Supplementary information

An asymmetrical A-DAD-A-Type Acceptor Simultaneously Enhances Voltage and Current for Efficient Organic Solar Cells

Hanjian Lai, [‡,a, b] Hui Chen, [‡,a] Yulin Zhu, [a] Lin Chen, [a] Hsin-Hsiang Huang, [d] and Feng He*[a, c]

[a] Shenzhen Grubbs Institute and Department of Chemistry, Southern University of Science and Technology, Shenzhen 518055, China

[b] School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin, 150001, China

[c] Guangdong Provincial Key Laboratory of Catalysis, Southern University of Science and Technology, Shenzhen 518055, China

[d] Department of Materials Science and Engineering, and Center for Condensed Matter Sciences, National Taiwan University, Taipei 10617, Taiwan

‡ These authors contributed equally

* E-mail: hef@sustech.edu.cn (F.H.)

GENERAL METHODS

Instruments. ^{1}H NMR spectra were recorded on Bruker AV 400 MHz spectrometer in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Preparative gel permeation chromatography purification was performed with a JAI LC-9104 recycling preparative high performance liquid chromatography, and the eluent was chloroform. Cyclic voltammetry (CV) measurements were performed on a CHI 660E potentiostat/galvanostat (Shanghai Chenhua Instrumental Co., Ltd. China) to determine the HOMO and LUMO levels of the polymers, in an acetonitrile solution of 0.1 mol·L^{-1} tetrabutylammonium hexafluorophosphate ([*n*-Bu_4N] $^{+}$ [PF_6] $^{-}$) at a potential scan rate of 100 mV s^{-1} with an Ag/Ag^{+} reference electrode and a platinum wire counter electrode under a argon atmosphere. Solution and film UV-Vis absorption spectra absorption spectra were recorded on a Shimadzu UV3600 spectrometer. Thermogravimetric analysis (TGA) plots were measured with a Discovery series instrument under a nitrogen atmosphere at heating and cooling rates of 10 ^{o}C min^{-1}. Different scanning calorimetry (DSC) measurements were performed on a Discovery series thermal analyzer at a scanning rate of 10 ^{o}C min^{-1} in N_2. Atom force microscopy (AFM) images were taken on a NanoScopeIIIa controller (Veeco Metrology Group/Digital Instruments, Sant a Barbara, CA), using built-in software (version V6.13R1) to capture images. Transmission electron microscopy (TEM) images were acquired using a HITACHI H-7650 electron microscope operating at an acceleration voltage of 100 kV.

Fabrication and Characterization of OSCs. The fabrication and measurement methods of OSCs devices are as follows: After a thorough cleaning of the indium-tin oxide (ITO)-coated glass substrate with detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 15 minutes each and subsequently dried in an oven at 80 °C. The ITO glass substrates were treated with UV-ozone for 15 minutes and then the sol-gel-derived ZnO films were spin-coated onto the ITO substrates followed by thermal treatment at 200 °C for 30 min. The total concentration of the **PBDB-TF**: **BDIC-γCl-2F** (1:1.2) blend solution for spin-coating was 11 mg mL^{-1} with chloroform as the processing solvent. The additive, chloronaphthalene (CN) (volume content：0.5%) was added into solution 30 minutes before the spin-coating process. The total concentration of the **PBDB-TF**: **ITIC-γCl-2F** (1:1.2) blend solution for spin-coating was 7 mg mL^{-1} with chlorobenzene as the processing solvent. The additive, 1, 8-diiodooctane (DIO) (volume content：0.5%) was added into solution 30 minutes before the spin-coating process. The blend was stirred at room temperature in the glove box overnight. The active layer was spin-coating at 3000 rpm for 30 s to get neat film. A 10 nm MoO_3 layer and a 100 nm Ag layer were subsequently evaporated through a shadow mask to define the active area of the devices. The integrated device structure is ITO/ZnO/**PBDB-TF**: Acceptors/MoO_3/Ag. A solar simulator (Enlitech.Inc) with an AM 1.5G filter was used as a light source to produce an intensity of 100 mW cm^{-2} for the illumination of

the photovoltaic cells. The light intensity was calibrated by a 2 cm × 2 cm calibrated silicon solar cell with KG-3 visible color filter. A shadow mask with a single aperture (4.15 mm^2) was placed onto the devices in order to accurately define the photoactive area.

