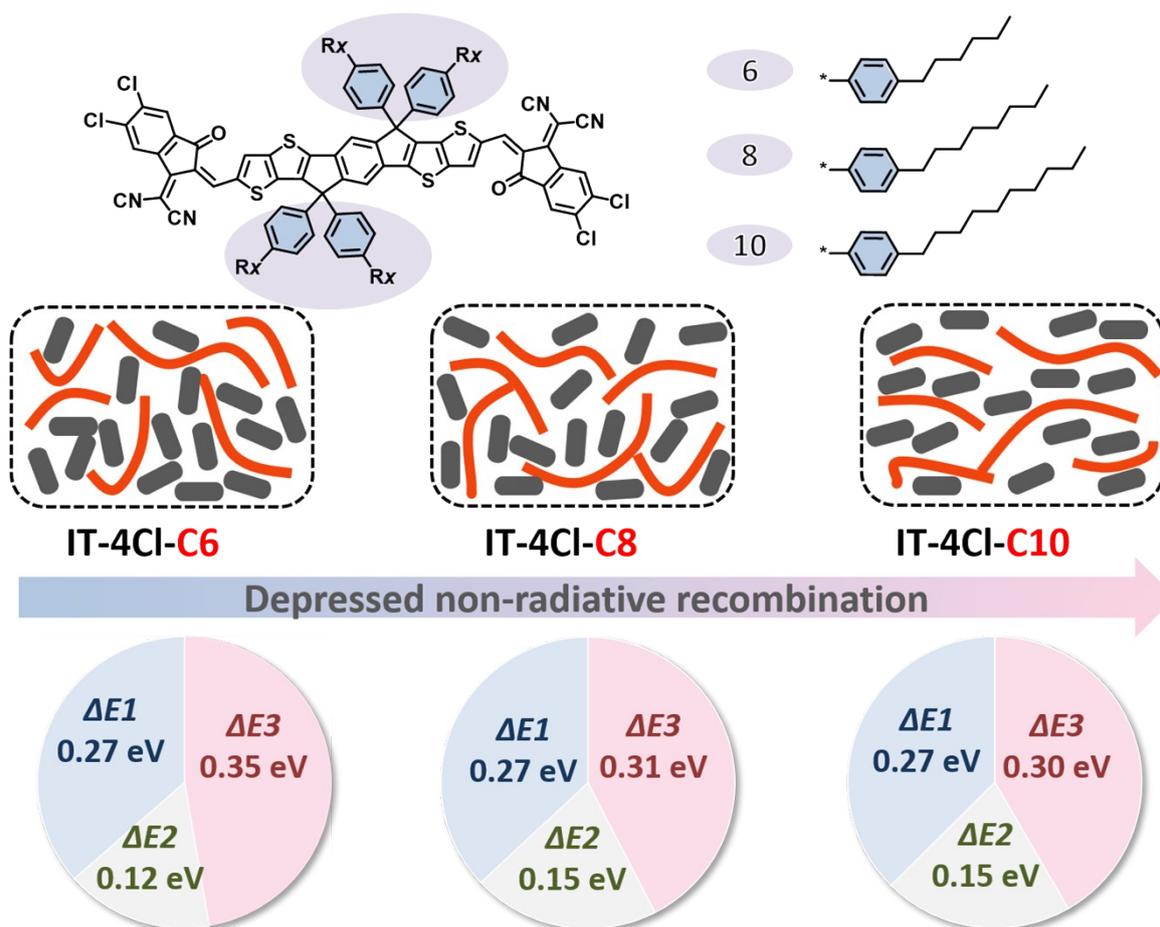
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Components of V_{oc} loss in organic solar cells were reasonably controlled by tuning the lengths of alkyl pendants on non-fullerene acceptors.



