

## Supporting information

### **Suppressing Electrostatic Potential Fluctuations to Achieve High-efficiency Organic Photovoltaic cells for Laser Wireless Energy Transfer**

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## **Materials**

Compound 1-2, PBQx-TCI, and NDI-Ph were purchased from Solarmer Materials Inc. PEDOT:PSS, Clevios™ P VP AI 4083, was purchased from Heraeus. The other reagents and solvents were commercially available and purchased from J&K chemicals, Innochem, Sinopharm Chemical Reagent Co, Ltd and Bei Jing TongGuang Fine Chemicals Company, and these reagents and solvents were used without further purification.

## **Materials characterization**

<sup>1</sup>H-, <sup>13</sup>C-NMR spectra were recorded on Bruker Fourier 300 or Avance III 400 HD spectrometer. Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS) was measured with a Bruker Reflex II-TOF spectrometer.

Ultraviolet-visible (UV-Vis) absorption spectra in solution and in solid films were measured using Hitachi UH5300 UV-vis spectrophotometer. The solid film samples were spin-coated with chloroform solution of the acceptors (AITO-Br, AITO-2F, and ITO-2F, 15mg/ml) or toluene solution of donor (PBQx-TCI, 7.5 mg/mL) on the quartz plates. The film thickness was obtained via a surface profilometer (Dektak XT, Bruker).

The molecular energy levels were measured by CHI650D electrochemical workstation with three-electrode cell in anhydrous acetonitrile solvents solution of Bu<sub>4</sub>NPF<sub>6</sub> (0.1 M) with scanning rate of 0.05 V·s<sup>-1</sup> under argon atmosphere. Ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) was used as an external standard in the measurement.

## **Morphology characterization**

### **In-situ UV-vis absorption spectra measurement**

In-situ UV-vis absorption spectra were measured by a home-made system consist a high sensitivity CCD spectrometer (QE Pro, Ocean Insight), a tungsten halogen light source (HL-2000FHSA, Ocean Insight), a spin coater (KW-4A), and a heating panel (C-MAG HS7, IKA).

### **AFM measurement**

Atomic force microscope (AFM) images were recorded on Bruker Nanoscope V AFM microscope by tapping mode.

### **GIWAXS measurement**

The GIWAXS data were obtained at in-house X-ray scattering beamline Xeuss 3.0 of National

Engineering Research Center for Colloidal Materials, Shandong University. The samples were prepared by spin-coating onto Si substrates.

### **Femtosecond transient absorption (TA) spectra**

Femtosecond transient absorption (TA) spectra were measured on an Ultrafast Helios pump-probe system in collaboration with a regenerative amplified laser system from Coherent. The pulses with a repetition rate of 1 kHz, a length of 100 fs, and an energy of 7 mJ/pulse, were generated by a Ti:sapphire amplifier (Astrella, Coherent). Then the pulses were separated into two parts by a beam splitter. One part was coupled into an optical parametric amplifier (TOPAS, Coherent) to generate the pump pulses at 380 and 720 nm. The other part was focused onto a sapphire plate and a YAG plate to generate white light supercontinuum as the probe beams with spectra covering 420-800 nm and 750-1600 nm, respectively. The time delay between pump and probe was controlled by a motorized optical delay line with a maximum delay time of 8 ns. The sample films were spin-coated onto the 1 mm-thick quartz plates and encapsulated by epoxy resin in nitrogen-filled glove box to resist water and oxygen in the air. The pump pulse is chopped by a mechanical chopper with 500 Hz and then focused on to the mounted sample with probe beams. The probe beam was collimated and focused into a fiber-coupled multichannel spectrometer with CCD sensor. The energy of pump pulse was measured and calibrated by a power meter (PM400, Thorlabs).

### **Device fabrication**

The OPV devices were fabricated with a structure of ITO/PEDOT: PSS/active layer/NDI-Ph/Ag. ITO glass ( $6\Omega\text{ cm}^{-2}$ ) was purchased from South China Xiang's Science & Technical Company Limited. PEDOT: PSS (4083) was purchased from the Clevios<sup>TM</sup>. PEDOT: PSS was diluted with the same volume of water. NDI-Ph was purchased from Solarmer Material Inc. The ITO glasses were treated with ultraviolet-ozone for 10 min. Afterward, about 10 nm PEDOT: PSS was spin-coated on the ITO glass at 3000 r.p.m. for 30 s. Subsequently, the ITO glasses were treated by thermal annealing for 15 min at 150°C. Then, the substrates were transferred to a glove box. PBQx-TCl: AITO-Br, PBQx-TCl: AITO-2F, and PBQx-TCl: ITO-2F with a weight ratio of 1:1.2 were dissolved in toluene at a polymer concentration of 7 mg mL<sup>-1</sup>. The active layer solutions need to be stirred at 90°C until completely dissolved. 0.5% 1,8-diiodooctane (DIO) (v/v) was added to the solutions 30 min before the spin-coating process. The active layer solutions were spin-coated onto the PEDOT: PSS layers at 5000 r.p.m. for 30 s. The best active layer thickness is about 110 nm.

Then, the films were treated with thermal annealing at 100°C for 10 min. NDI-Ph was dissolved in methanol at a concentration of 1.5 mg mL<sup>-1</sup> at 50°C and then spin-coated on the top of the active layers at 3000 rpm for 30 s with a thickness about 15 nm. Finally, 100 nm Ag was deposited under a high vacuum ( $\sim 9 \times 10^{-4}$  Pa). The SCLC devices have same active layers while containing different electrodes and charge transfer layers with structures of ITO/ZnO/active layers/Al for the electron-only devices. The photovoltaic device has an area of 0.09 cm<sup>2</sup> and a mask of 0.0617 cm<sup>2</sup>.

### **Device characterization and measurement**

The testing conditions are under a nitrogen atmosphere at 25 °C, with an oxygen content of less than 200 ppm and a water content of less than 1 ppm.  $J$ - $V$  measurements were performed using solar simulator (SS-F5-3A, Enli Technology Co. Ltd.) with AM 1.5G spectra (100 mW cm<sup>-2</sup>). Exciton dissociation was also determined by measuring  $J_{ph}$ - $V_{eff}$  curve.  $J_{ph}$  is defined as  $J_{ph} = J_L - J_D$ , where  $J_L$  and  $J_D$  stand for the current density under illumination and in dark, respectively. The  $V_{eff}$  is defined as  $V_{eff} = V_0 - V$ , where  $V_0$  is voltage when the  $J_{ph}$  is zero,  $V$  is the applied voltage. The  $J_{sat}$  is the saturation photocurrent density. The exciton dissociation probability ( $P_{diss}$ ) is calculated from the equation  $P_{diss} = J_{ph}/J_{sat}$ . The external quantum efficiency (EQE) tests were measured by using an integrated IPCE measurement system of QE-R3011 (Enli Technology Co. Ltd.). Highly sensitive EQE was obtained with an integrated system (PECT-600, Enli Technology Co. Ltd.).

### **TD-SCLC measurement**

The temperature-dependence electron mobility of neat acceptor films and blend films were measured by homo-made device including a continuous-flow cryostats (ST-100, Janis Research Company Inc.), a source meter (Keithley 2400) and testing software from Enli Technology Co. Ltd.

### **PL and TDPL measurement**

The PL spectra were recorded using a fiber-connected spectrometer (DU420A-OE, ANDOR). The pump power density was maintained at a constant value of 5 μJ cm<sup>-2</sup>. For the temperature depended PL measurements, the sample temperature was controlled by Model 325 Cryogenic Temperature Controller (Lake Shore Cryotronics, Inc.) in a Liquid nitrogen thermostatic chamber. All samples were fabricated on quartz substrates.

### **Impedance measurement and DoS calculation**

The  $\epsilon_r$  of the active layers can be determined by the following equation,

$$\varepsilon_r = \frac{C_g L}{\varepsilon_0 A}$$

where  $C_g$  is the geometry capacitance of the active layer measured at a reverse bias of -3 V in dark environment,  $L$  is the thickness of the active layer about 100 nm,  $A$  is the effective area of the OPV cells.

The DoS can be calculated from capacitance spectroscopy measured in dark environment. The frequency axis can be scaled to energy axis through the follows

$$E_\omega = kT \ln \left( \frac{2\nu_0}{\omega} \right)$$

where  $\omega$  is the angular frequency calculated by  $\omega = 2\pi f$ ,  $\nu_0$  is the attempt-to-escape frequency. The trap density at energy  $E_\omega$  can be acquired as

$$N(E_\omega) = -\frac{V_{bi} d C \omega}{q d d \omega k T}$$

$d$  is the thickness of the active layer and  $V_{bi}$  is the built-in voltage. Then the energy distribution can be described with Gaussian shape distribution

$$N(E) = \frac{N}{\sqrt{2\pi}\sigma} \exp \left[ -\frac{(E_t - E)^2}{2\sigma^2} \right]$$

Where  $N$  is the total density,  $E_t$  is the center of the DoS,  $\sigma$  is the disorder parameter.

### Theoretical calculation

The theoretical calculations, including electrostatic potential (ESP), electrostatic potential fluctuation (ESPF), and distribution of  $\pi$  electron were conducted using the Gaussian 09 program based on the density functional theory method using B3LYP/6-31G (d, p). The convergence criteria followed the default settings in Gaussian. In addition, Multiwfn software is used to assist in calculating ESPF and  $\pi$  electron distributions. The ESPFs were determined by calculating the average ESP of C atoms in different fragments. Taking IT-4F as an example, the carbon atom of fragments from left to right are as follows: the terminal benzene ring, four carbon atoms at the double bond, bithiophene, the central benzene ring plus two adjacent  $sp^3$  carbon atoms, bithiophene, four carbon atoms at the double bond, and the terminal benzene ring.

### Laser measurement

The wavelength selected for laser measurement is 660 nm, and the detailed laser spectrum is shown in Figure 5c. The laser light source was purchased from Beijing Blueprint Optoelectronic Technology Co., Ltd., and the laser intensity was measured

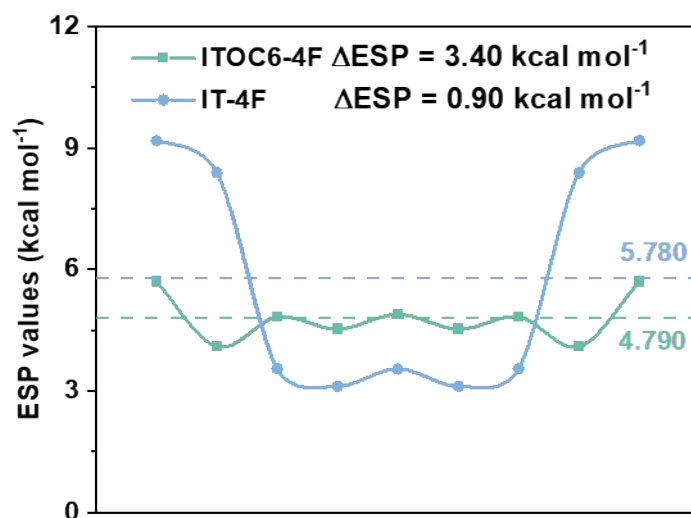
by a power meter (S142C, Thorlabs). The average value of 30 seconds of continuous testing is selected as the incident light power. For the  $J$ - $V$  measurements under laser lighting, the OPV cells are placed just below the laser source and their  $J$ - $V$  curves are harvested by using Keithley 2400. The area of OPV cells used in laser measurements is 0.0617 cm<sup>2</sup>. The EQE value at 660 nm represents the conversion efficiency from photon to electron at corresponding wavelength. The integrated current density ( $J_{cal}$ ) is calculated from the corresponding

EQE spectra based on the following equation:

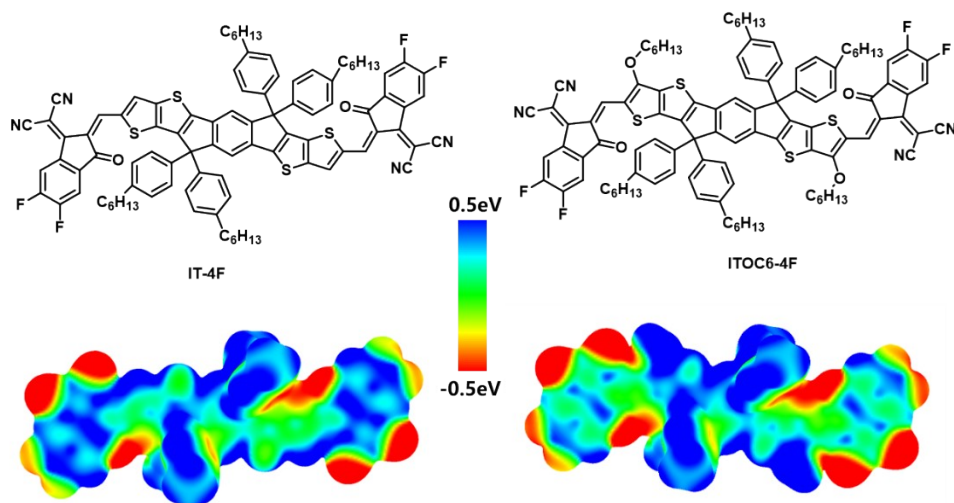
$$J_{cal} = \frac{q}{hc} \phi(660) EQE(660)$$

where  $q$  is the elementary charge,  $\phi(660)$  is the emission spectrum of 660 nm,  $h$  is Planck constant,  $c$  is light velocity.

