

Supporting Information

Halogenated Conjugated Molecules for Ambipolar Field-Effect Transistors and Non-Fullerene Organic Solar Cells

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1. Materials and measurements

All synthetic procedures were performed under argon atmosphere. Commercial chemicals were used as received. THF and toluene were distilled from sodium under an N₂ atmosphere. ¹H-NMR and ¹³C-NMR spectra were recorded at 400 MHz and 100 MHz on a Bruker AVANCE spectrometer with CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. Optical absorption spectra were recorded on a JASCO V-570 spectrometer with a slit width of 2.0 nm and a scan speed of 1000 nm min⁻¹. TGA measurement was performed on a Perkin-Elmer TGA-7 apparatus. Cyclic voltammetry was performed under an inert atmosphere at a scan rate of 0.1 V s⁻¹ and 1 M tetrabutylammonium hexafluorophosphate in acetonitrile as the electrolyte, a glassy-carbon working electrode coated with samples, a platinum-wire auxiliary electrode, and an Ag/AgCl as a reference electrode. X-Ray diffraction (XRD) measurements were obtained in reflection mode at 40 kV and 200 mA with Cu Kα radiation using a 2-kW Rigaku D/max-2500 X-ray diffractometer. Atomic force microscopy (AFM) images were recorded using a Digital Instruments Nanoscope IIIa multimode atomic force microscope in tapping mode under ambient conditions.

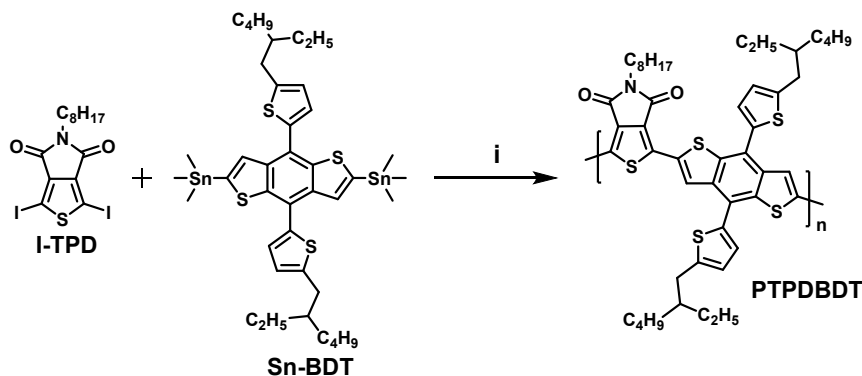
The organic field-effect transistors were fabricated on a commercial Si/SiO₂/Au substrate purchased from First MEMS Co. Ltd. A heavily N-doped Si wafer with a SiO₂ layer of 300 nm served as the gate electrode and dielectric layer, respectively. The Ti (2 nm)/Au (28 nm) source–drain electrodes were sputtered and patterned by a lift-off technique. Before deposition of the organic semiconductor, the gate dielectrics were treated with octadecyltrichlorosilane (OTS) in a vacuum oven at a temperature of 120 °C, forming an OTS self-assembled monolayers. The treated substrates were rinsed successively with hexane, chloroform, and isopropyl alcohol. Polymer thin films were spin coated on the substrate from CHCl₃/10% *n*-hexane solution with a thickness of around 30 – 50 nm. The devices were thermally annealed at certain temperature for 10 min in a glovebox filled with N₂ before measurement. The devices were measured on a Keithley 4200 SCS semiconductor parameter analyzer at room temperature. The mobilities were calculated from the saturation region with the following equation: $I_{SD} = (W/2L)C_i\mu(V_G - V_T)^2$, where I_{SD} is the drain–source current, W is the channel width (1400 μm), L is the channel length (50 μm for H, F, Cl and I based ITIC, 5 μm for Br-ITIC), μ is the field-effect mobility, C_i is the capacitance per unit area of the gate dielectric layer, and V_G and V_T are the gate voltage and threshold voltage, respectively. This equation defines the important characteristics of electron

mobility (μ), on/off ratio ($I_{\text{on}}/I_{\text{off}}$), and threshold voltage (V_T), which could be deduced by the equation from the plot of current–voltage.

Photovoltaic devices with inverted configuration were made by spin-coating a ZnO sol-gel at 4000 rpm for 60 s onto pre-cleaned, patterned ITO substrates. The photoactive layer was deposited by spin coating a CHCl_3 solution containing PTPDBDT and X-ITIC and the appropriate amount of DIO as processing additive in air. MoO_3 (10 nm) and Ag (100 nm) were deposited by vacuum evaporation at ca. 4×10^{-5} Pa as the back electrode.

The active area of the cells was 0.04 cm^2 . The J - V characteristics were measured by a Keithley 2400 source meter unit under AM1.5G spectrum from a solar simulator (Enlitech model SS-F5-3A). Solar simulator illumination intensity was determined at 100 mW cm^{-2} using a monocrystal silicon reference cell with KG5 filter. Short circuit currents under AM1.5G conditions were estimated from the spectral response and convolution with the solar spectrum. The external quantum efficiency was measured by a Solar Cell Spectral Response Measurement System QE-R3011 (Enli Technology Co., Ltd.). The thickness of the active layers in the photovoltaic devices was measured on a Veeco Dektak XT profilometer.

2. Synthesis of PTPDBDT



Scheme S1. Chemical Structures of the donor polymer PTPDBDT and its synthetic route. i) Stille polymerization by using $\text{Pd}_2(\text{dba})_3/\text{P}(o\text{-tol})_3$ in toluene at 115 $^\circ\text{C}$.

PTPDBDT. To a degassed solution of the monomer **I-TPD**^{S1} (57.76 mg, 0.112 mmol), **Sn-BDT** (101.03 mg, 0.112 mmol) in toluene (2.5 mL), tris(dibenzylideneacetene)dipalladium (3.07 mg, 3.4 μmol) and $\text{P}(o\text{-tol})_3$ (8.16 mg, 26.8 μmol) were added. The mixture was stirred at 115 for 24 h, after which it was precipitated in methanol and filter through a Soxhlet thimble. The polymer was extracted with acetone, hexane and CHCl_3 , which was then precipitated into acetone. The

polymer was collected by filtering over a 0.45 μm PTFE membrane filter and dried in a vacuum oven to yield PTPDBDT (75 mg, 80%).