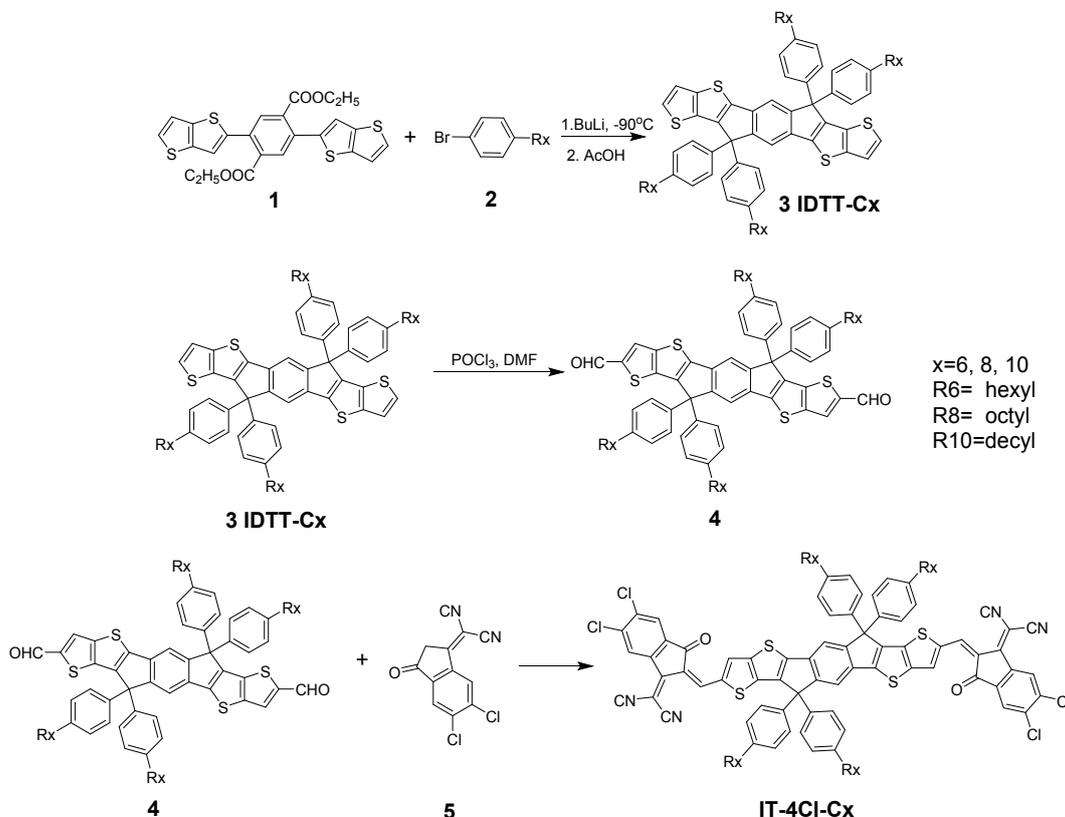
Keywords: non-fullerene organic solar cells, alkyl pendant, energy loss, morphology, power conversion efficiency

Experimental

Materials:

PBDB-TF and PFN-Br were purchased from Solarmer Material Inc. IT-4Cl-C6, IT-4Cl-C8 and IT-4Cl-C10 were synthesized in our lab. PEDOT: PSS was purchased from Heraeus (CLEVIOS™ P VP Al 4083). All these solvents used here were commercially available from Acros.

The three non-fullerene based acceptors, IT-4Cl-C6, IT-4Cl-C8 and IT-4Cl-C10, were synthesized by the reported methods. Compound 1, 2 and 5 were purchased from Solarmer Materials, Inc. All of the commercial available reagents were used without any further treatment.



Scheme S1. Synthesis of IT-4Cl-Cx.

Compound 3. (IDTT-C6, IDTT-C8, IDTT-C10)

Compound 2 (0.01 mol) was dissolved into 200 mL of dry-tetrahydrofuran in a 500 mL two-neck round-bottom flask under protection of inert atmosphere. After cooling the solution down to $-90\text{ }^{\circ}\text{C}$, BuLi (2.5 M, 0.05 mol) was added into the flask dropwise, and then the reactant was kept stirring at $-80\text{ }^{\circ}\text{C}$ to $-90\text{ }^{\circ}\text{C}$ for 1 hour. Afterwards, compound 1 (16.9 g, 0.07 mmol) was added into the flask in one portion, and the mixture was kept stirring overnight. The reactant was then poured into 200 mL of deionized water and extracted by 150 mL*2 of dichloromethane and concentrated by rotary evaporation. The raw product was then mixed with acetic acid (200 mL) and concentrated H_2SO_4 (4 mL), the mixture was stirred at $120\text{ }^{\circ}\text{C}$ for 2 hours and then precipitated in water. The product was extracted by dichloromethane and purified by chromatographic column (petroleum ether: dichloromethane=5:1). The pure product was obtained as light yellow solid with a yield of ~65%.