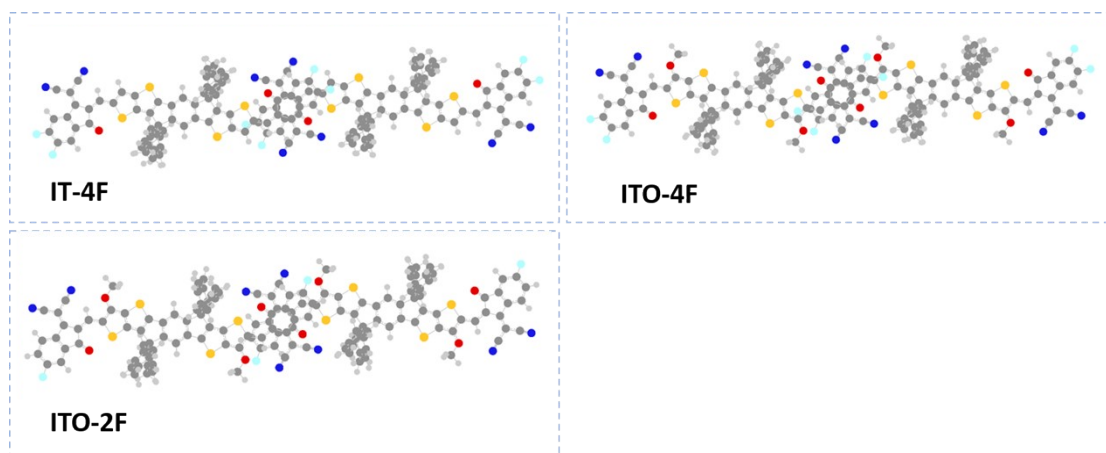
## Supplementary Figures



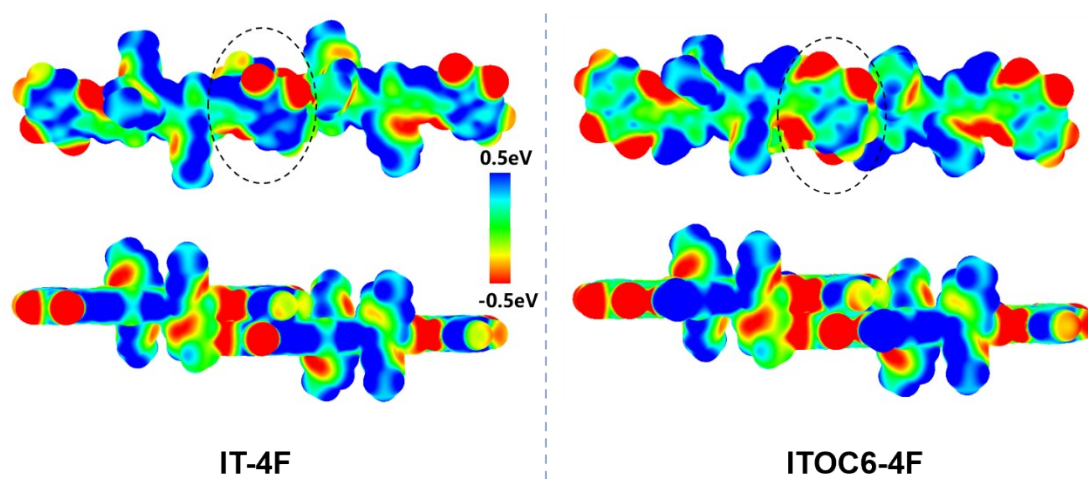
**Figure S1.** The ESPF of ITOC6-4F and IT-4F in monomeric state.



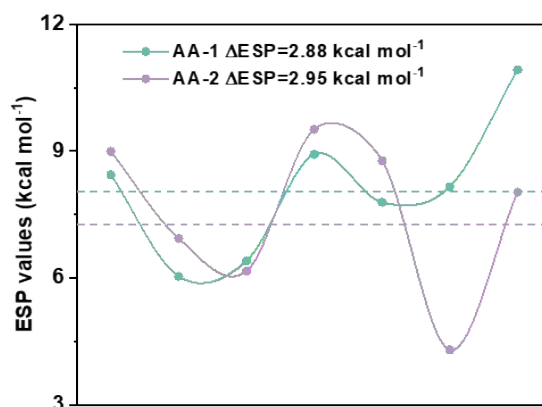
**Figure S2.** The molecular structure and ESP of IT-4F and ITOC6-4F in monomeric state.



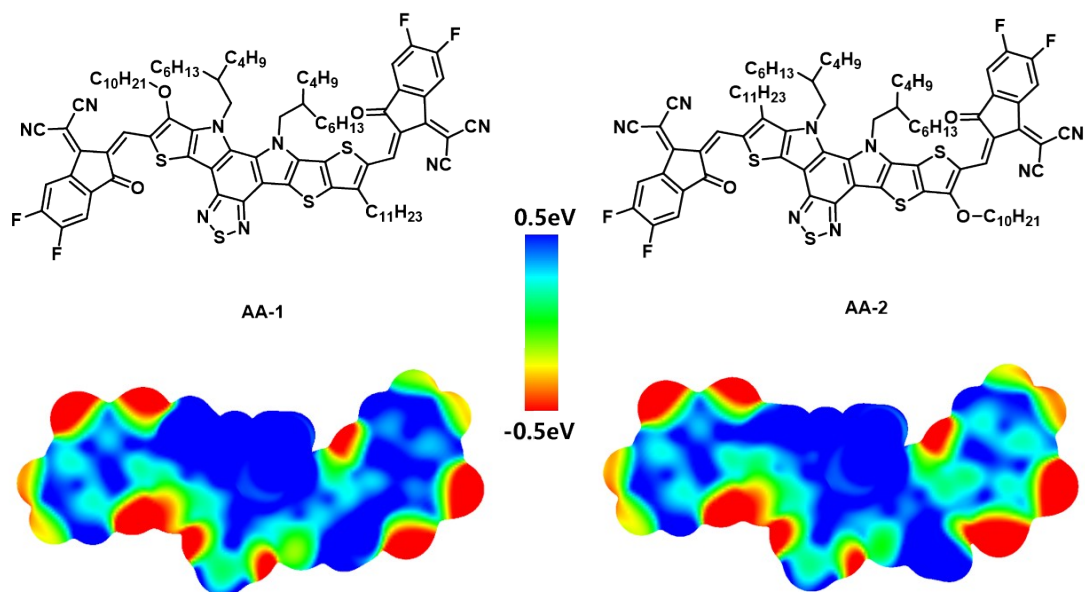
**Figure S3.** The aggregation patterns of IT-4F, ITOC6-4F, and ITO-2F.



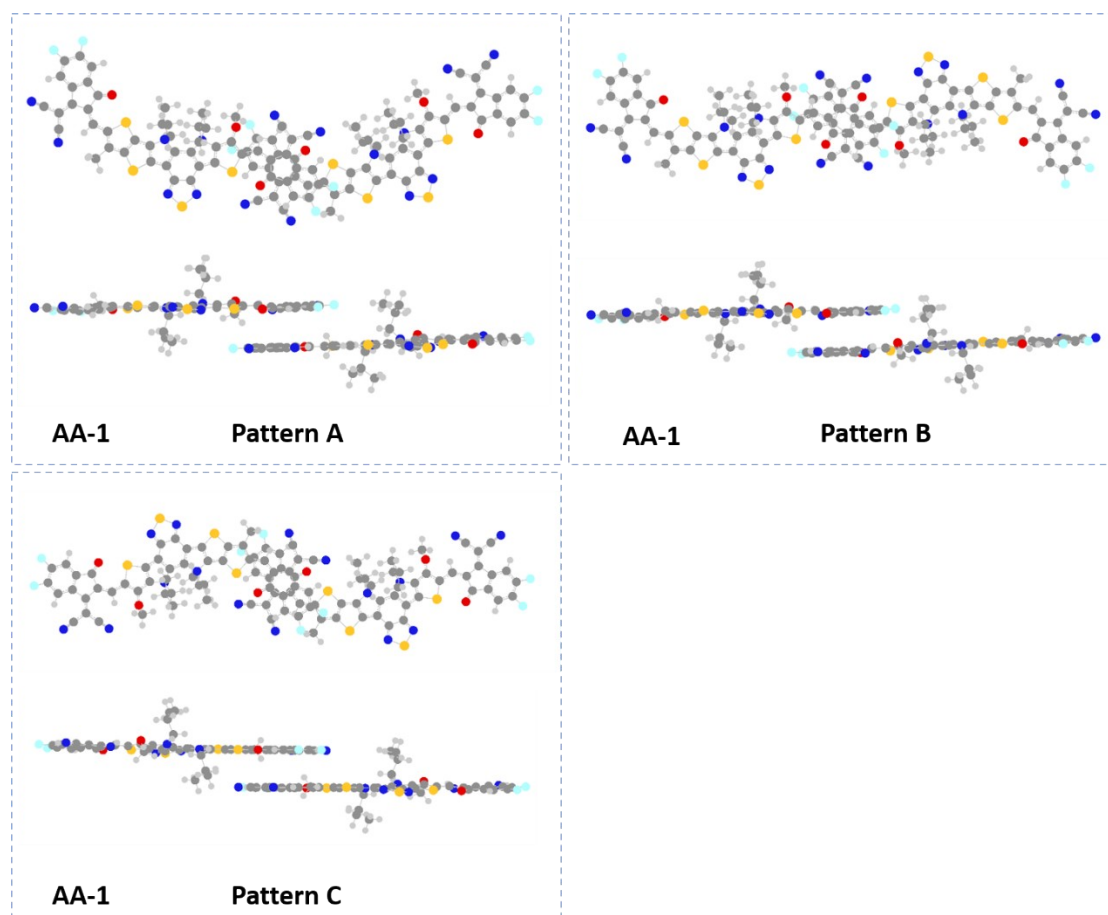
**Figure S4.** The ESP of IT-4F and ITOC6-4F after dimerization.



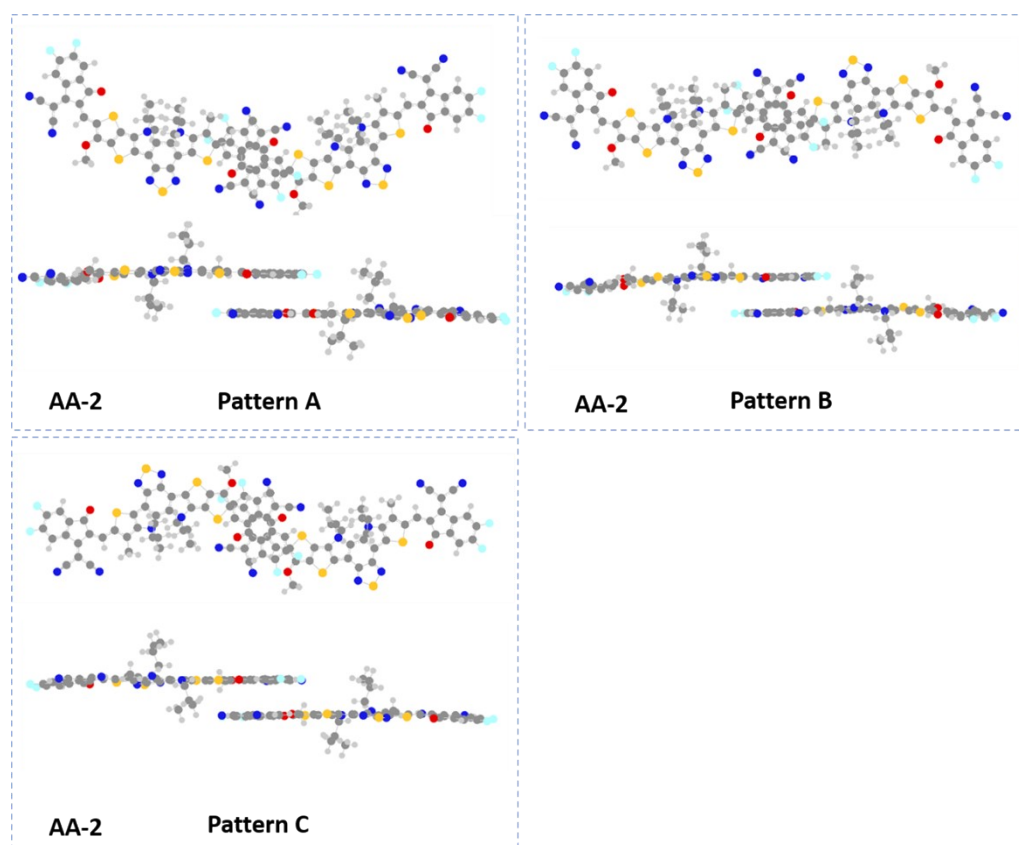
**Figure S5.** The ESPF of AA-1 and AA-2 in monomeric state.