3. Characterization of X-ITIC

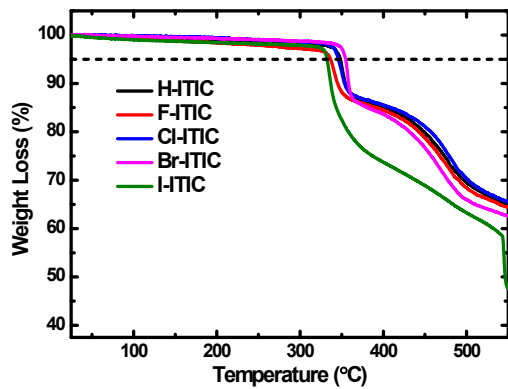


Fig. S1 TGA plots of the ITIC and its derivatives with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under N_2 atmosphere. Temperatures with 5% weight loss for H-ITIC, F-ITIC, Cl-ITIC, Br-ITIC and I-ITIC are 348, 337, 346, 355 and 332 $^{\circ}\text{C}$.

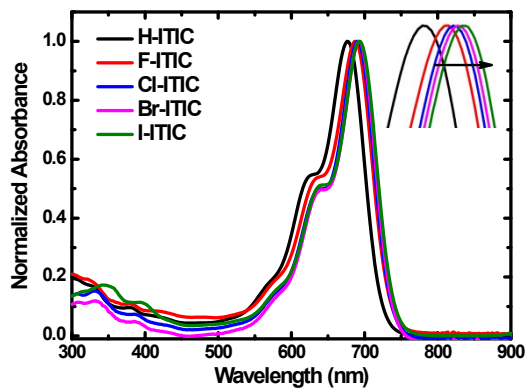
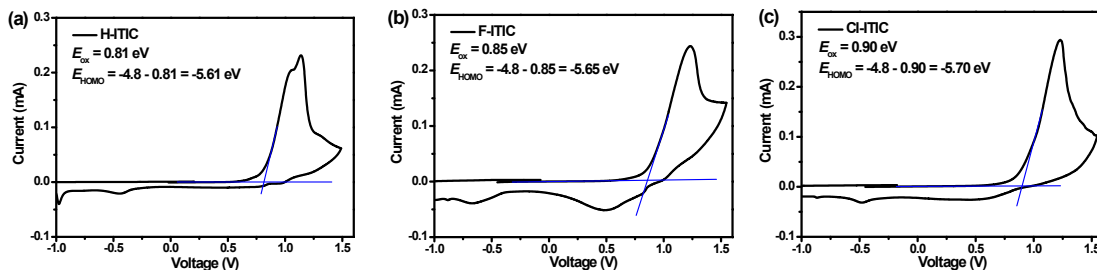


Fig. S2 Absorption spectra of X-ITIC in chloroform. The graph inset shows the absorption around 700 nm. The absorption peaks for H-, F-, Cl-, Br- and I-ITIC are 677 nm, 687 nm, 691 nm, 692 nm and 695 nm.



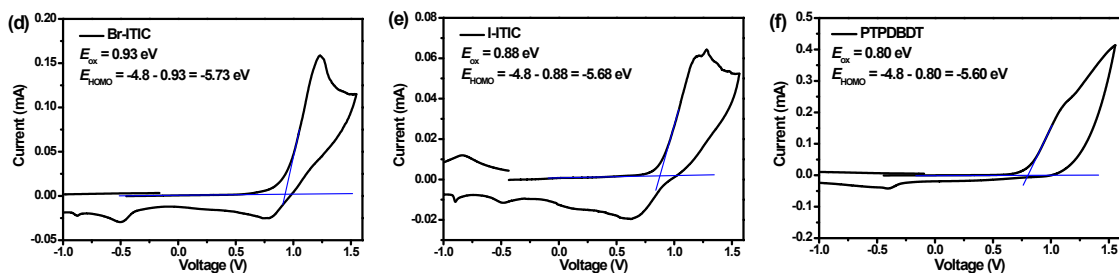


Fig. S3 Cyclic voltammogram of (a) H-ITIC, (b) F-ITIC, (c) Cl-ITIC, (d) Br-ITIC, (e) I-ITIC and (f) the donor polymer PTPDBDT. Potential vs. Fc/Fc^+ . Oxidation potential and HOMO levels are also included.

Table S1. 2θ and d -spacings calculated from XRD patterns.

	2θ (1)	d -spacing [Å]	2θ (2)	d -spacing [Å]
H-ITIC	6.04°	14.6	-	-
F-ITIC	6.05°	14.6	-	-
Cl-ITIC	5.76°	15.3	7.68°	11.5
Br-ITIC	5.73°	15.4	7.65°	11.5
I-ITIC	5.73°	15.4	7.64°	11.6