IDTT-C6: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ (ppm): 7.50 (s, 2H), 7.28 (d, 2H), 7.25 (d, 2H), 7.19 (d, 8H), 7.08 (d, 8H), 2.55 (t, 8H), 1.58 (m, 8H), 1.29 (m, 24H), 0.86 (t, 12H)

IDTT-C8: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ (ppm): 7.50 (s, 2H), 7.28 (d, 2H), 7.25 (d, 2H), 7.19 (d, 8H), 7.08 (d, 8H), 2.56 (t, 8H), 1.58 (m, 8H), 1.27 (m, 40H), 0.86 (t, 12H)

IDTT-C10: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ (ppm): 7.50 (s, 2H), 7.29 (d, 2H), 7.24 (d, 2H), 7.19 (d, 8H), 7.08 (d, 8H), 2.55 (t, 8H), 1.58 (m, 8H), 1.29 (m, 56H), 0.86 (t, 12H)

Compound 4. (IDTT-CHO-C6, IDTT-CHO-C8, IDTT-CHO-C10)

Compound 3 (5.9 mmol) was dissolved into 50 mL of DMF in a 250 mL flask at room temperature, and then phosphorus oxychloride (7.2 g, 47.2 mmol) was added into the flask in one portion. The reactant was stirred at room temperature for 30 min and then reflux at $145\text{ }^{\circ}\text{C}$ for another 30 min. The mixture was poured into 150 mL of water and the raw product was precipitated as brown

solid. The residue was purified by column chromatography by using mixed solvent of petroleum ether: dichloromethane=1:1 as eluent, yielding a yellow solid. (yield \approx 70%)

IDTT-CHO-C6: ^1H NMR (300 MHz, CDCl_3) δ (ppm): 9.89 (s, 2H), 7.94 (s, 2H), 7.61 (s, 2H), 7.16 (d, 8H), 7.11 (d, 8H), 2.56 (t, 8H), 1.60 (m, 8H), 1.30 (m, 24H), 0.86 (m, 12H)

IDTT-CHO-C8: ^1H NMR (300 MHz, CDCl_3) δ (ppm): 9.89 (s, 2H), 7.94 (s, 2H), 7.61 (s, 2H), 7.16 (d, 8H), 7.11 (d, 8H), 2.55 (t, 8H), 1.58 (m, 8H), 1.27 (m, 40H), 0.87 (m, 12H)

IDTT-CHO-C10: ^1H NMR (300 MHz, CDCl_3) δ (ppm): 9.89 (s, 2H), 7.94 (s, 2H), 7.61 (s, 2H), 7.16 (d, 8H), 7.11 (d, 8H), 2.55 (t, 8H), 1.58 (m, 8H), 1.29 (m, 56H), 0.87 (m, 12H)

IT-4CI-C6, IT-4CI-C8, IT-4CI-C10

Compound 4 (IDTT-CHO-Rx, 2.8 mmol) and compound 5 (5.94 g, 22.4 mmol) was dissolved into 300 mL of chloroform under the protection of inert atmosphere. The solution was stirred at room temperature for 10 min and then pyridine (3 mL) was added into the mixture in one portion. The reactant was stirred at 70 °C for 1 hour and concentrated by rotary evaporator. The residue was purified by silica gel column using petroleum ether: dichloromethane=1:1 as eluent. The product was obtained as dark blue solid with a yield of \approx 35%.