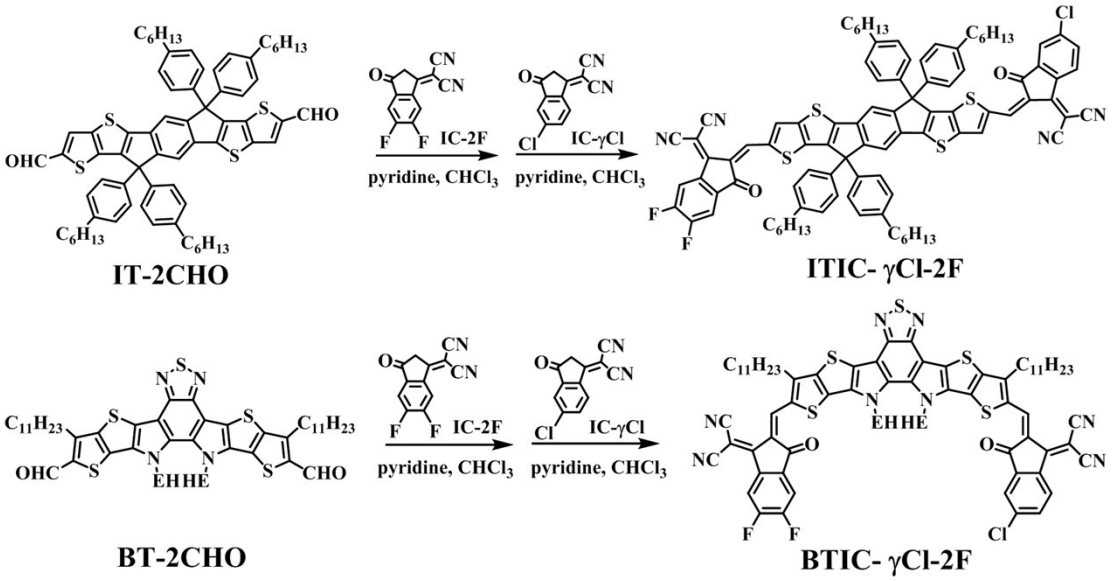
Steady-state current-voltage (*J*-*V*) curves were measured by a Keithley 2400 source-measurement unit under AM 1.5 G spectrum from a solar simulator (Enlitech.Inc) calibrated by a silicon reference cell (Hamamatsu S1133 color, with KG-5 visible fiith). The relationship of *J*sc to the light intensity were measured by steady-state current-voltage measurement, the light intensity was modulated by neutral density filters (NDF) with different values of optical density (OD). The external quantum efficiency (EQE) was measured by a solar cells–photodetector responsibility measurement system (Enlitech.Inc).

Electron-only and hole-only devices fabrication. Electron-only devices were fabricated with the device structure of ITO/ZnO/PBDB-TF: Acceptors/Ca/Al, while the hole-only devices were fabricated with the device structure of ITO/PEDOT: PSS/blends/MoO_3/Ag. The mobilities were determined by fitting the dark current to the model of a single carrier SCLC, [1,2] which is described by the equation:

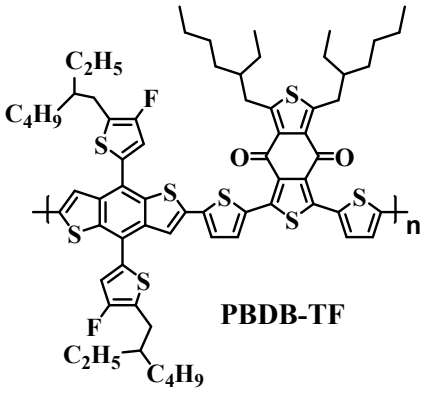
$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu_h\frac{V^2}{d^3}$$

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

EXPERIMENTAL SECTION



Scheme S1. The synthetic routes of **ITIC-γCl-2F** and **BTIC-γCl-2F**.



Scheme S2. The structure of polymer donor PBDB-TF.

Materials: Compound **IT-2HO**, **BT-2CHO**, **IC-2F** and **IC-γCl** were synthesized according previously reported approaches.[3-5] All the other chemicals were purchased as reagent grade from J&K, Energy, Macklin, and Sigma-Aldrich, and used without

further purification. All solvents for reactions were freshly distilled immediately prior to use.

Compound ITIC-γCl-2F: A mixture of **IT-2CHO** (200 mg, 0.186 mmol), **IC-2F** (42.8 mg, 0.186 mmol) in chloroform/pyridine (30 ml/0.5 ml) was reacted 6 hours under Argon at 50 °C, then the **IC-γCl** (42.5mg, 0.186mmol) was added for further 6 hours. The reaction mixture was then cooled to room temperature and then extracted with chloroform. The organic layer was washed with brine and dried over $MgSO_4$. The crude product was purified by flash column chromatography with chloroform as eluent and further purified with cycling preparative HPLC to get the product (103 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.85-8.87 (d, 2H), 8.60-8.63 (d, 1H), 8.51-8.55 (dd, 1H), 8.23 (s, 2H), 7.85-7.86 (s, 1H), 7.65-7.71 (m, 4H), 7.13-7.22 (m, 16H), 2.55-2.59(t, 8H), 1.57-1.63(m, 8H), 1.26-1.37(m, 24H), 0.84-0.87(m, 12H). MALDI-TOF-MS calcd for C94H79ClF2N4O2S4 (M+): 1496.474, found: 1497.561.