4. FETs of X-ITIC

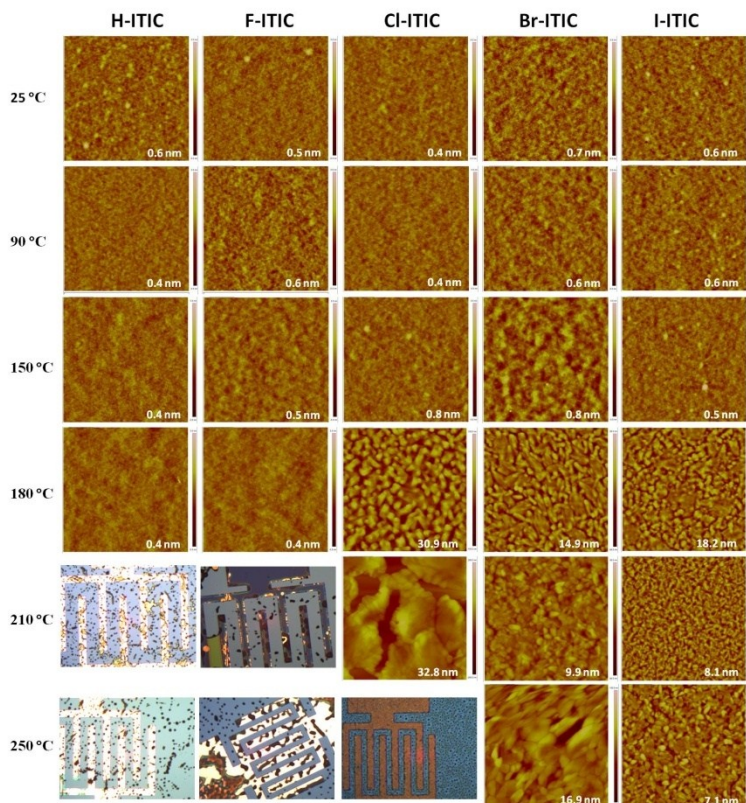
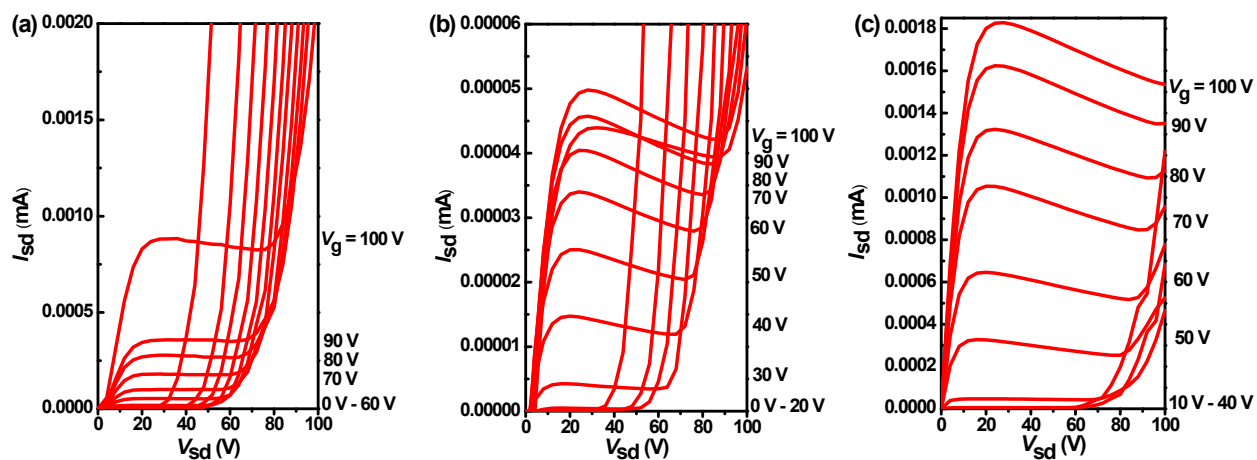


Fig. S4 AFM height images ($3 \times 3 \mu\text{m}^2$) of X-ITIC thin films on OTS-modified Silica substrates. The thin films were thermal annealed under certain temperature for 10 min. RMS roughness is included. AFM images of H-ITIC, F-ITIC and Cl-ITIC thin films thermal annealed at 210 °C or 250 °C are replaced by optical images of devices in order to show the melting condition of the X-ITIC.



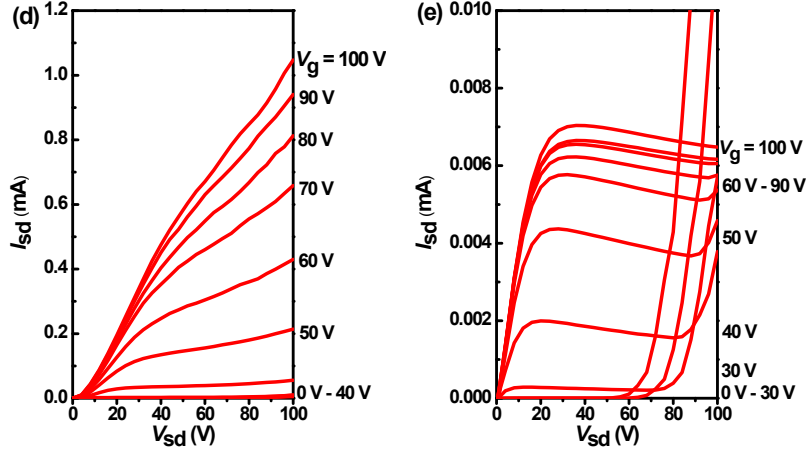


Fig. S5 n-Type Output curves obtained from BGBC FET devices. X-ITIC thin films were fabricated from $\text{CHCl}_3/\text{n-hexane}$ (10%) and thermal annealed for 10 min before measurement. 90 °C for F-ITIC and 180 °C for other ITIC derivatives. (a) H-ITIC, (b) F-ITIC, (c) Cl-ITIC, (d) Br-ITIC and (e) I-ITIC.