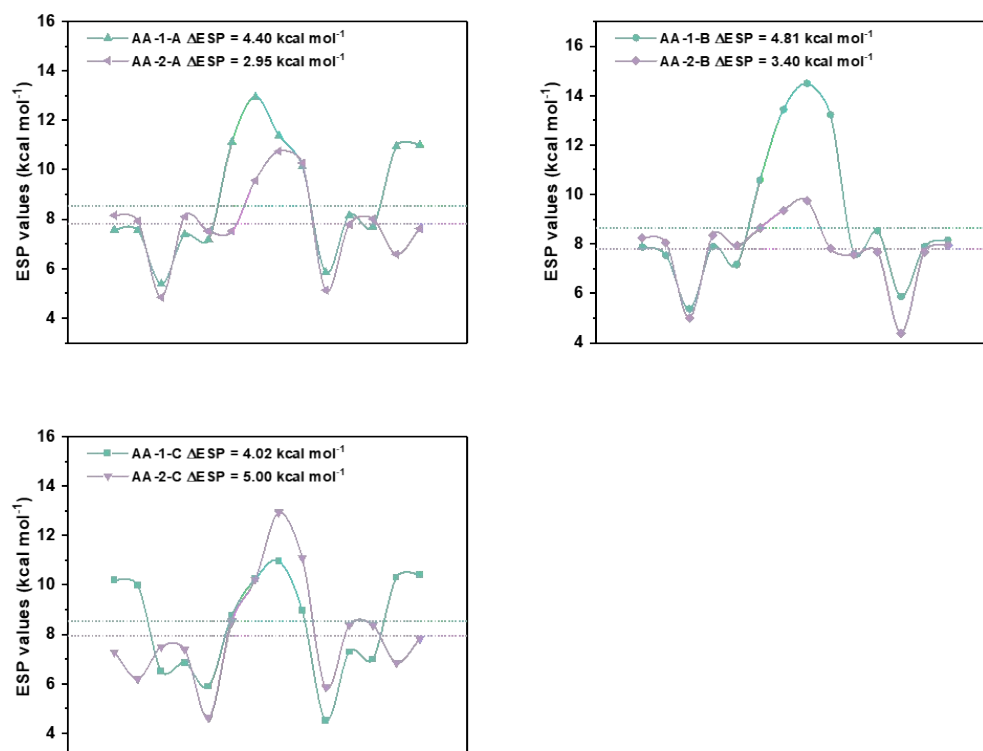
**Figure S6.** The molecular structure and ESP of AA-1 and AA-2 in monomeric state.



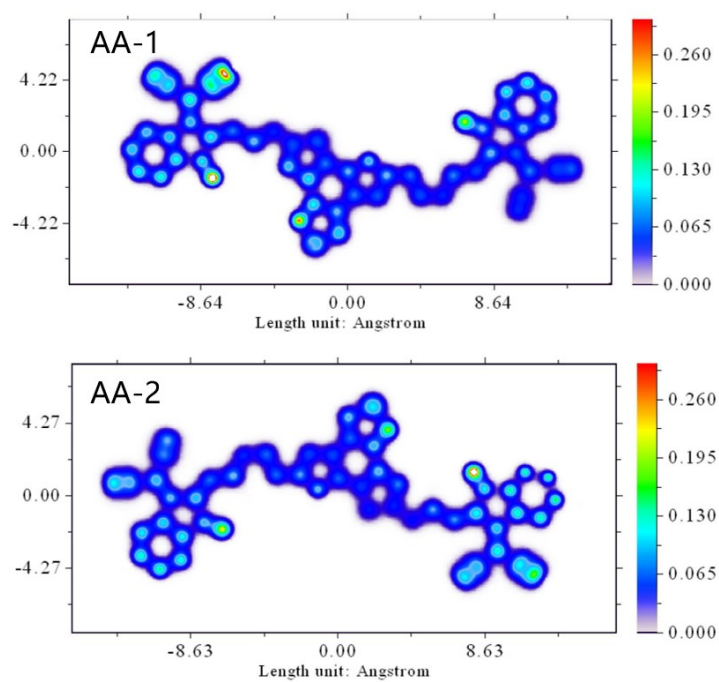
**Figure S7.** Three distinct dimeric aggregation patterns of AA-1.



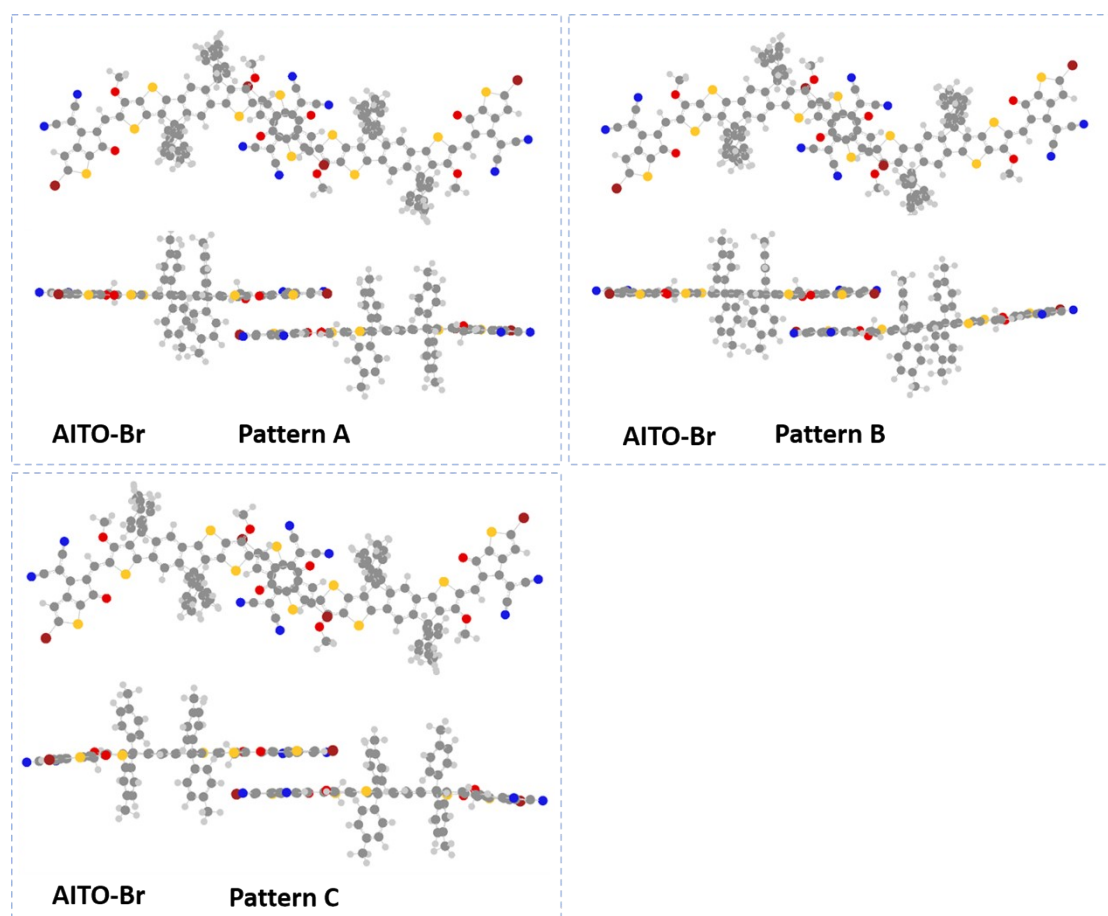
**Figure S8.** Three distinct dimeric aggregation patterns of AA-2.



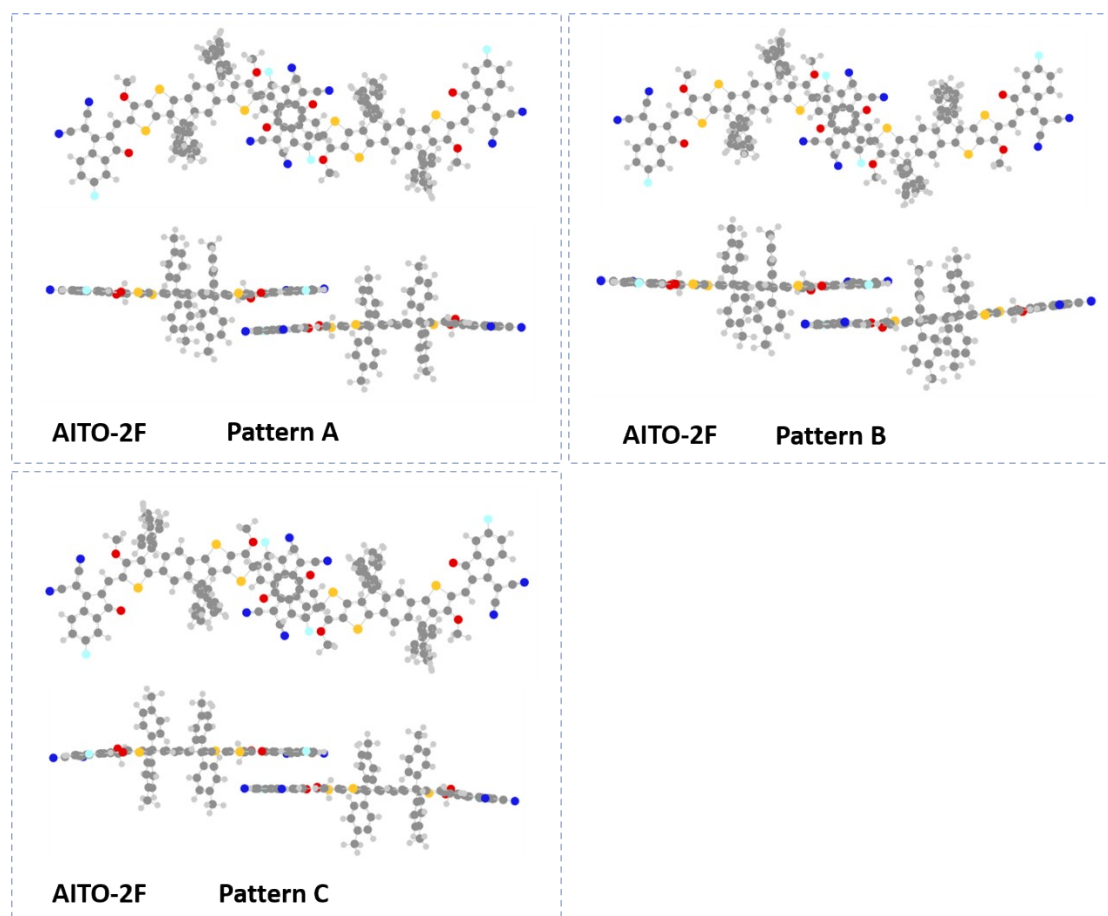
**Figure S9.** The ESPF of AA-1 and AA-2 after dimerization.



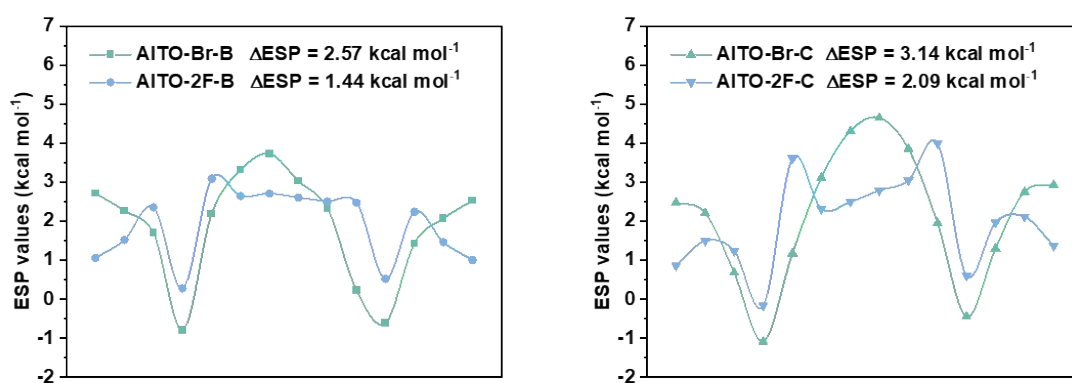
**Figure S10.** The  $\pi$  electrons distribution of AA-1 and AA-2 in monomeric state.