Compound BTIC-γCl-2F: A mixture of **BT-2CHO** (200 mg, 0.194 mmol), **IC-2F** (44.6 mg, 0.194 mmol) in chloroform/pyridine (30 ml/0.5 ml) was reacted 6 hours under Argon at 50 °C, then the **IC-γCl** (44.3mg, 0.194mmol) was added for further 6 hours. The reaction mixture was then cooled to room temperature and then extracted with chloroform. The organic layer was washed with brine and dried over $MgSO_4$. The crude product was purified by flash column chromatography with chloroform as eluent and further purified with cycling preparative HPLC to get the product (110 mg, 39.1%). ^{1}H NMR (400 MHz, $CDCl_3$) δ : 9.13-9.15 (d, 2H), 8.61-8.63 (d, 1H), 8.52-

8.56 (dd, 1H), 7.87-7.88 (s, 1H), 7.67-7.71(m, 2H), 4.78-4.80(d, 4H), 3.19-3.23(t, 4H), 2.12(s, 2H), 1.85-1.89(m, 4H), 0.96-1.52(m, 48H), 0.86-0.88(m, 6H), 0.74-0.80(m, 6H), 0.65-0.69(m, 6H). MALDI-TOF-MS calcd for C82H87ClF2N8O2S5 (M+): 1448.521, found: 1450.199.

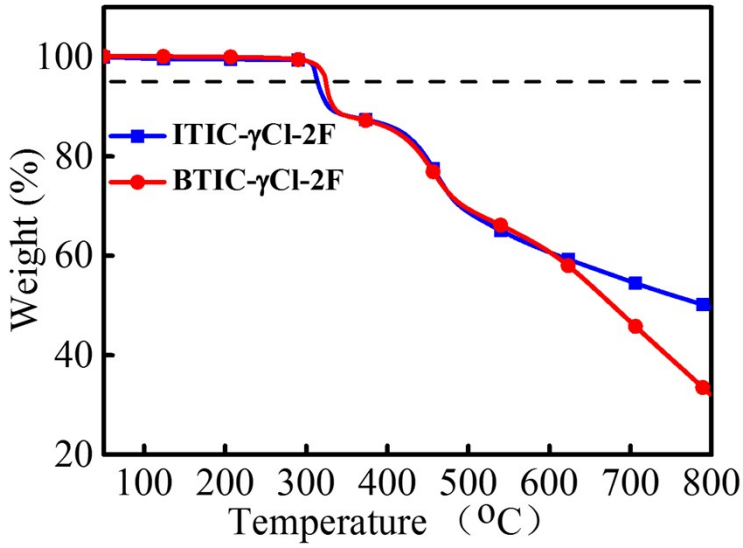


Figure S1. Thermogravimetric analysis (TGA) results of **ITIC-γCl-2F** and **BTIC-γCl-2F** with a heating rate of 10 °C min^{-1} under nitrogen purge.

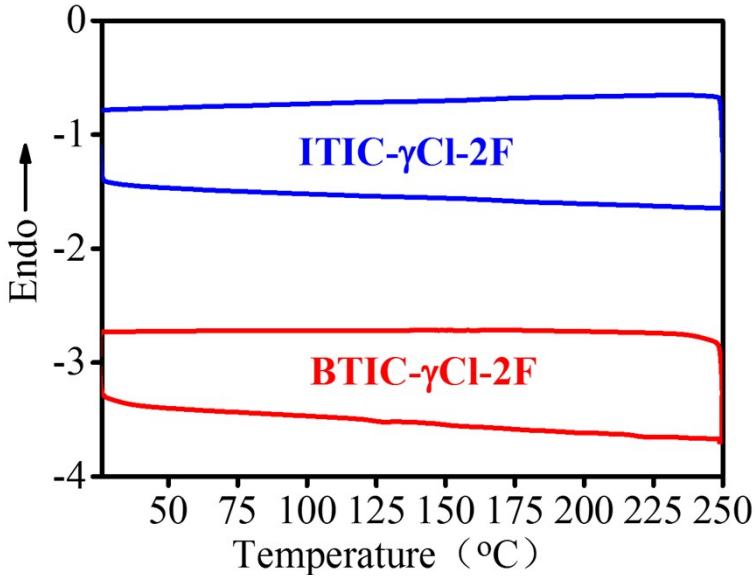


Figure S2. Differential scanning calorimetry (DSC) results of two molecules with heating and cooling rates of 10 °C min^{-1} under nitrogen purge.