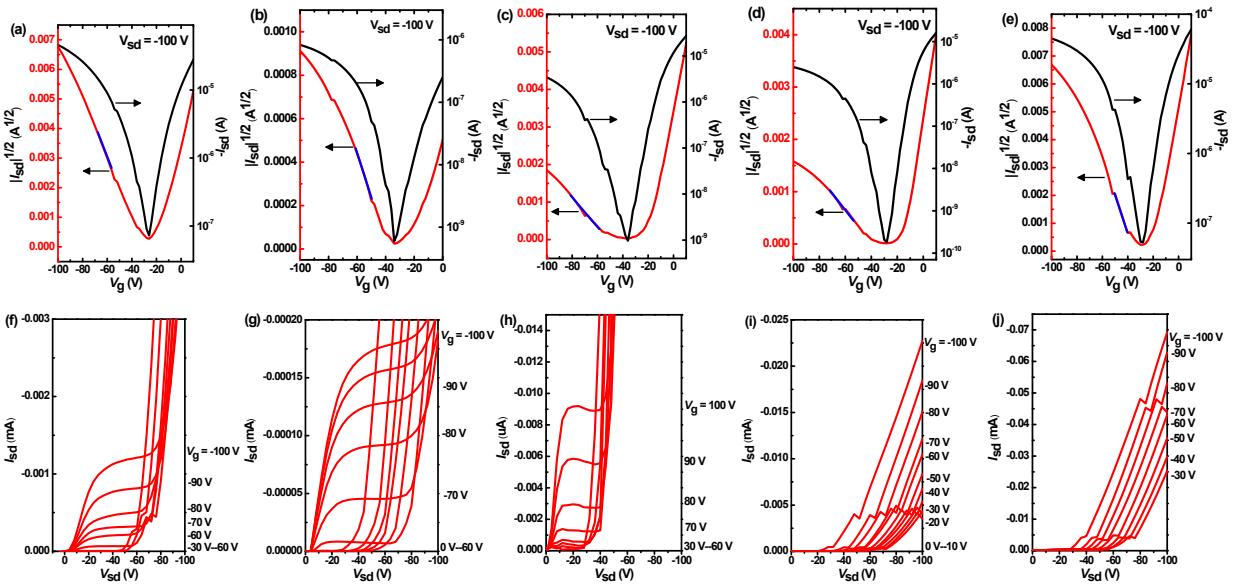


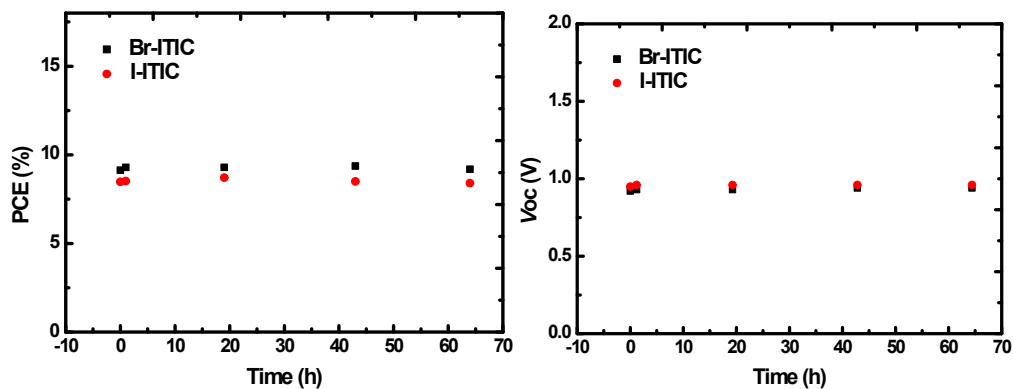
Fig. S6 p-Type transfer (a-e) and Output (f-j) curves obtained from BGBC FET devices. X-ITIC thin films were fabricated from $\text{CHCl}_3/\text{n-hexane}$ (10%) and thermal annealed for 10 min before measurement. 90 °C for F-ITIC and 180 °C for other ITIC derivatives. (a,f) H-ITIC, (b,g) F-ITIC, (c,h) Cl-ITIC, (d,i) Br-ITIC and (e,j) I-ITIC.

5. Solar cells of PTPDBDT:X-ITIC

Table S2. Influence of thermal annealing of PTPDBDT:X-ITIC (1:1) thin films fabricated from CHCl_3/DIO (0.5%) on the device performance of solar cells.

Acceptor	Thermal Anneal	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF	PCE [%]
H-ITIC	No	10.6	1.04	0.58	6.4
	Yes ^a	9.1	1.04	0.59	5.6
F-ITIC	No	14.8	0.94	0.61	8.5
	Yes ^a	14.1	0.94	0.66	8.8
Cl-ITIC	No	15.3	0.95	0.61	8.8
	Yes ^a	15.6	0.94	0.65	9.5
Br-ITIC	No	15.4	0.93	0.62	8.9
	Yes ^a	15.4	0.93	0.66	9.4
I-ITIC	No	13.6	0.94	0.61	7.8
	Yes ^a	14.5	0.95	0.65	8.9

^aPhotoactive layers were thermal annealed at 150 °C for 30 min before metal evaporation.



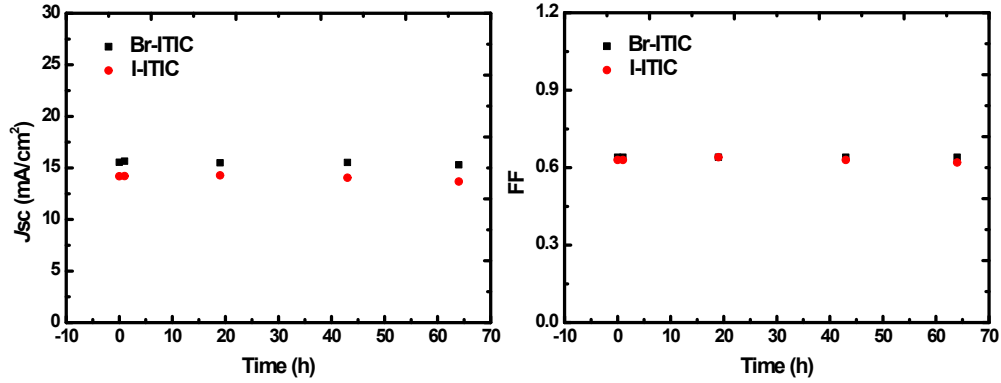


Fig. S7 Stability test of Br-ITIC and I-ITIC based solar cells. The cells were stored in the N_2 filled glove box in the dark and measured under AM1.5 G simulated solar spectrum.