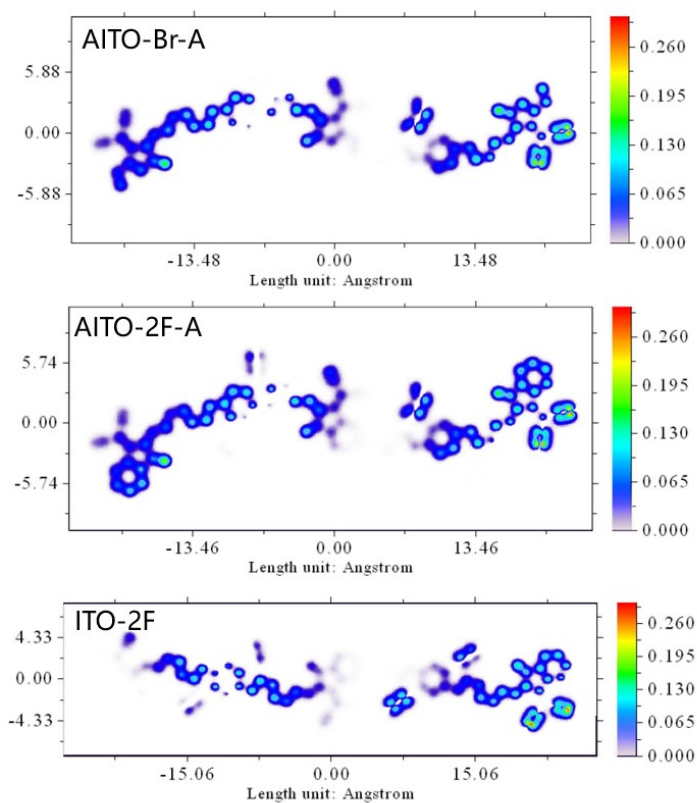
**Figure S11.** Three distinct dimeric aggregation patterns of AITO-Br.



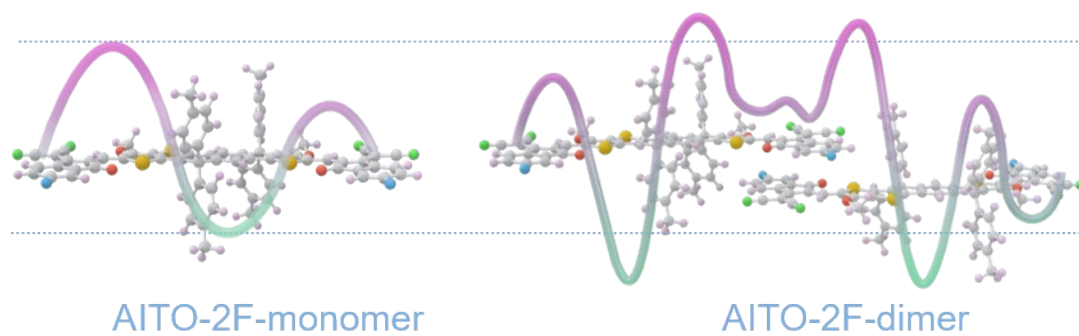
**Figure S12.** Three distinct dimeric aggregation patterns of AITO-2F.



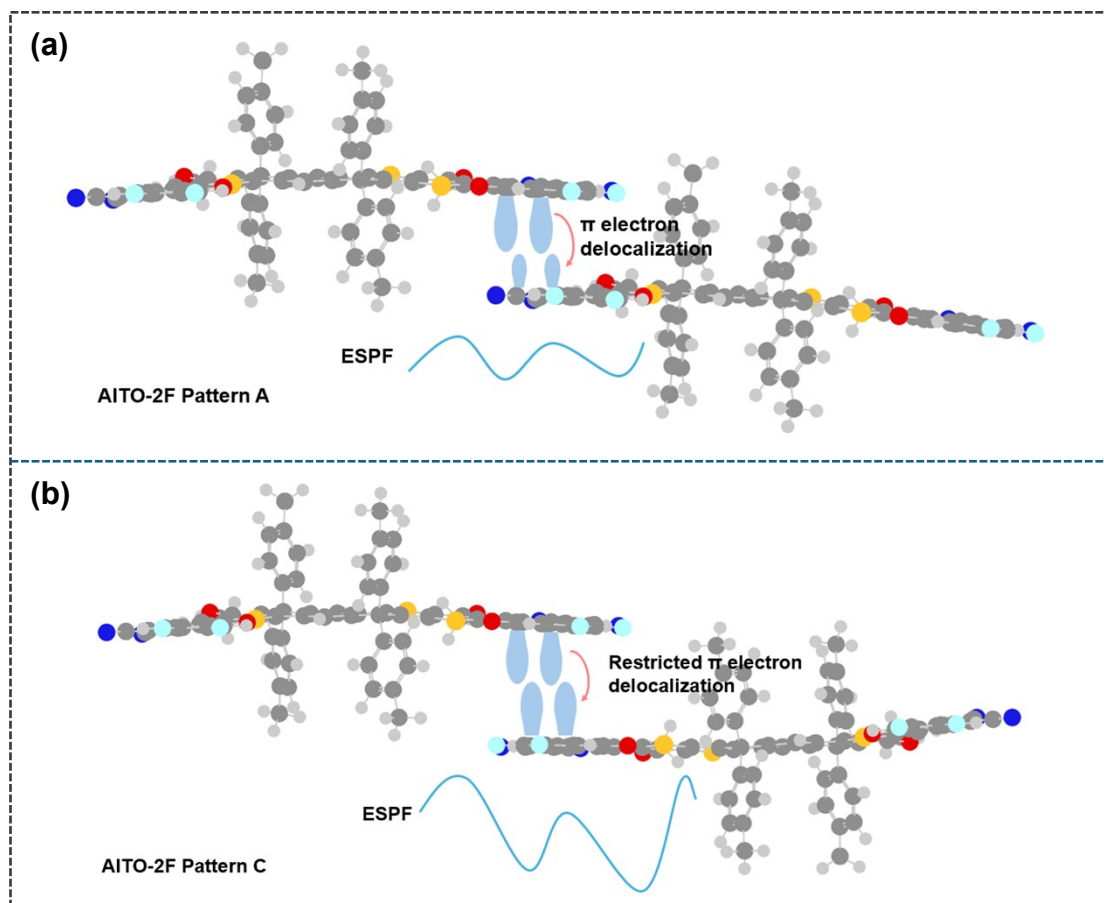
**Figure S13.** The ESPF of AITO-Br and AITO-2F after dimerization.



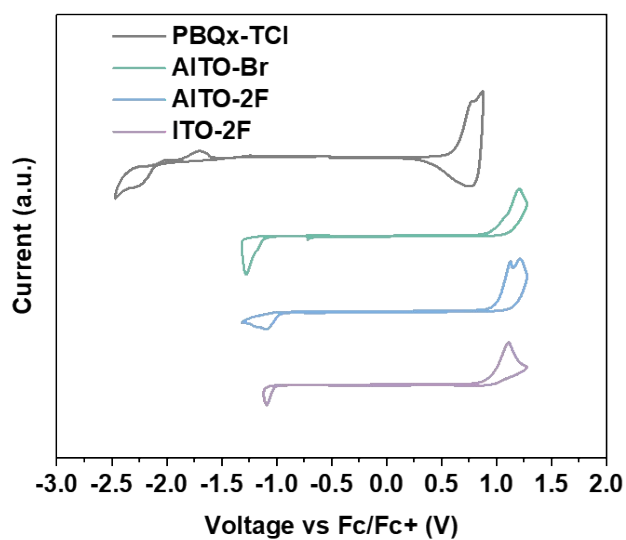
**Figure S14.** The  $\pi$  electrons distribution of AITO-Br, AITO-2F, and ITO-2F after dimerization.



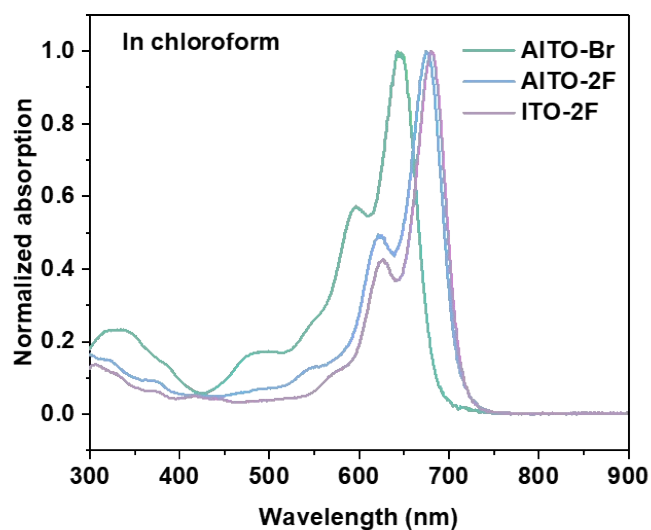
**Figure S15.** Schematic diagram of ESPF comparison between AITO-2F monomer and dimer.



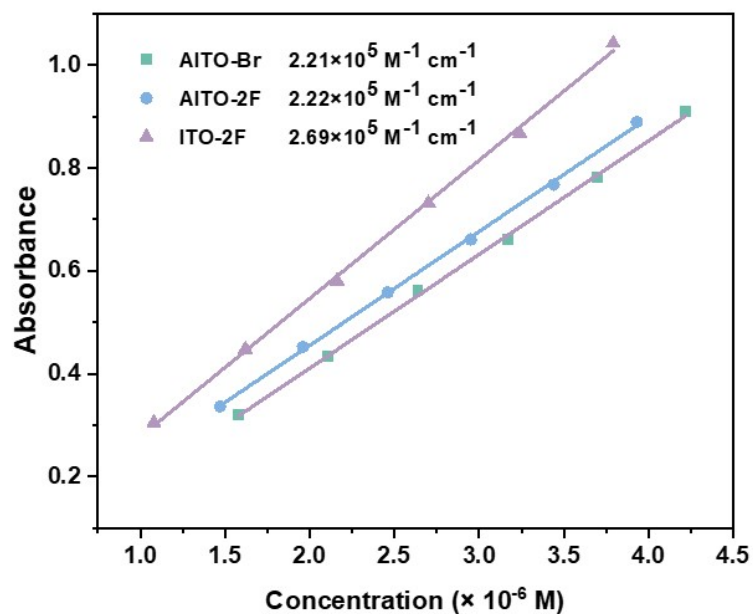
**Figure S16.** Schematic diagram of the effect of  $\pi$  electron delocalization on ESPF. (For AITO-2F pattern A, the ESP difference between the stacked terminal groups is relatively large, which results in more pronounced  $\pi$ -electron delocalization, facilitating ESP homogenization and achieving a smaller ESPF. In contrast, for AITO-2F pattern C, the ESP difference between the stacked terminal groups is small, restricting  $\pi$ -electron delocalization and leading to a greater ESP difference in the aggregated state.)



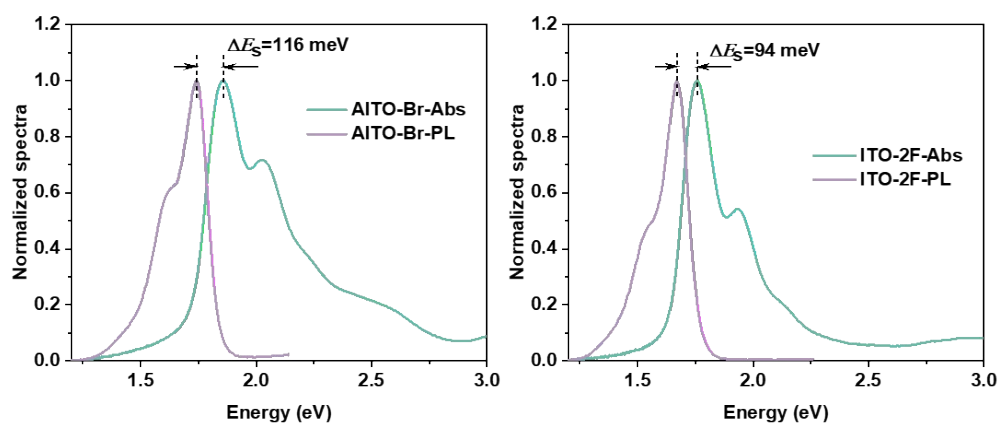
**Figure S17.** The electrochemical curves of AITO-Br, AITO-2F, ITO-2F, and PBQx-TCI neat films measured by cyclic voltammetry.