IT-4CI-C6: ^1H NMR (300 MHz, CDCl_3) δ (ppm): 8.87 (s, 2H), 8.76 (s, 2H), 8.24 (s, 2H), 7.95 (s, 2H), 7.65 (s, 2H), 7.22-7.19 (d, 8H), 7.16-7.13 (d, 8H), 2.57 (t, 8H), 1.60 (m, 8H), 1.29 (m, 24H), 0.86 (t, 12H)

IT-4CI-C8: ^1H NMR (300 MHz, CDCl_3) δ (ppm): 8.87 (s, 2H), 8.76 (s, 2H), 8.24 (s, 2H), 7.95 (s, 2H), 7.65 (s, 2H), 7.22-7.19 (d, 8H), 7.15-7.13 (d, 8H), 2.57 (t, 8H), 1.59 (m, 8H), 1.25 (m, 40H), 0.85 (t, 12H)

IT-4CI-C10: ^1H NMR (300 MHz, CDCl_3) δ (ppm): 8.87 (s, 2H), 8.76 (s, 2H), 8.24 (s, 2H), 7.95 (s, 2H), 7.66 (s, 2H), 7.22-7.19 (d, 8H), 7.15-7.13 (d, 8H), 2.57 (t, 8H), 1.59 (m, 8H), 1.27 (m, 56H), 0.86 (t, 12H)

Device fabrication and characterization:

Device fabrication: Indium-tin-oxide (ITO) ($115 \Omega/\square$) substrates were cleaned with detergent, deionized (DI) water, acetone and isopropanol. After 15 min UV-ozone, the ITO substrates were cooled down for further using. The solution of PEDOT: PSS (CLEVIOSTM P VP Al 4083) was spin-coated on top of ITO at 4000 rpm, followed by 15 minutes annealing at 160 °C. After annealing, the PEDOT: PSS coated ITO substrates were transferred into N_2 glove box. Then the BHJ solution was spin-coated, followed by 100°C annealing for 10 minutes. The BHJ precursor solutions were prepared using total concentration 20 mg/mL in chlorobenzene, together with 1:1 donor/acceptor ratio by weight. After thermal annealing, the PFN-Br solution was spin coated on the active layer at 4000 rpm for 30 sec. Then 100 nm of Al cathode was thermally evaporated under high vacuum (ca. 3×10^{-4} Pa). The device area, as defined by the aperture area on mask, was 1.938 mm².

Characterization: The J-V characteristics of all the devices were measured with a KEITHLEY 2400 Precision Source/Measure unit. The PCE of the resulting single-junction and tandem solar cells were measured under AM1.5G (100 mW/cm²) using a XES-70S1 solar simulator ((SAN-EI Electric Co., Ltd., AAA grade, 70 mm \times 70 mm photo-beam size). A 20 mm \times 20 mm single-crystal Si diode was used to calibrate the irradiation power of the simulator. The EQE was measured by Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech, Taiwan). The light intensity at each wavelength was calibrated with a single-crystal Si photovoltaic cell. The UV-visible absorption spectroscopy measurements were carried out using a Purkinje General TU-1901 UV-vis spectrophotometer. AFM images were taken on a IIIa atomic force microscope (Vecoo). The charge-carrier mobility of the blended films were measured using photo-induced charge-carrier extraction by linearly increasing voltage (photo-CELIV) measurements by using a device architecture of ITO / PEDOT: PSS / BHJ / PFN-Br / Al. The electrochemical cyclic voltammetry was conducted on a Zahner IM6e Electrochemical Workstation with glassy carbon disk, Pt wire, and Ag/Ag⁺ electrode as working electrode, counter electrode and reference electrode respectively in a 0.1 mol/L tetrabutylammoniumhexafluorophosphate (Bu₄NPF₆) acetonitrile solution. TEM measurements were carried out by using the instrument HT7700 purchased from Hitachi, Ltd. Electroluminescence (EL) spectroscopy measurement. EL spectra and EQEEL were measured by a Solar-Luminescence-EQE system (Enli Technology, SLE-1100). SLE-1100 combines a Keysight B2912a two-channel SMU (10fA resolution), a NIST-traceable spectrometer (wavelength calibrated), and a calibrated large area Si photodetector. For EL spectra, Keysight B2912a was used for