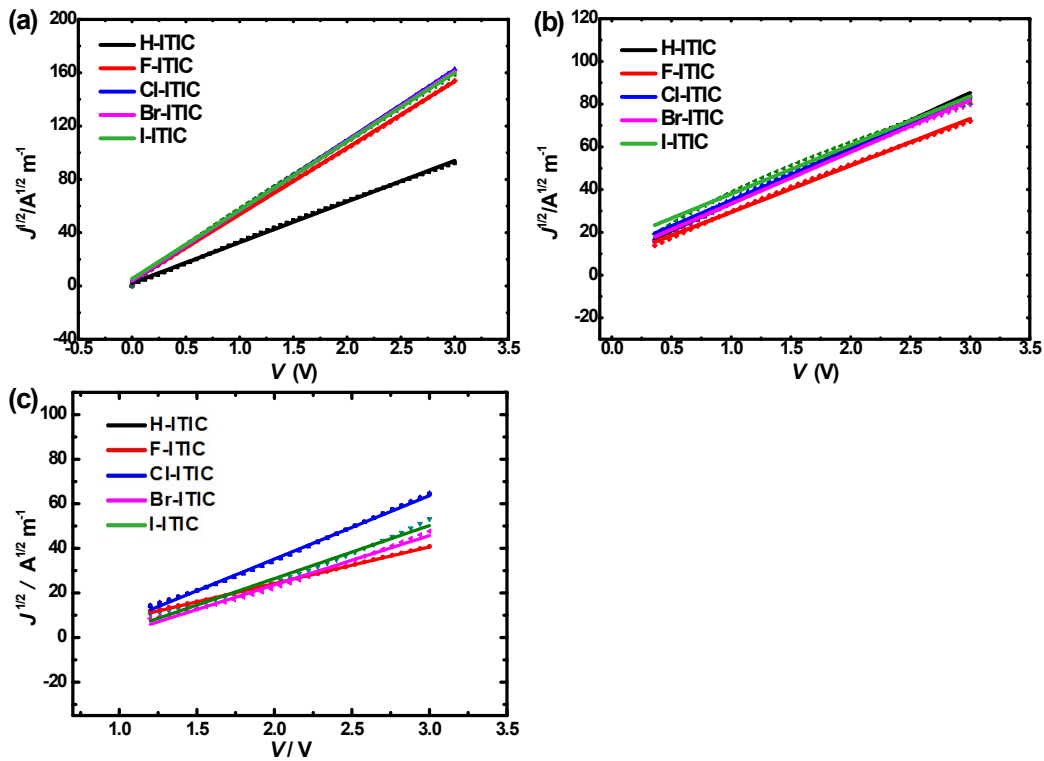


Fig. S8 J - V characteristics of the pure materials by SCLC measurement under dark for (a) hole-only devices and (b) electron-only devices of PTPDBDT:X-ITIC blended thin films. (c) Electron-only devices of pure X-ITIC. ITO/PEDOT:PSS/thin film/ MoO_3 /Ag for hole-only devices. ITO/ZnO/thin film/Ca/Al for electron-only devices.

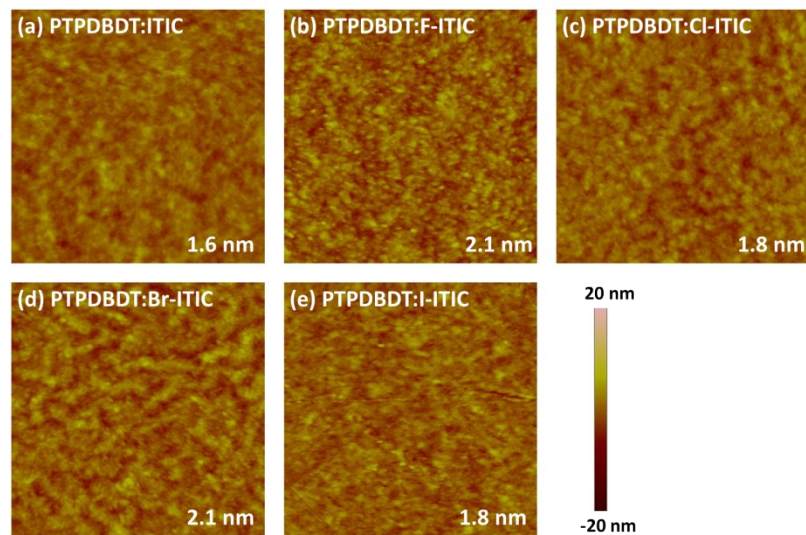
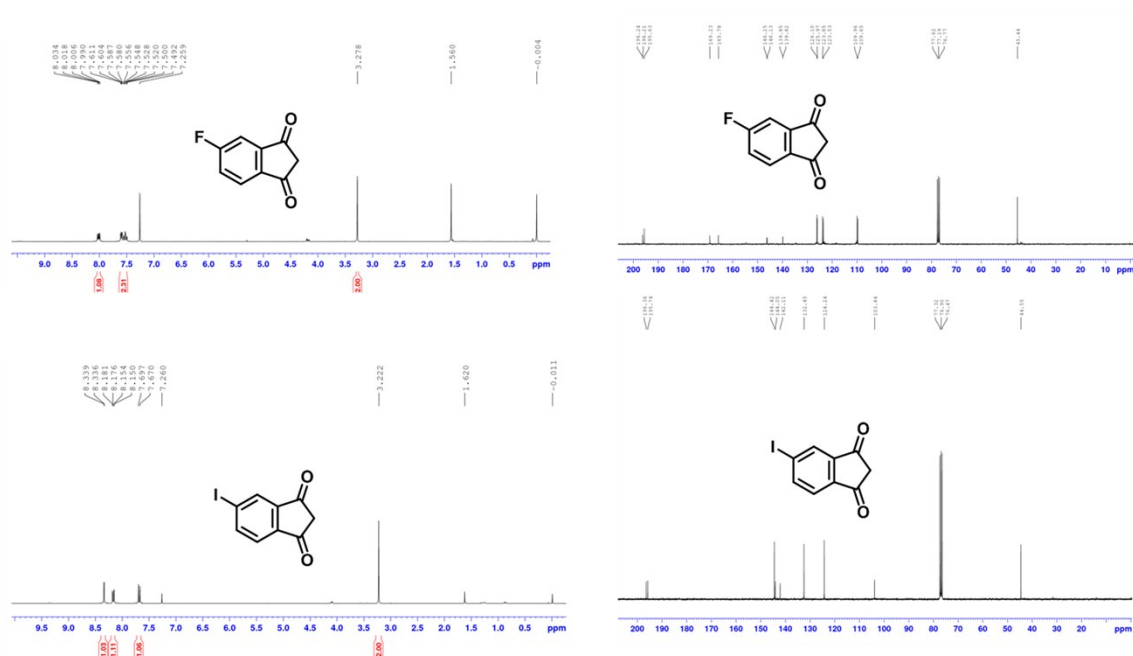


Fig. S9 AFM height images ($3 \times 3 \mu\text{m}^2$) of the optimized blended thin films. RMS roughness is also included.