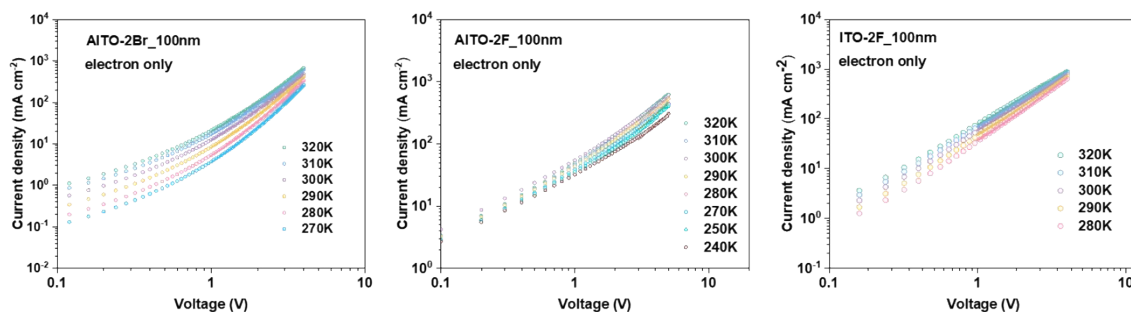
**Figure S18.** The UV-Vis absorption spectroscopy in chloroform of AITO-Br, AITO-2F, and ITO-2F.



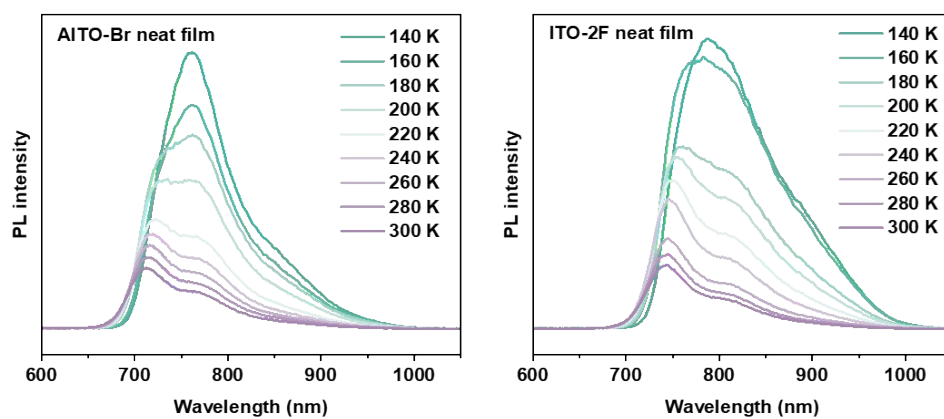
**Figure S19.** The absorption coefficients in chloroform of AITO-Br, AITO-2F, and ITO-2F.



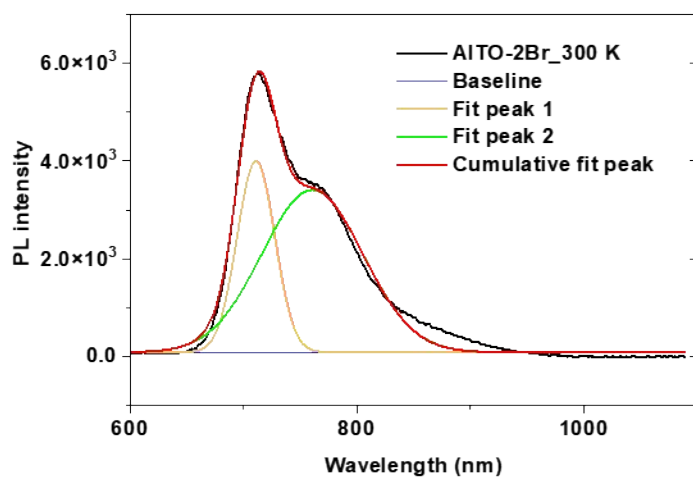
**Figure S20.** The Stokes shifts in the neat films of AITO-Br and ITO-2F.



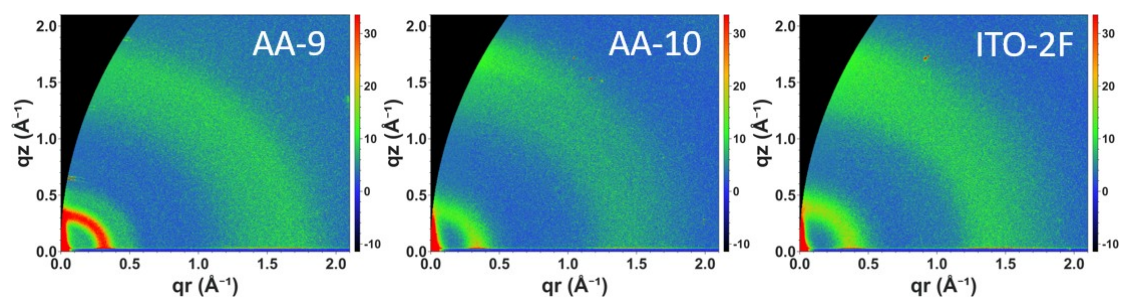
**Figure S21.** The temperature-dependent space-charge limited current curves of AITO-Br, AITO-2F, and ITO-2F neat films.



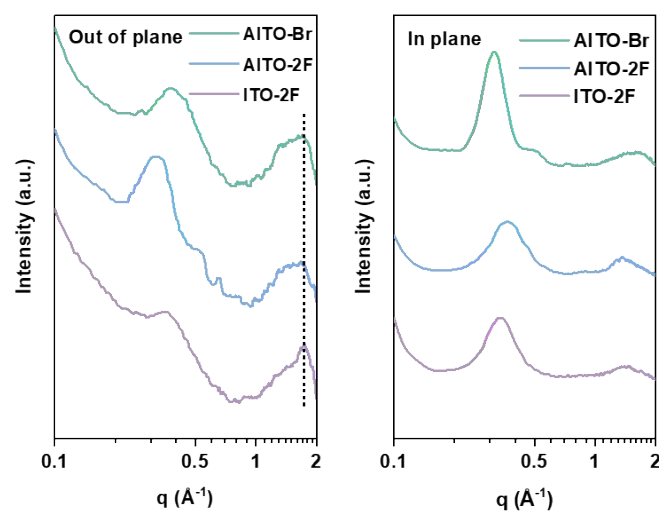
**Figure S22.** The temperature-dependent photoluminescence spectra of AITO-Br, and ITO-2F neat films.



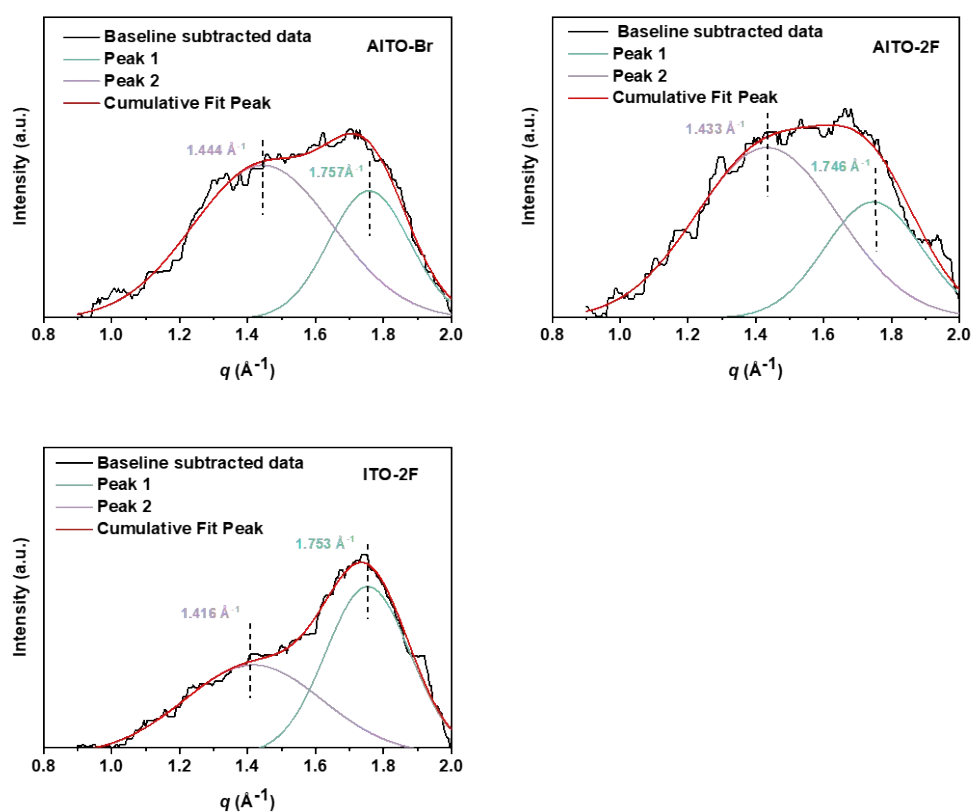
**Figure S23.** The schematic diagram of bimodal fitting of temperature dependent fluorescence spectra.



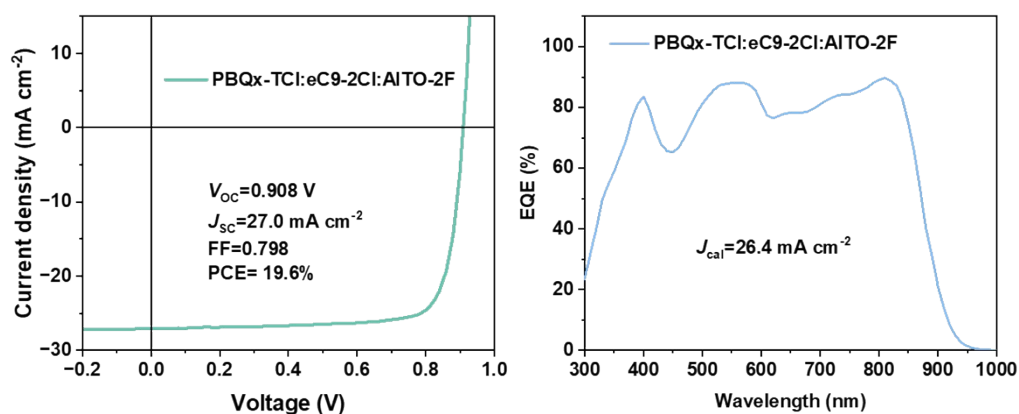
**Figure S24.** The 2D-GIWAXS patterns of AITO-Br, AITO-2F, and ITO-2F-based neat films.



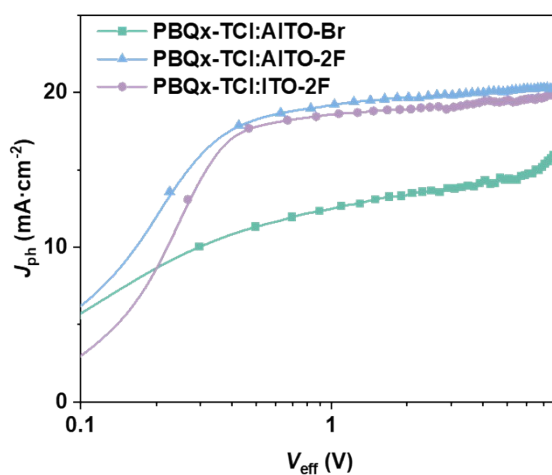
**Figure S25.** The line-cut profiles of AITO-Br, AITO-2F, and ITO-2F-based neat films in OOP and IP directions.