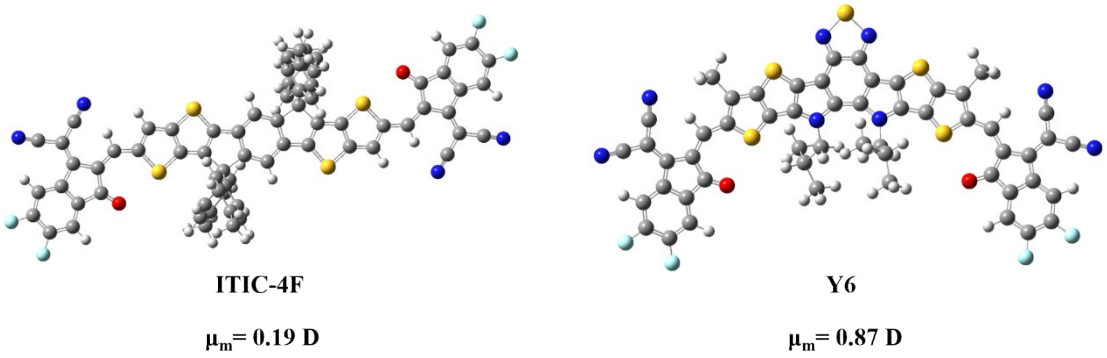


Figure S3. The dipole moments of ITIC-4F and Y6.

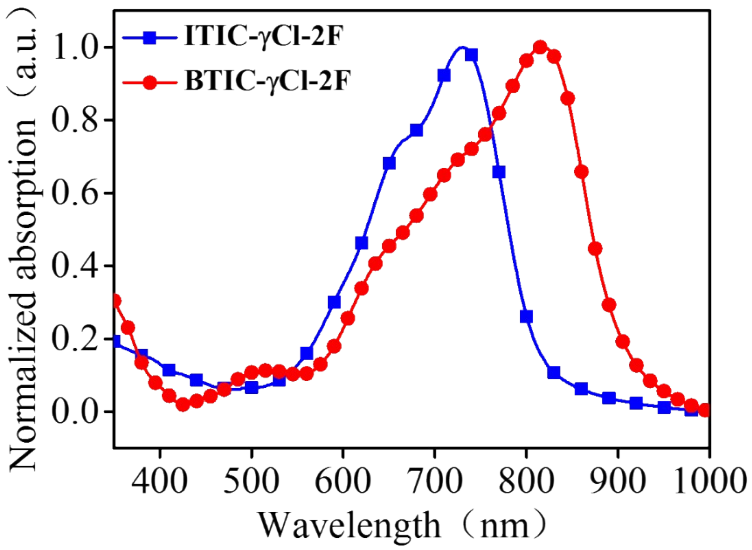


Figure S4. Normalized UV-vis absorption of two acceptors in films.

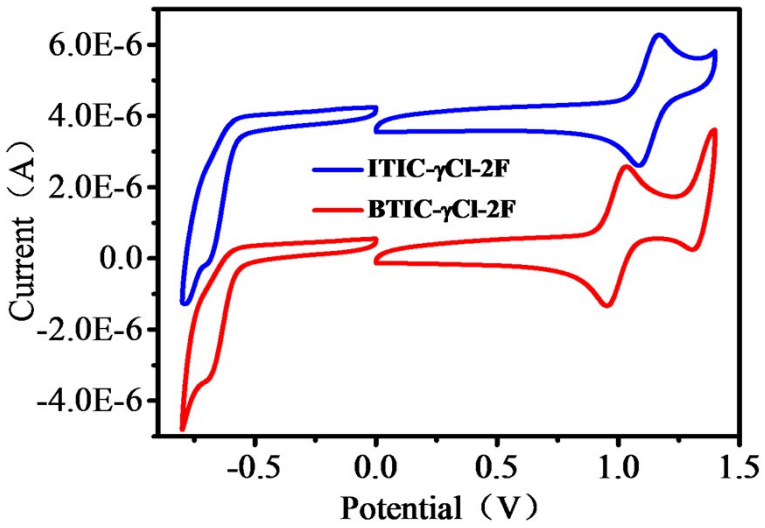


Figure S5. Cyclic voltammograms of two molecules in dichloromethane with (n-Bu)$_4$NPF$_6$ (0.1 M) as supporting electrolyte, Pt wire as counter electrode, and Ag/Ag$^+$ as reference electrode.