6. NMR and MALDI-TOF



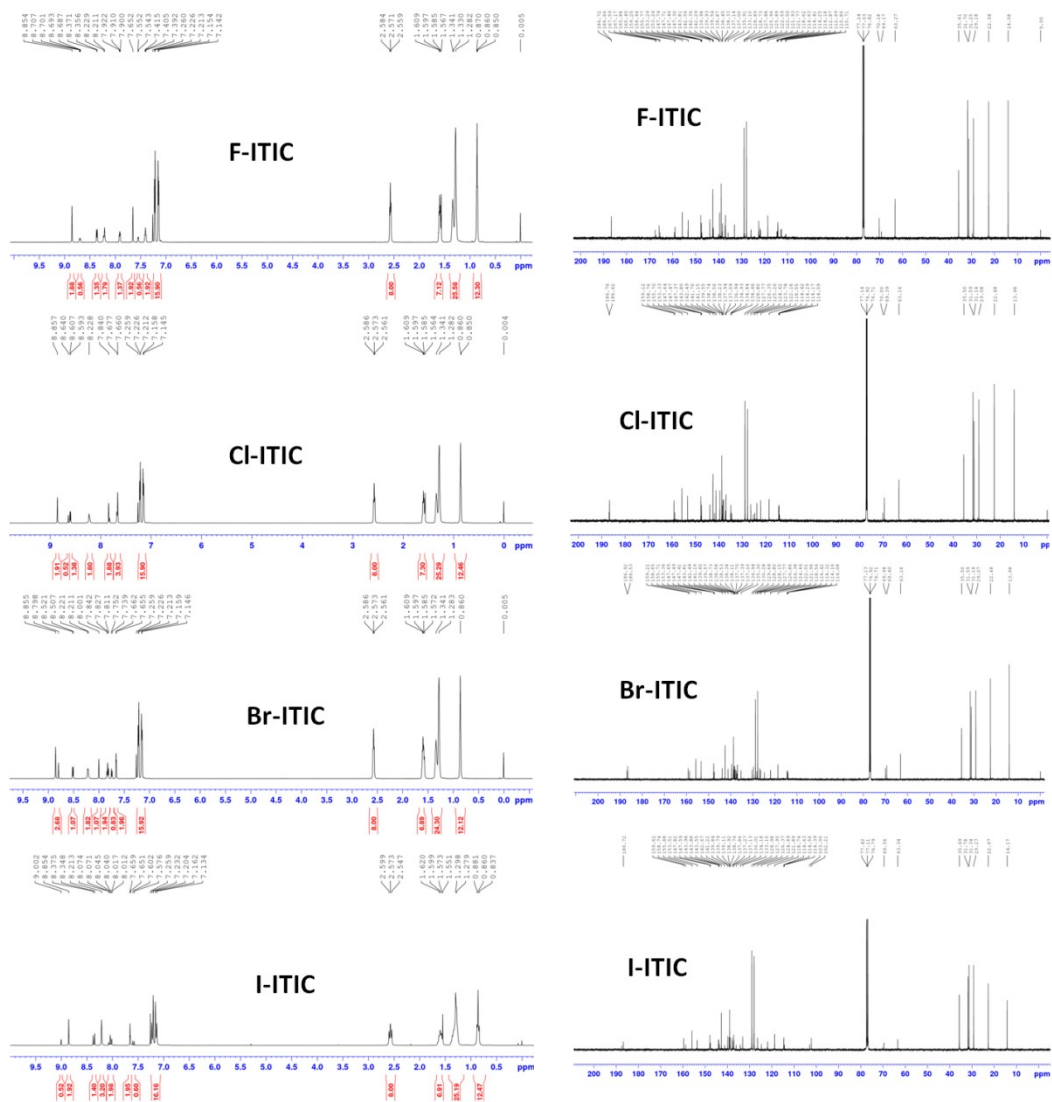


Fig. S12 $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ of halogenated ITIC.

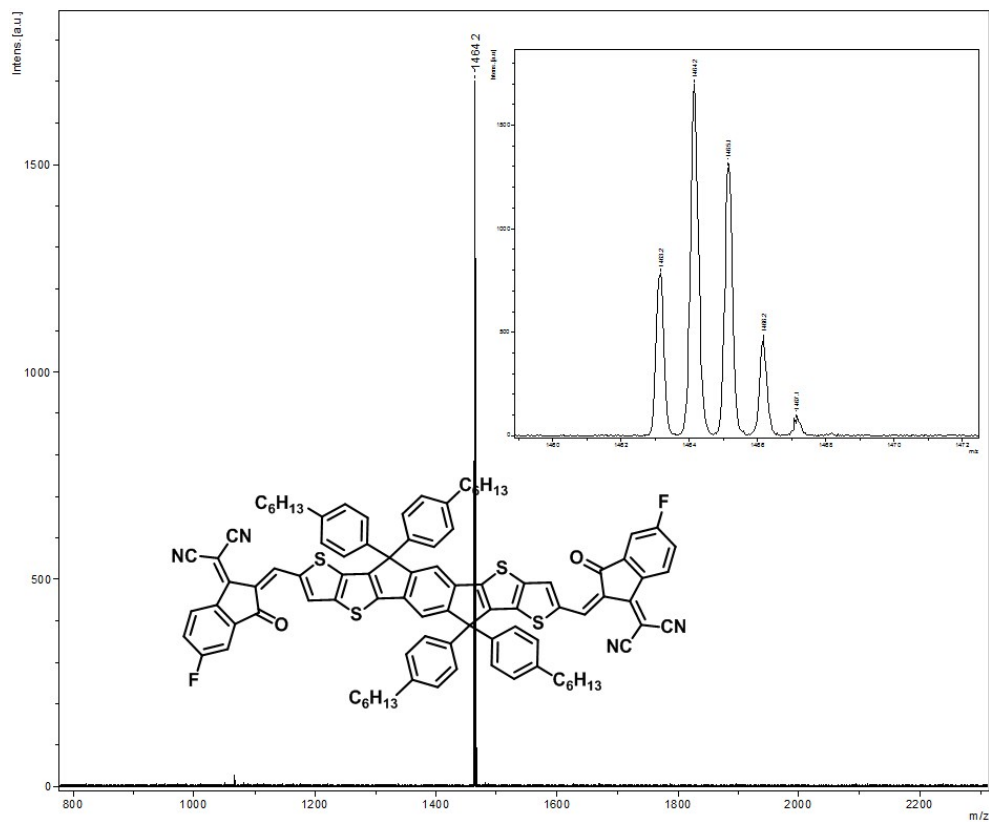


Fig. S13 MALDI-TOF spectra of F-ITIC.