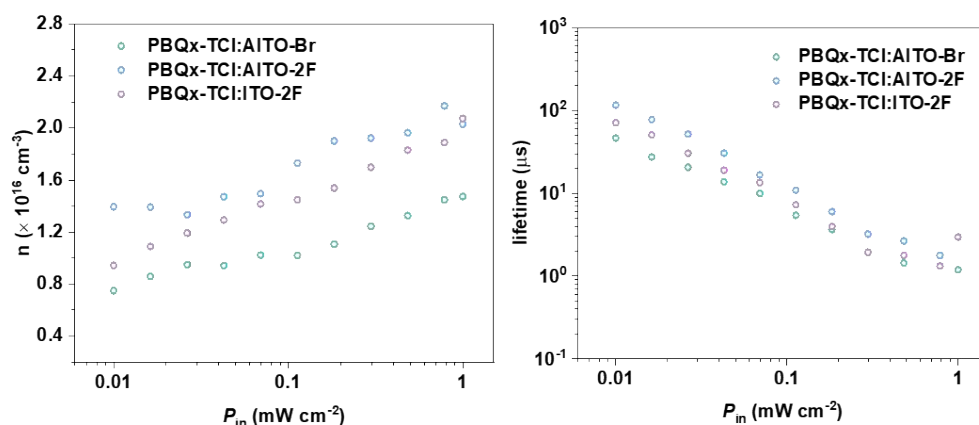
**Figure S26.** The double-peak fitting for the  $\pi$ - $\pi$  stacking peaks in the OOP direction.



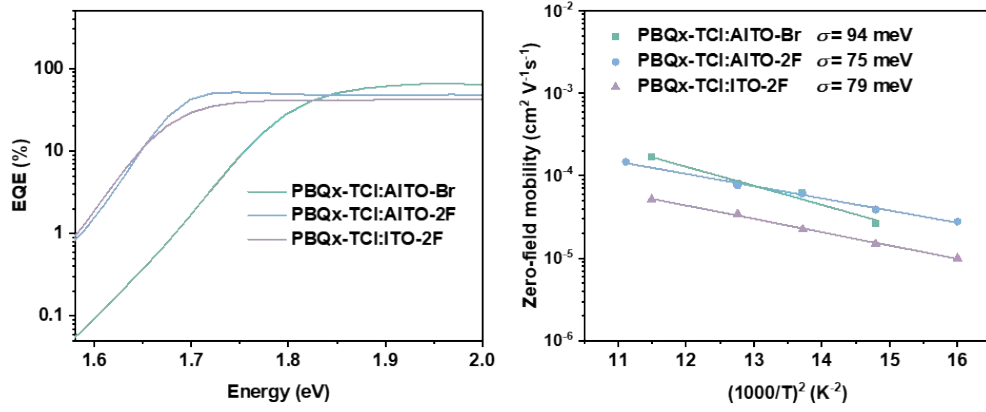
**Figure S27.** The  $J$ - $V$  and EQE curves of PBQx-TCI:eC9-2Cl:AITO-2F-based ternary device.



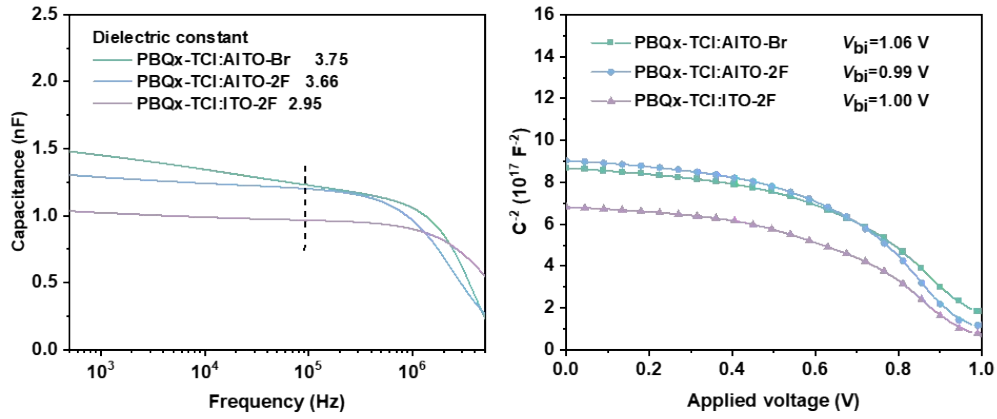
**Figure S28.** The exciton dissociation efficiency curves of PBQx-TCI:AITO-Br, PBQx-TCI:AITO-2F, and PBQx-TCI:ITO-2F-based devices.



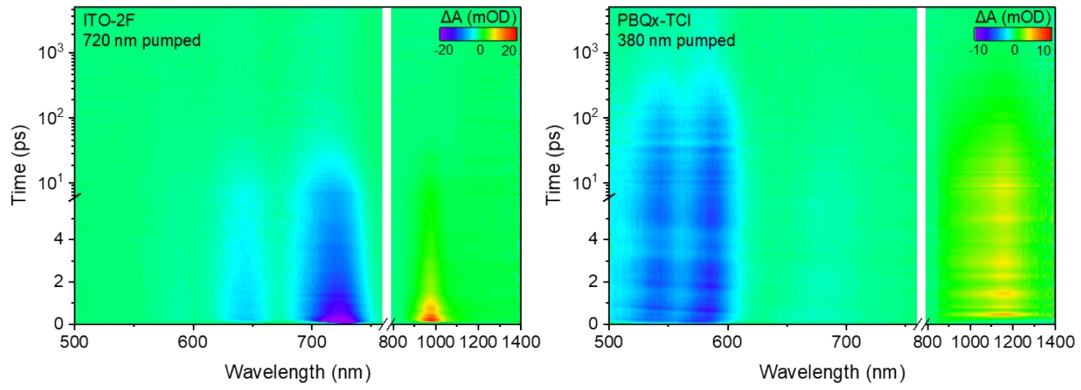
**Figure S29.** The charge carrier density ( $n$ ) and the charge carrier lifetime ( $\tau$ ) under different light intensities.



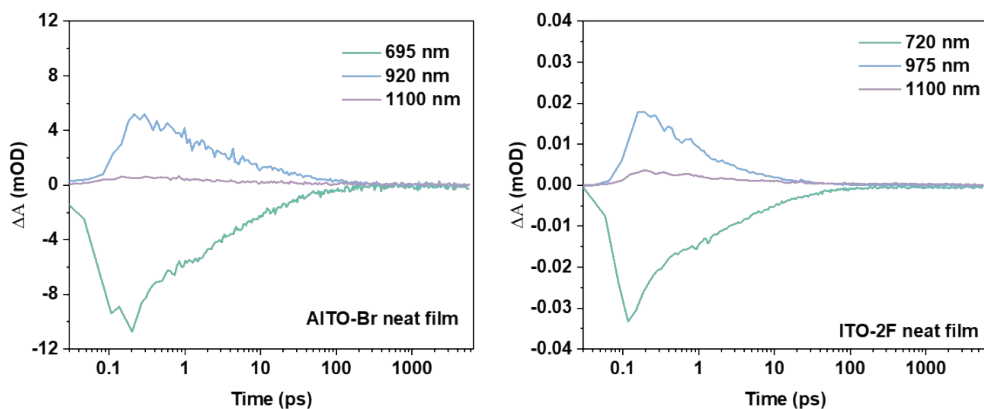
**Figure S30.** The s-EQE curves and The TD electron mobility of the AITO-Br, AITO-2F, and ITO-2F-based devices.



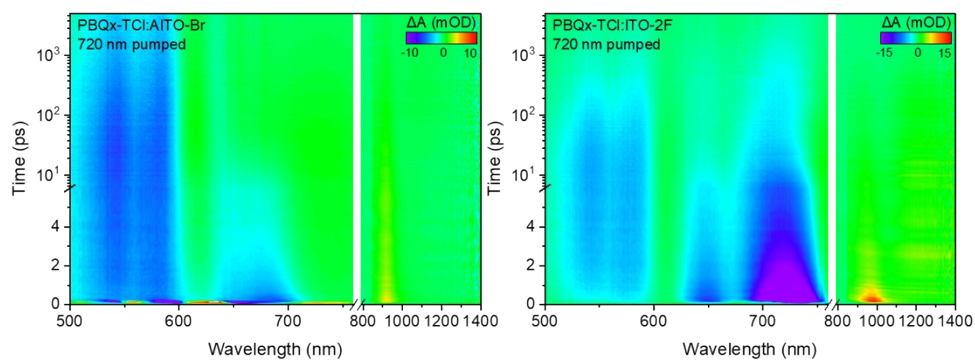
**Figure S31.** The dielectric constant ( $\epsilon_r$ ) and built-in electric field ( $V_{bi}$ ) of the AITO-Br, AITO-2F, and ITO-2F-based blend films.



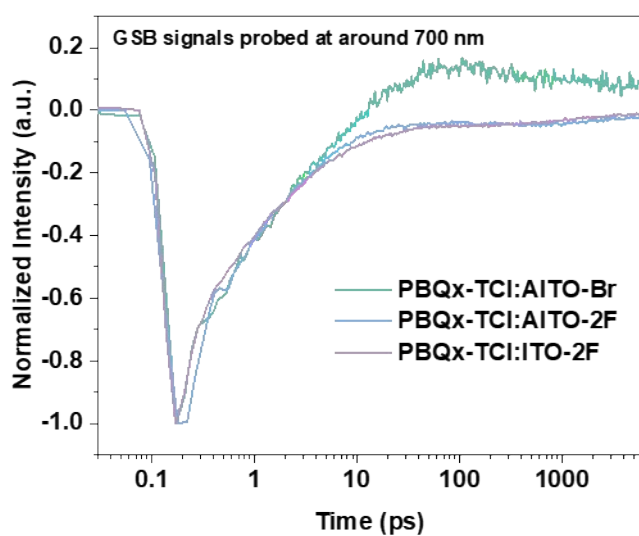
**Figure S32.** The 2D TA profiles of the ITO-2F and PBQx-TCI neat films.



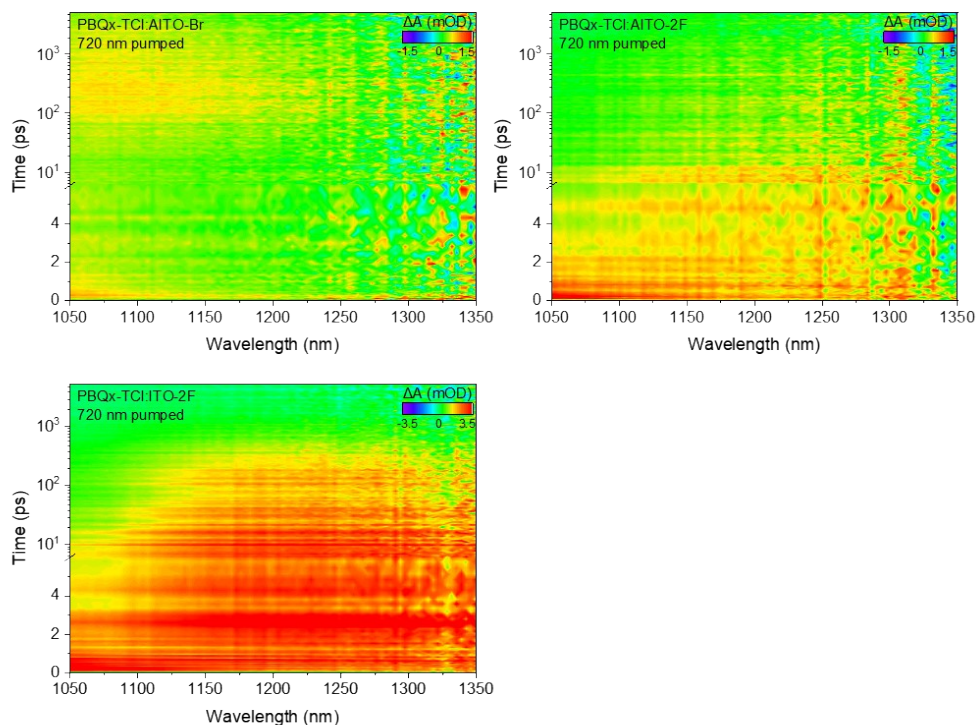
**Figure S33.** The TA dynamics of AITO-Br and ITO-2F neat film probed at corresponding wavelengths.



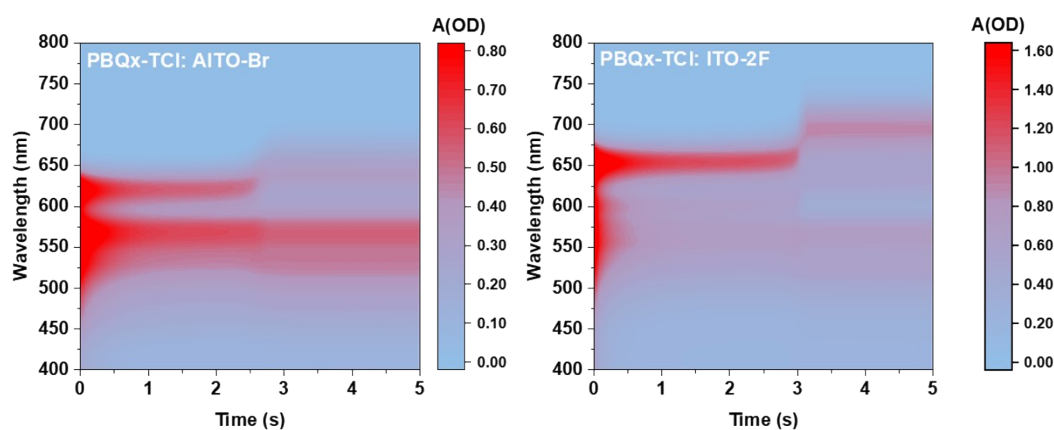
**Figure S34.** The 2D TA profiles of the PBQx-TCI:AITO-Br and PBQx-TCI:ITO-2F blend films.