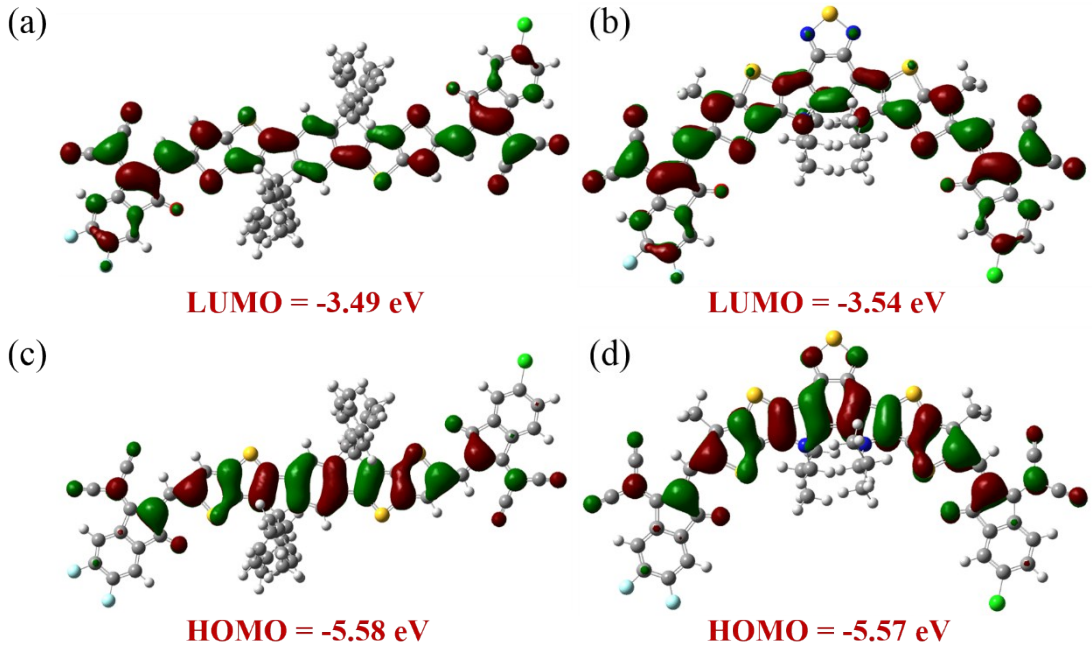


Figure S6. The density functional theory (DFT) calculation of molecules.

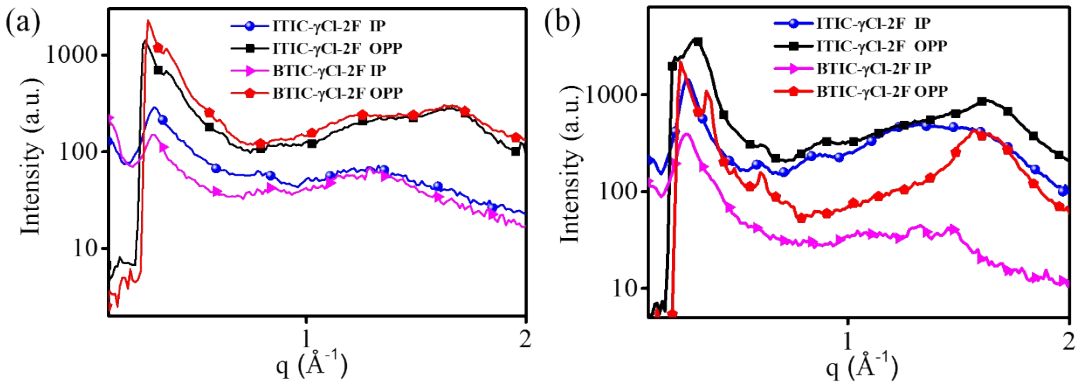


Figure S7. GIWAXS data of two acceptors-based neat films and blend films. (a) The intensity profiles of in-plane (IP) and out of plane (OPP) of four neat films, (b) The intensity profiles of IP and OPP of blend films.