supplying voltage and current to the devices. The device luminescence was coupled into an optical fiber and guided to a spectrometer (with a low-temperature cooled back-thinned CCD array sensor, 300nm~1100nm) to record the EL spectra. The whole system was wavelength calibrated by a NIST-traceable standard lamp from 300 nm to 1100 nm. For bias-dependent EQE_{EL} measurements, the current-voltage-luminescence curves were measured using Keysight B2912a two-channel SMU and a calibrated large area Si photodetector to collect all photons from the device. PL spectra of the studied films were obtained by a FLS980 fluorescence spectrophotometer. The grazing incident wide-angle X-ray diffraction (GIWAXS) data were measured by X-ray scattering system (XEUSS, FRANCE Xenocs SA) at the National Center for Nanoscience and Technology (NCNST, Beijing). The detector was Pilatus 3R 300k. The scattered X-rays were detected using wavelength of 1.54 Å, bandwidth of $\Delta E/E=3e^{-3}$ and spot size of 0.8mm.

Supplementary Figures:

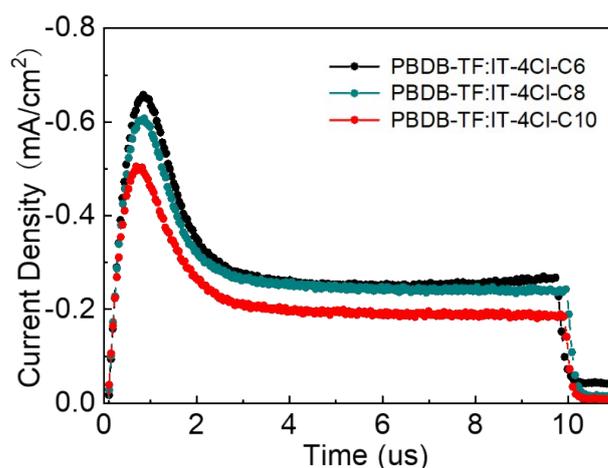


Figure S1. Carrier extraction by linearly increasing voltage(Photo-CELIV) plots of studied devices.

Table S1. The data of Photo-CELIV in Figure S1.

BHJs	Carrier mobility ($\text{cm}^2\text{V}^{-1}\text{S}^{-1}$)
PBDB-TF:IT-4CI-C6	2.0×10^{-4}
PBDB-TF:IT-4CI-C8	2.6×10^{-4}
PBDB-TF:IT-4CI-C10	4.5×10^{-4}