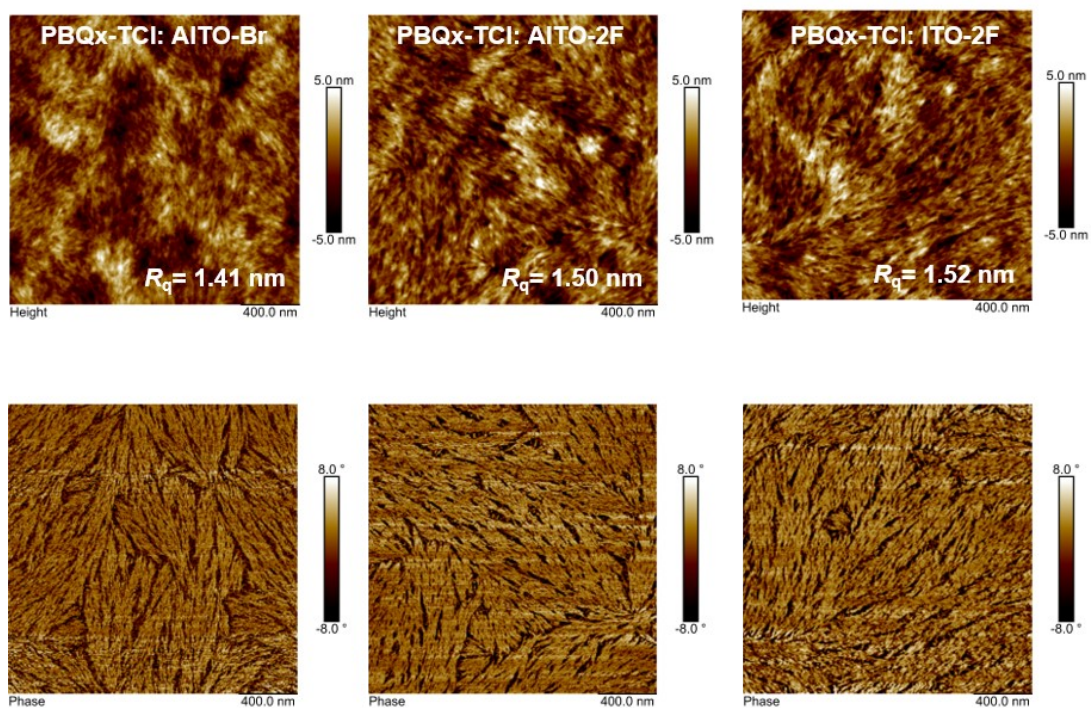
**Figure S35.** The GSB signals of the PBQx-TCI:AITO-Br, PBQx-TCI:AITO-2F and PBQx-TCI:ITO-2F blend films.



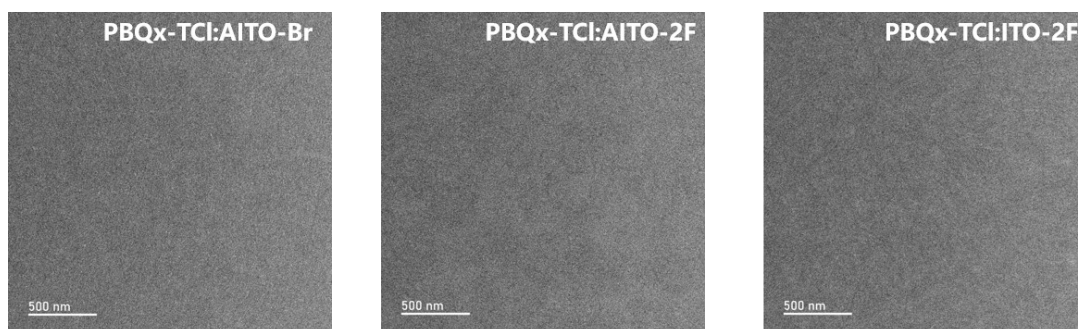
**Figure S36.** The 2D i-EX signals of the PBQx-TCl:AITO-Br, PBQx-TCl:AITO-2F and PBQx-TCl:ITO-2F blend films. (Note: In the blend film, PBQx-TCl:AITO-Br with the highest ESPF exhibits no i-EX signal, but both PBQx-TCl:AITO-2F and PBQx-TCl:ITO-2F exhibit i-EX state signal. And the i-EX signal of PBQx-TCl:AITO-2F decays faster, indicating that it is more easily dissociated into free carriers.)



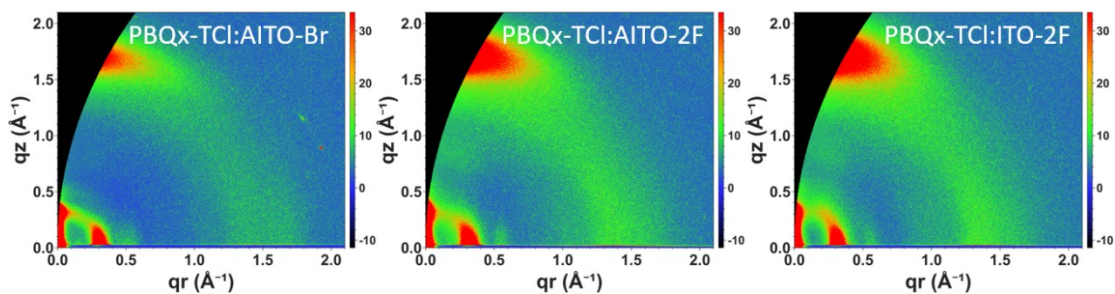
**Figure S37.** The 2D in situ absorption spectra of PBQx-TCl:AITO-Br- and PBQx-TCl:ITO-2F-based blend film.



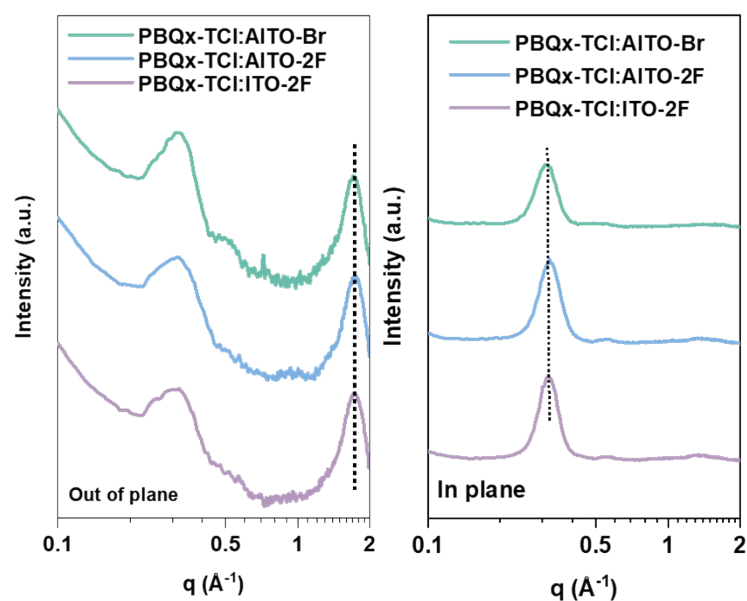
**Figure S38.** The AFM height images and phase images.



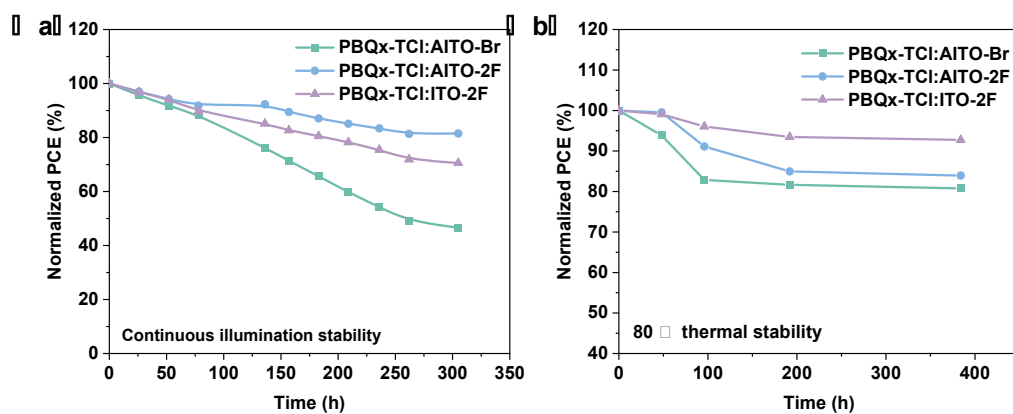
**Figure S39.** The TEM images of three blend films.



**Figure S40.** The 2D-GIWAXS patterns of AITO-Br, AITO-2F, and ITO-2F-based blend films.



**Figure S41.** The line-cut profiles of AITO-Br, AITO-2F, and ITO-2F-based blend films in IP directions.



**Figure S42.** The continuous illumination stability and 80 °C thermal stability of PBQx-TCI:AITO-Br-, PBQx-TCI:AITO-2F-, and PBQx-TCI:ITO-2F-based devices.

## Supplementary Tables

**Tables S1.** The detailed GIWAXS parameters for AITO-Br, AITO-2F, and ITO-2F-based neat films.

|         | $q_z$ ( $\text{\AA}^{-1}$ ) | $\pi$ - $\pi$ distance ( $\text{\AA}$ ) | $q_{xy}$ ( $\text{\AA}^{-1}$ ) | Lamellar distance ( $\text{\AA}$ ) |
|---------|-----------------------------|-----------------------------------------|--------------------------------|------------------------------------|
| AITO-Br | 1.757                       | 3.58                                    | 0.315                          | 20.0                               |
| AITO-2F | 1.746                       | 3.60                                    | 0.365                          | 17.2                               |
| ITO-2F  | 1.753                       | 3.58                                    | 0.34                           | 18.5                               |

**Tables S2.** Summary of photovoltaic parameters for the best PCEs of PBQx-TCl:AITO-2F-based devices with different additives.

| Additives    | $V_{OC}$ (V) | $J_{SC}$ (mA cm <sup>-2</sup> ) | FF    | PCE (%) |
|--------------|--------------|---------------------------------|-------|---------|
| without      | 1.00         | 18.0                            | 0.659 | 11.9    |
| 0.5% Vol CN  | 0.994        | 18.0                            | 0.680 | 12.1    |
| 0.5% Vol DIO | 1.00         | 20.0                            | 0.803 | 16.1    |

**Tables S3.** Summary of photovoltaic parameters for the best PCEs of PBQx-TCl:AITO-2F-based devices with different thickness.

| Thickness (nm) | $V_{OC}$ (V) | $J_{SC}$ (mA cm <sup>-2</sup> ) | FF    | PCE (%) |
|----------------|--------------|---------------------------------|-------|---------|
| 85             | 0.989        | 20.0                            | 0.773 | 15.3    |
| 110            | 1.00         | 20.0                            | 0.803 | 16.1    |
| 125            | 0.988        | 20.3                            | 0.775 | 15.6    |
| 150            | 0.981        | 20.3                            | 0.708 | 14.1    |

**Tables S4.** Summary of photovoltaic parameters for the best PCEs of PBQx-TCl:AITO-2F-based devices with different annealing temperatures.

| annealing temperature ( $^{\circ}\text{C}$ ) | $V_{OC}$ (V) | $J_{SC}$ (mA cm <sup>-2</sup> ) | FF    | PCE (%) |
|----------------------------------------------|--------------|---------------------------------|-------|---------|
| without                                      | 1.00         | 19.0                            | 0.768 | 14.6    |
| 80                                           | 1.00         | 19.6                            | 0.767 | 15.0    |
| 100                                          | 1.00         | 20.0                            | 0.803 | 16.1    |
| 120                                          | 0.987        | 20.3                            | 0.774 | 15.5    |
| 140                                          | 0.973        | 20.0                            | 0.690 | 13.5    |