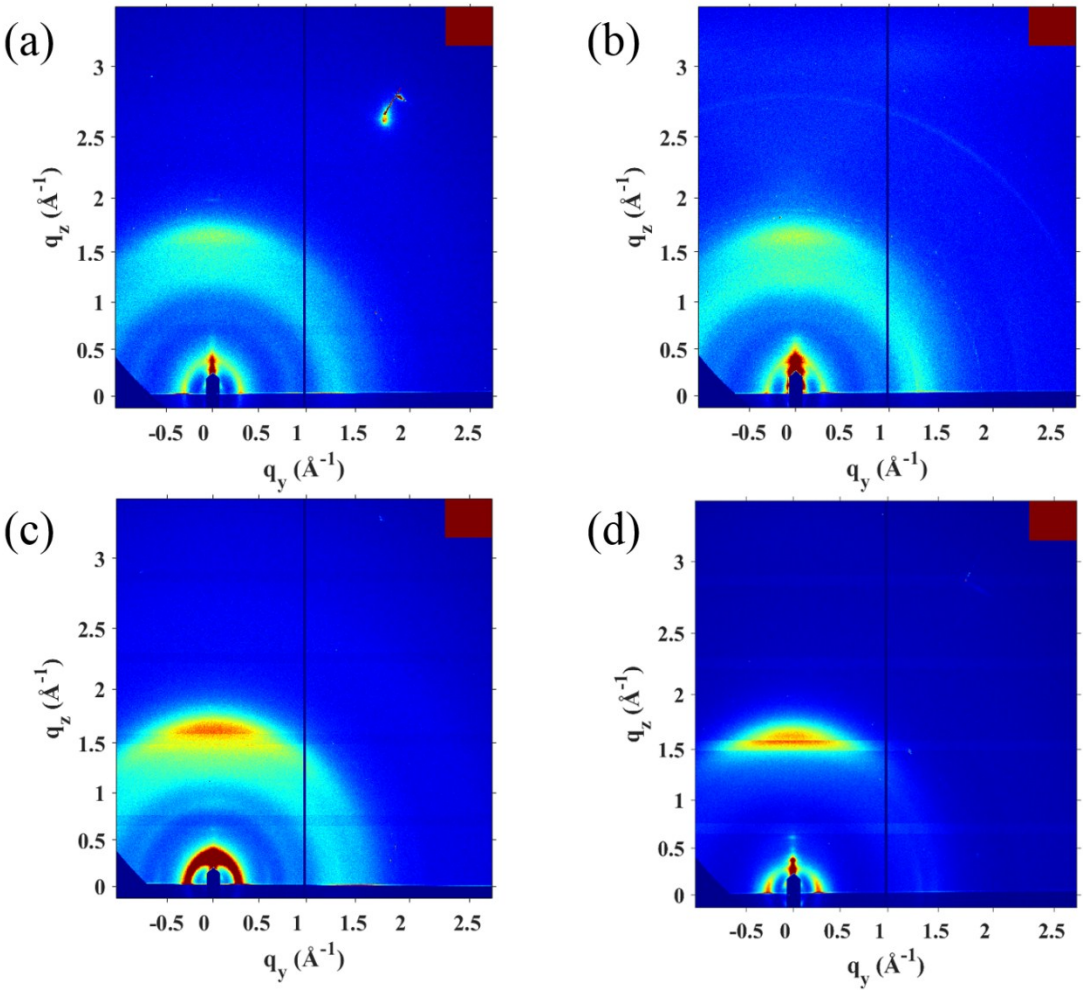


Figure S8. GIWAXS images of two acceptors-based neat films and blend films. (a) **ITIC-γCl-2F** neat film, (b) **BTIC-γCl-2F** neat film, (c) **ITIC-γCl-2F** blend film, (b) **BTIC-γCl-2F** blend film.