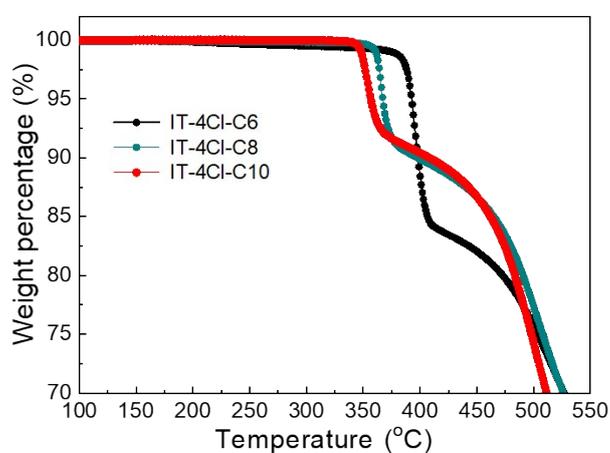
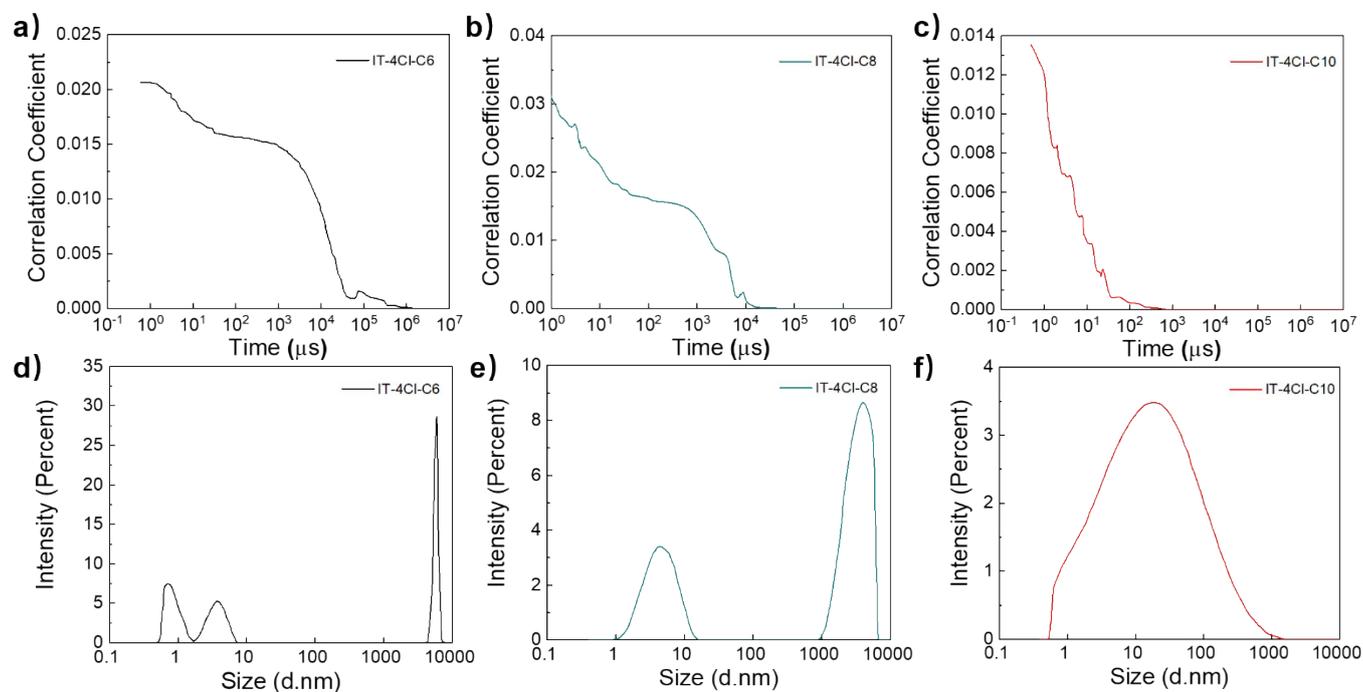
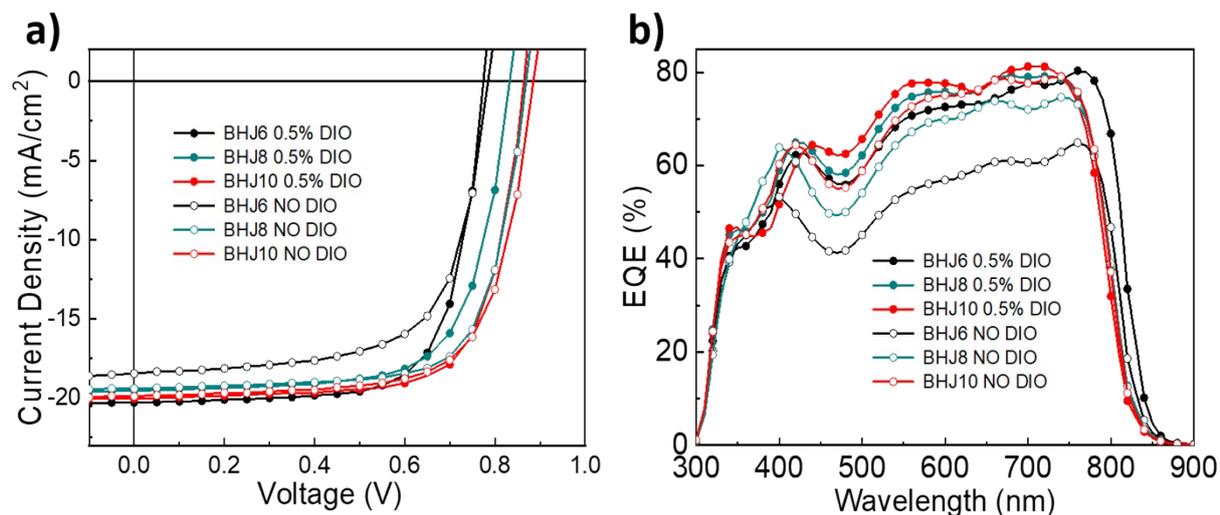


Figure S2. TGA curves of three NFAs.