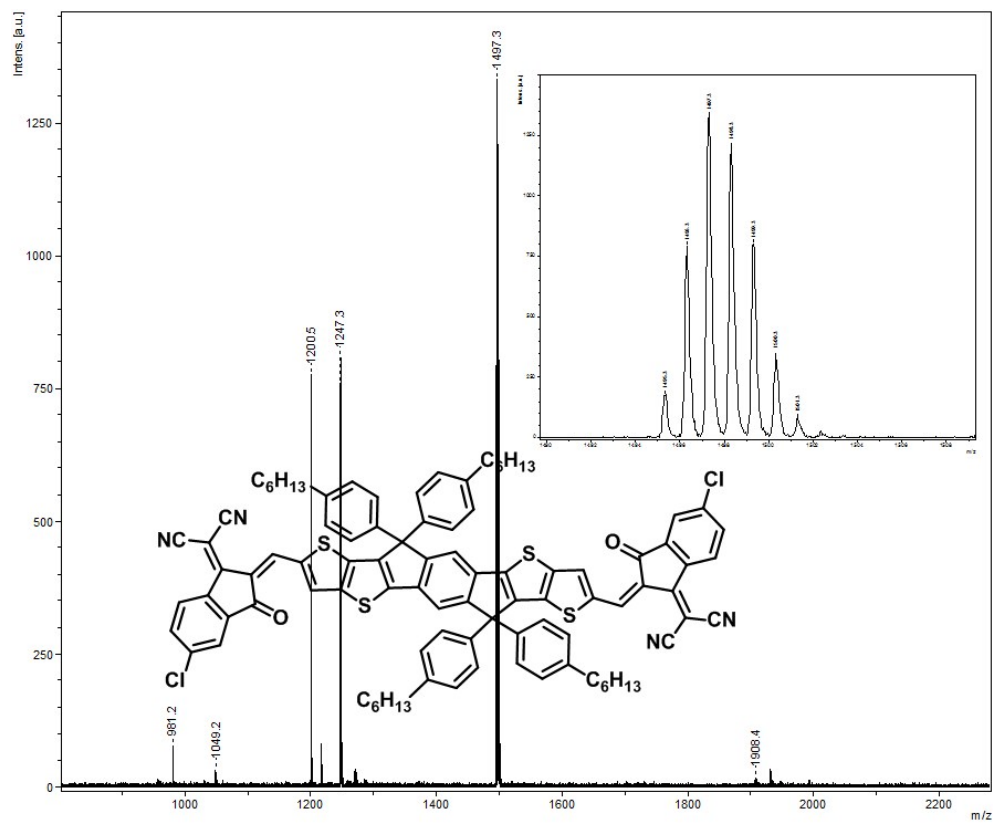


Fig. S14 MALDI-TOF spectra of Cl-ITIC.

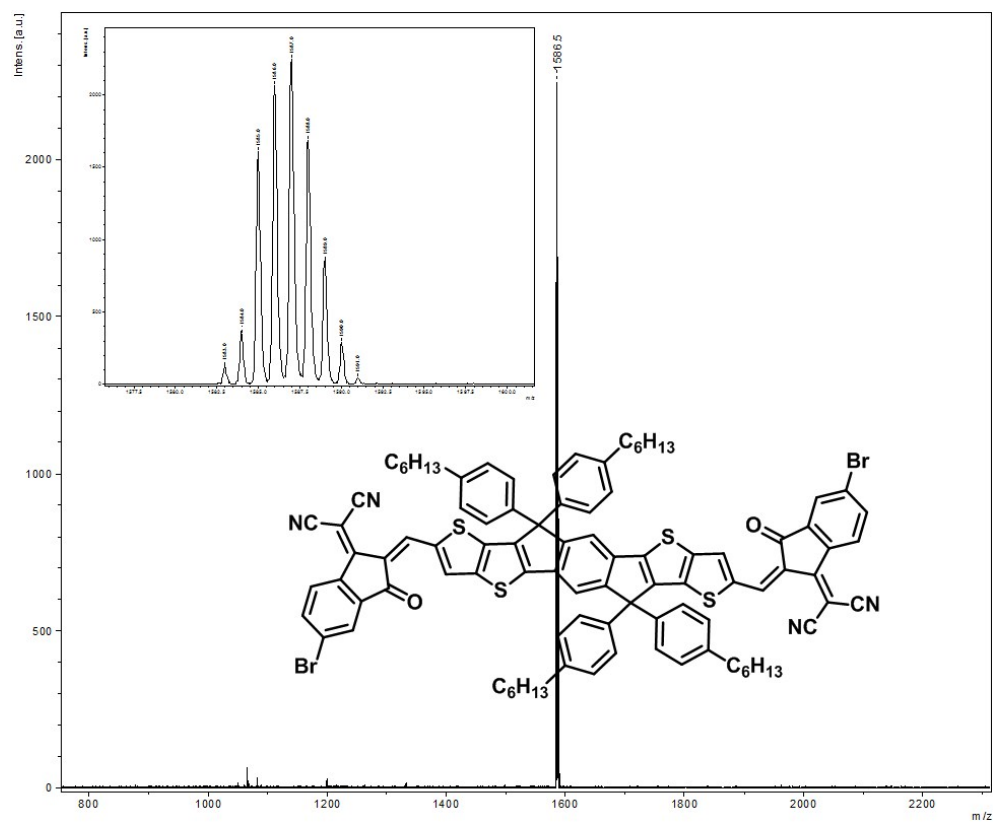


Fig. S15 MALDI-TOF spectra of Br-ITIC.