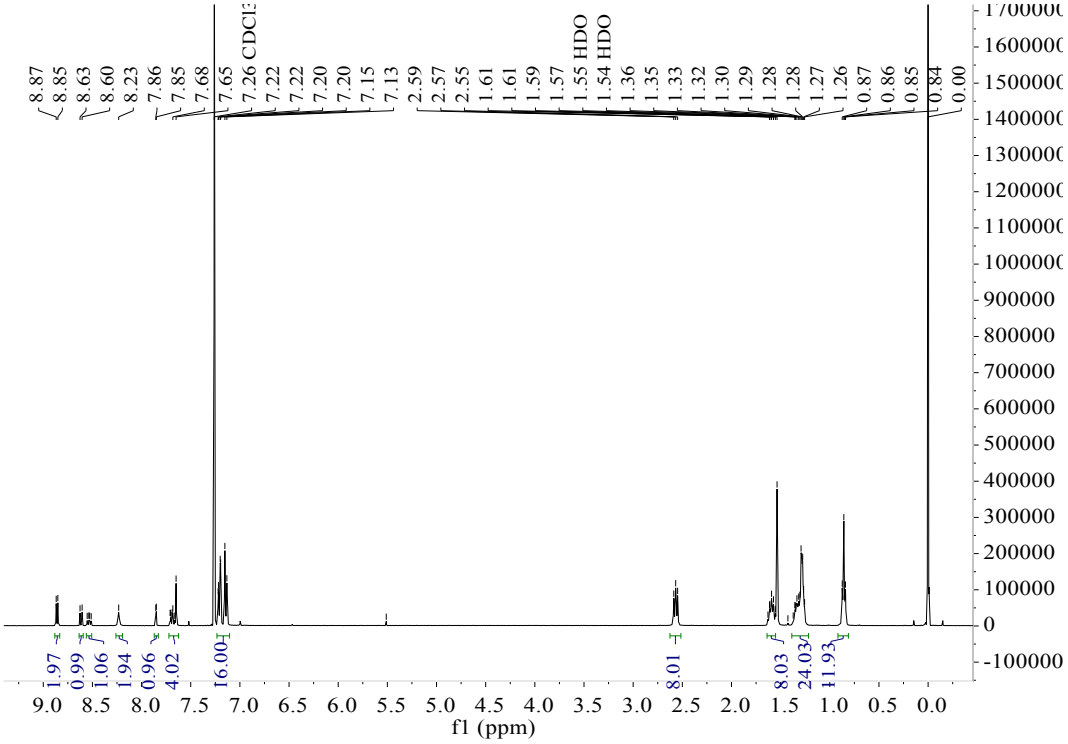


Figure S9. ^{1}H NMR of **ITIC-γCl-2F** in $CDCl_3$.

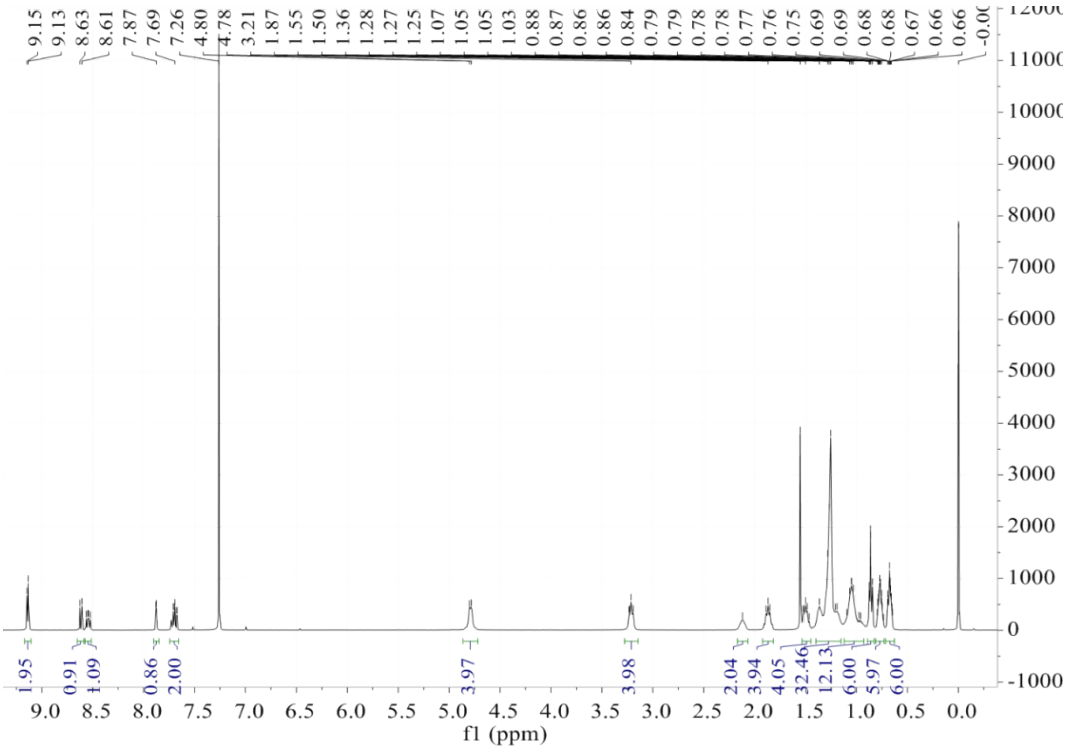


Figure S10. ^{1}H NMR of **BTIC-γCl-2F** in $CDCl_3$.