Table S2. Summary of TGA data for these NFAs.

acceptors	T_d (°C)
IT-4Cl-C6	383
IT-4Cl-C8	356
IT-4Cl-C10	338

**Figure S3.** The data of dynamic light scattering experiments of the three studied acceptors in CB solutions with concentrations of 10 mg/mL, which is the same as the concentration used in device fabrication.**Figure S4.** Additive optimization results of devices with BHJs of PBDB-TF:IT-4Cl-C6, PBDB-TF:IT-4Cl-C8 and PBDB-TF:IT-4Cl-C10.

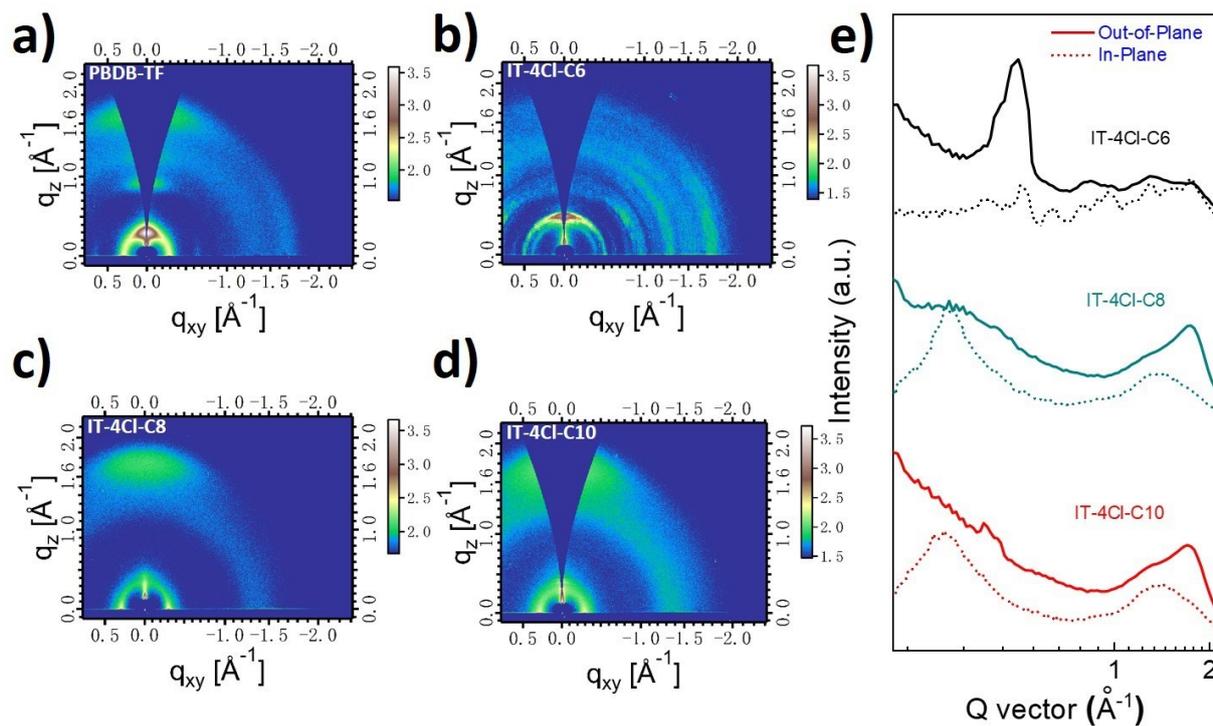


Figure S5. GIWAXS patterns and the line-cuts of the corresponding GIWAXS patterns of PBDB-TF, IT-4Cl-C6, IT-4Cl-C8 and IT-4Cl-C10.