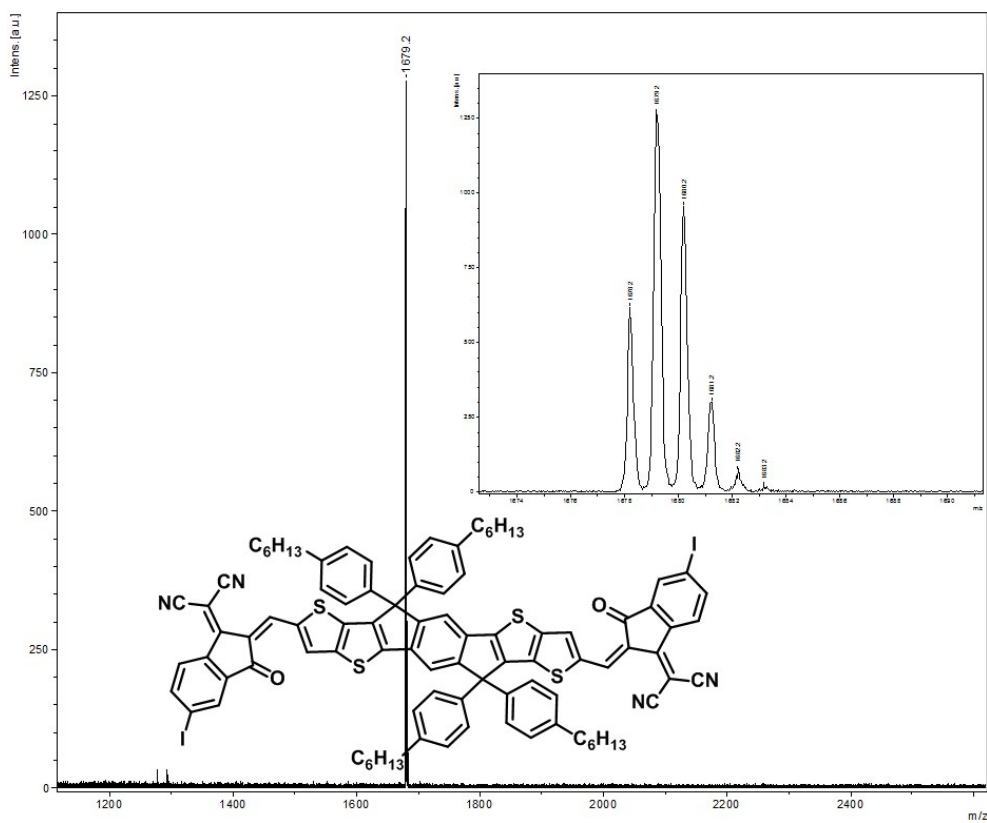


Fig. S16 MALDI-TOF spectra of I-ITIC.

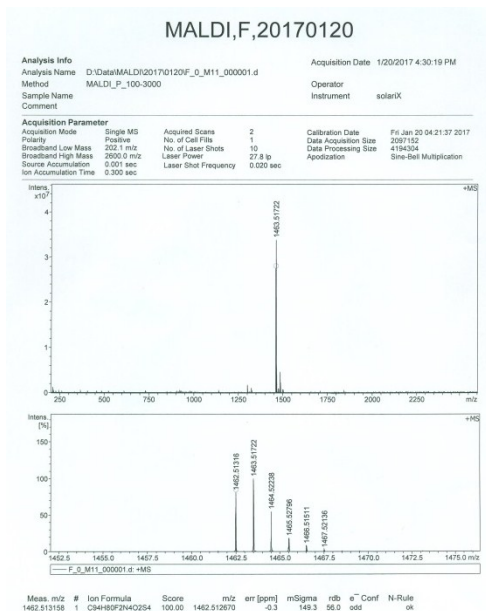


Fig. S17 High resolution MALDI-TOF spectra of F-ITIC.

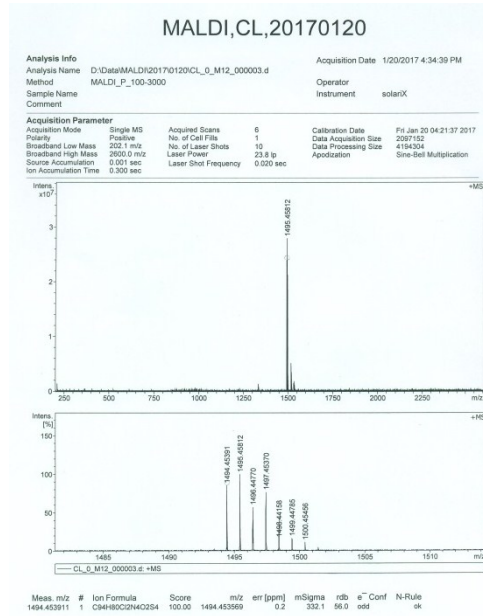


Fig. S18 High resolution MALDI-TOF spectra of Cl-ITIC.

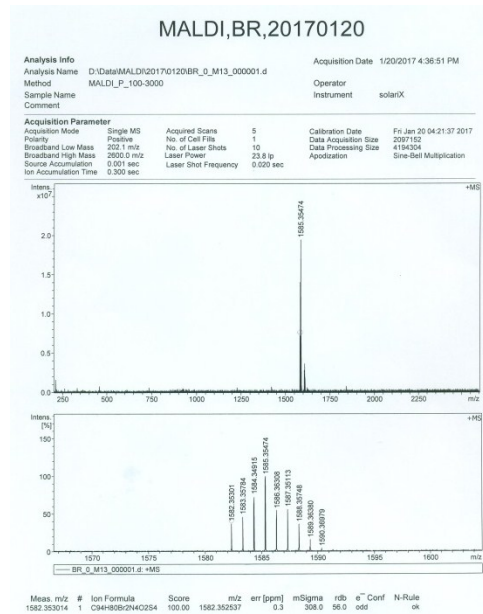


Fig. S19 High resolution MALDI-TOF spectra of Br-ITIC.

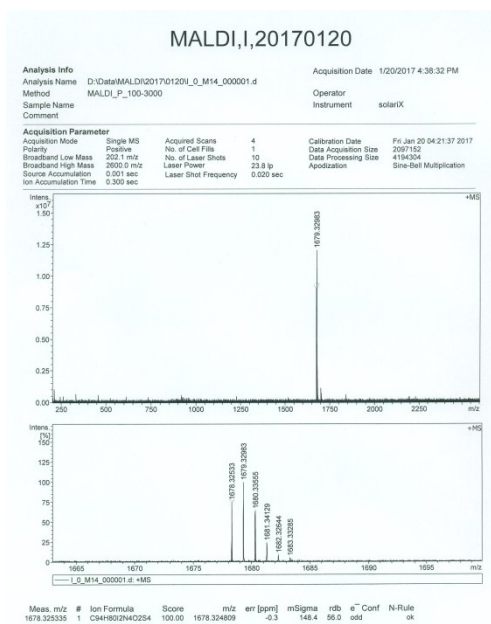


Fig. S20 High resolution MALDI-TOF spectra of I-ITIC.

7. References

- (1) Shi, Q.; Zhang, S.; Zhang, J.; Oswald, V. F.; Amassian, A.; Marder, S. R.; Blakey, S. B. *J. Am. Chem. Soc.* **2016**, *138*, 3946-3949.