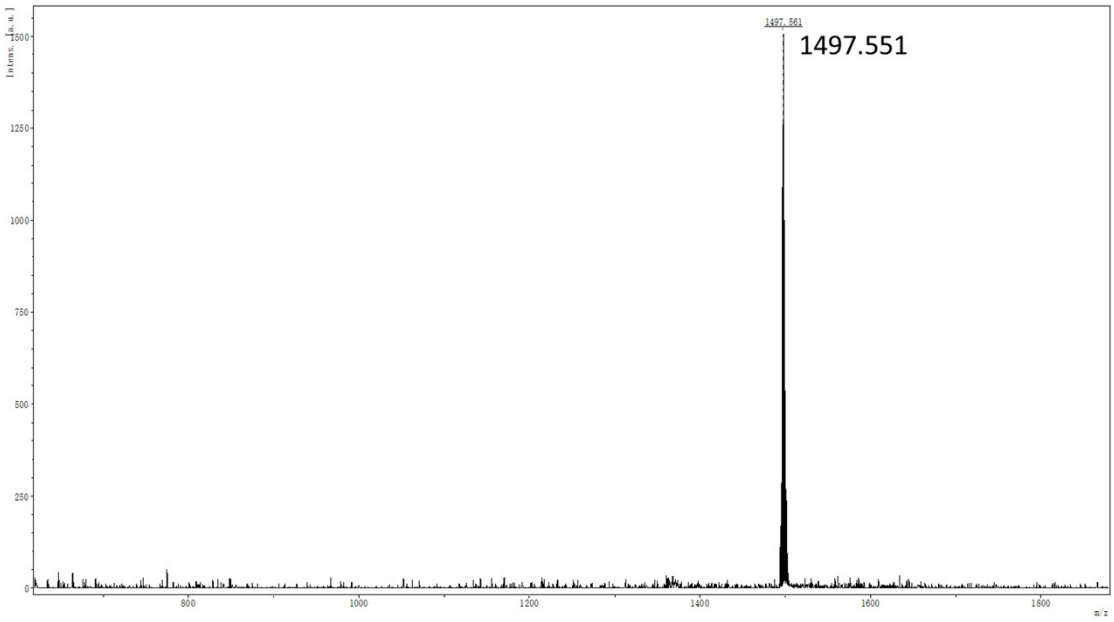


Figure S11. The MALDI-TOF-MS spectrum of **ITIC-γCl-2F**.

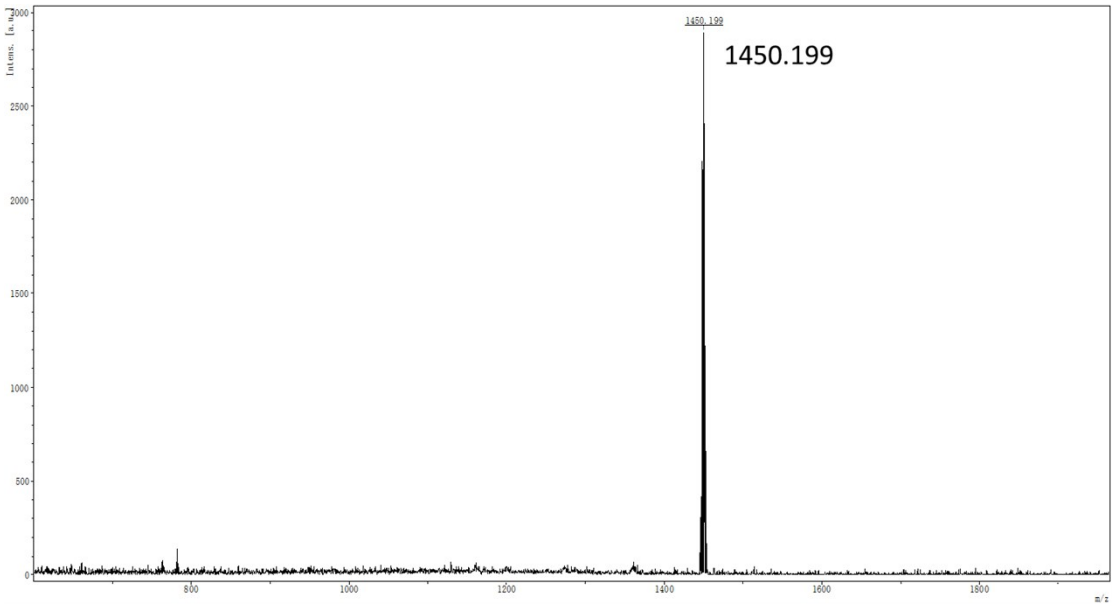


Figure S12. The MALDI-TOF-MS spectrum of **BTIC-γCl-2F**.

References

1. Mihailetchi, V. D., Wildeman, J., Blom, P. W. (2005). Space-Charge Limited Photocurrent. Phys. Rev. Lett. *94*, 126602-126605.
2. Davids, P. S., Campbell, I. H., Smith, D. L. (1997). Device Model for Single Carrier Organic Diodes. J. Appl. Phys. *82*, 6319-6325.
3. Lin, Y., Wang, J., Zhang, Z. G., Bai, H., Li, Y., Zhu, D., Zhan, X. (2015). An Electron Acceptor Challenging Fullerenes for Efficient Polymer Solar Cells. Adv. Mater. *27*, 1170-1174.
4. Yao, H., Cui, Y., Yu, R., Gao, B., Zhang, H., Hou, J. (2017). Design, Synthesis, and Photovoltaic Characterization of a Small Molecular Acceptor with an Ultra-Narrow Band Gap. Angew. Chem. Int. Ed. *56*, 3045-3049.
5. Li, Y., Lin, J.-D., Che, X., Qu, Y., Liu, F., Liao, L. S., Forrest, S. R. (2017). High Efficiency Near-Infrared and Semitransparent Non-Fullerene Acceptor Organic Photovoltaic Cells. J. Am. Chem. Soc. *139*, 17114-17119.