**Table S5.** The efficiency and FF statistics of wide-bandgap acceptors below 750nm.

| Donors   | Acceptors  | Absorption cut-off edge (nm) | PCE   | FF    | References |
|----------|------------|------------------------------|-------|-------|------------|
| J52-F    | BTA3       | 705                          | 9.04  | 0.657 | 1          |
| J52-F    | BTA3b      | 735                          | 9.81  | 0.614 | 1          |
| PBQx-TF  | F-BTA3     | 710                          | 11.5  | 0.756 | 2          |
| PBQx-TCI | BTA3       | 700                          | 12.2  | 0.741 | 3          |
| J61      | BTA1       | 663                          | 3.02  | 0.467 | 4          |
| J61      | BTA2       | 620                          | 0.26  | 0.239 | 4          |
| J61      | BTA3       | 704                          | 8.25  | 0.662 | 4          |
| PE25     | Cl-BTA3    | 717                          | 10.75 | 0.646 | 5          |
| D18      | FCC-Cl     | 725                          | 13.1  | 0.760 | 6          |
| PM6      | FCC-Cl     | 725                          | 13.0  | 0.780 | 6          |
| PB2      | FTCC-Br    | 721                          | 14.8  | 0.788 | 7          |
| PB2      | ITCC       | 715                          | 11.0  | 0.654 | 7          |
| PBDB-TF  | GS-ISO     | 685                          | 11.62 | 0.704 | 8          |
| PBDB-TF  | GS-OC6     | 697                          | 8.69  | 0.614 | 8          |
| PBDB-TF  | GS-OEH     | 693                          | 8.44  | 0.613 | 8          |
| PB2      | FCC-Cl     | 725                          | 14.4  | 0.770 | 9          |
| P3HT     | SF-DPPEH   | 693                          | 3.63  | 0.426 | 10         |
| PDBT-T1  | SdiPBI-S   | 700                          | 7.16  | 0.655 | 11         |
| PDBT-T1  | IC-1IDT-IC | 700                          | 7.39  | 0.600 | 12         |
| PSEHTT   | DBFI-EDOT  | 700                          | 8.10  | 0.630 | 13         |
| P3HT     | F4TBT4     | 653                          | 4.12  | 0.561 | 14         |
| PDBT-T1  | SdiPBI-BT  | 689                          | 6.61  | 0.676 | 15         |
| PB2      | TIDC-Cl    | 743                          | 13.8  | 0.782 | 16         |
| PB2      | ITCC-Cl    | 737                          | 13.4  | 0.731 | 16         |
| PBDB-TCI | AITC       | 700                          | 11.1  | 0.726 | 17         |
| PBQx-TCI | ITO-2F     | 765                          | 13.4  | 0.712 | This work  |
| PBQx-TCI | AITO-Br    | 720                          | 8.5   | 0.580 | This work  |
| PBQx-TCI | AITO-2F    | 750                          | 16.1  | 0.803 | This work  |

**Tables S6.** The photovoltaic parameters of PBQx-TCl:eC9-2Cl:AITO-2F-based ternary devices.

| Blends                       | $V_{OC}$<br>(V) | $J_{SC}$<br>(mA cm <sup>-2</sup> ) | $J_{cal}^{a)}$<br>(mA cm <sup>-2</sup> ) | FF    | PCE <sup>b)</sup> (%) |
|------------------------------|-----------------|------------------------------------|------------------------------------------|-------|-----------------------|
| PBQx-TCl:eC9-<br>2Cl:AITO-2F | 0.908           | 27.0                               | 26.4                                     | 0.798 | 19.6 (19.3±0.3)       |

<sup>a)</sup>The calculated current density obtained from corresponding EQE spectra; <sup>b)</sup> The average PCEs obtained from 5 independent devices.

**Tables S7.** The detailed GIWAXS parameters for AITO-Br, AITO-2F, and ITO-2F-based blend films.

|                  | $q_z$ (Å <sup>-1</sup> ) | $\pi$ - $\pi$ distance (Å) | $q_{xy}$ (Å <sup>-1</sup> ) | Lamellar distance (Å) |
|------------------|--------------------------|----------------------------|-----------------------------|-----------------------|
| PBQx-TCl:AITO-Br | 1.715                    | 3.66                       | 0.310                       | 20.3                  |
| PBQx-TCl:AITO-2F | 1.730                    | 3.63                       | 0.320                       | 19.6                  |
| PBQx-TCl:ITO-2F  | 1.730                    | 3.63                       | 0.315                       | 19.9                  |

**Tables S8.** The photovoltaic parameters of PBQx-TCl: AITO-Br-based devices under different laser incident power density.

| $P_{in}$<br>(mW cm <sup>-2</sup> ) | $V_{OC}$ (V) | $J_{SC}$<br>(mA cm <sup>-2</sup> ) | FF    | $J_{Cal}^{a)}$<br>(mA cm <sup>-2</sup> ) | $P_{out}$<br>(mW cm <sup>-2</sup> ) | PCE (%) |
|------------------------------------|--------------|------------------------------------|-------|------------------------------------------|-------------------------------------|---------|
| 5.89                               | 0.988        | 1.78                               | 0.660 | 2.03                                     | 1.16                                | 19.7    |
| 9.12                               | 0.998        | 2.65                               | 0.657 | 3.15                                     | 1.73                                | 19.0    |
| 14.5                               | 1.01         | 4.44                               | 0.595 | 5.00                                     | 2.66                                | 17.6    |
| 25.0                               | 1.02         | 7.53                               | 0.557 | 8.62                                     | 4.28                                | 17.1    |
| 41.9                               | 1.03         | 12.1                               | 0.523 | 14.5                                     | 6.52                                | 15.6    |
| 65.6                               | 1.04         | 18.5                               | 0.493 | 22.6                                     | 9.49                                | 14.5    |
| 99.0                               | 1.04         | 27.3                               | 0.474 | 34.2                                     | 13.5                                | 13.6    |
| 143.9                              | 1.04         | 38.6                               | 0.439 | 49.6                                     | 17.6                                | 12.2    |
| 224.7                              | 1.05         | 59.2                               | 0.404 | 77.5                                     | 25.04                               | 11.1    |

<sup>a)</sup>The calculated current density obtained from incident power density and the EQE response at 660nm (64.9%).

**Tables S9.** The photovoltaic parameters of PBQx-TCl: AITO-2F-based devices under different laser incident power density.

| $P_{in}$<br>(mW cm <sup>-2</sup> ) | $V_{OC}$ (V) | $J_{SC}$<br>(mA cm <sup>-2</sup> ) | FF    | $J_{Cal}^{a)}$<br>(mA cm <sup>-2</sup> ) | $P_{out}$<br>(mW cm <sup>-2</sup> ) | PCE (%) |
|------------------------------------|--------------|------------------------------------|-------|------------------------------------------|-------------------------------------|---------|
| 5.89                               | 0.931        | 2.66                               | 0.806 | 2.71                                     | 2.00                                | 33.9    |
| 9.12                               | 0.944        | 4.10                               | 0.817 | 4.20                                     | 3.16                                | 34.7    |
| 14.5                               | 0.959        | 6.57                               | 0.838 | 6.68                                     | 5.28                                | 36.4    |
| 25.0                               | 0.970        | 11.2                               | 0.779 | 11.5                                     | 8.46                                | 33.9    |
| 41.9                               | 0.981        | 18.1                               | 0.776 | 19.3                                     | 13.8                                | 32.9    |
| 65.6                               | 0.995        | 27.8                               | 0.778 | 30.2                                     | 21.5                                | 32.8    |
| 99.0                               | 1.01         | 43.0                               | 0.744 | 45.6                                     | 32.2                                | 32.5    |
| 143.9                              | 1.01         | 65.6                               | 0.697 | 66.3                                     | 46.2                                | 32.1    |
| 224.7                              | 1.02         | 101.4                              | 0.649 | 103.5                                    | 67.1                                | 29.9    |

<sup>a)</sup>The calculated current density obtained from incident power density and the EQE response at 660nm (86.7%).

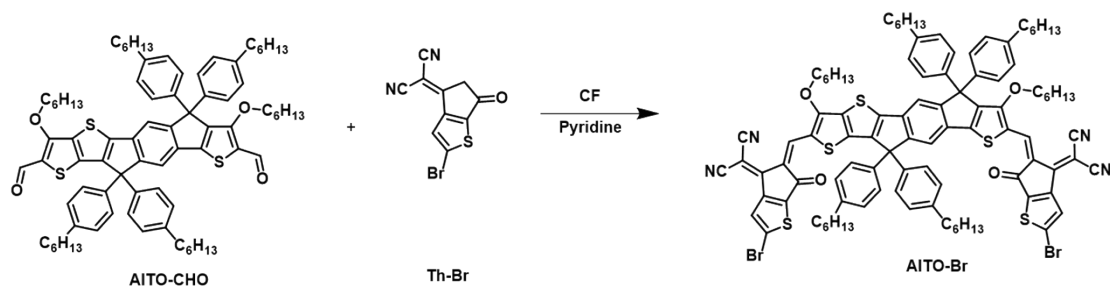
**Tables S10.** The photovoltaic parameters of PBQx-TCl: ITO-2F-based devices under different laser incident power density.

| $P_{in}$<br>(mW cm <sup>-2</sup> ) | $V_{OC}$ (V) | $J_{SC}$<br>(mA cm <sup>-2</sup> ) | FF    | $J_{Cal}^{a)}$<br>(mA cm <sup>-2</sup> ) | $P_{out}$<br>(mW cm <sup>-2</sup> ) | PCE (%) |
|------------------------------------|--------------|------------------------------------|-------|------------------------------------------|-------------------------------------|---------|
| 5.89                               | 0.953        | 2.63                               | 0.755 | 2.61                                     | 1.89                                | 32.1    |
| 9.12                               | 0.965        | 4.03                               | 0.759 | 4.04                                     | 2.95                                | 32.3    |
| 14.5                               | 0.978        | 6.34                               | 0.765 | 6.42                                     | 4.74                                | 31.3    |
| 25.0                               | 0.992        | 11.0                               | 0.710 | 11.1                                     | 7.73                                | 30.9    |
| 41.9                               | 1.01         | 18.2                               | 0.698 | 18.6                                     | 12.8                                | 30.5    |
| 65.6                               | 1.01         | 28.8                               | 0.678 | 29.1                                     | 19.8                                | 30.2    |
| 99.0                               | 1.03         | 41.9                               | 0.648 | 43.9                                     | 27.8                                | 28.1    |
| 143.9                              | 1.03         | 62.6                               | 0.610 | 63.8                                     | 39.4                                | 27.4    |
| 224.7                              | 1.04         | 97.9                               | 0.570 | 99.6                                     | 57.9                                | 25.8    |

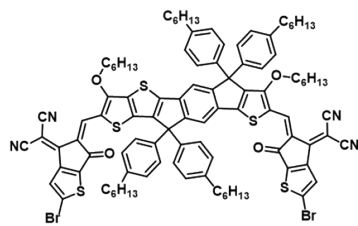
<sup>a)</sup>The calculated current density obtained from incident power density and the EQE response at 660nm (83.4%).

# Synthetic routes

## AITO-Br



In a 50 mL of two-neck round bottom flask, AITO-CHO (100mg, 0.082 mmol) and Th-Br (91.5 mg, 0.328 mmol) were dissolved in 5 mL of CHCl<sub>3</sub>, and then 0.20 mL of pyridine was added into the mixture by syringe. The reaction was stirred at room temperature overnight. The solvent was removed under vacuum and the residue was purified by silica gel column using CHCl<sub>3</sub> as eluent. The product AITO-CHO was obtained as blue black solid (117.1 mg, 82%). <sup>1</sup>H NMR (700 MHz, Chloroform-*d*) δ 8.95 (d, *J* = 23.6 Hz, 1H), 8.80 (d, *J* = 18.6 Hz, 1H), 7.94 (d, *J* = 19.5 Hz, 2H), 7.69 (d, *J* = 6.0 Hz, 1H), 7.45 (s, 1H), 7.23 (d, *J* = 8.1 Hz, 4H), 7.13 (dt, *J* = 18.4, 8.2 Hz, 12H), 4.57 (t, *J* = 6.6 Hz, 2H), 3.48 (t, *J* = 7.4 Hz, 2H), 2.57 (q, *J* = 6.6, 5.2 Hz, 8H), 1.94 – 1.89 (m, 2H), 1.60 – 1.48 (m, 12H), 1.38 – 1.25 (m, 28H), 1.22 (d, *J* = 7.4 Hz, 2H), 1.10 (s, 2H), 1.00 (s, 2H), 0.87 (d, *J* = 6.2 Hz, 18H). <sup>13</sup>C NMR (176 MHz, Chloroform-*d*) δ 162.62, 160.67, 158.46, 157.62, 156.20, 156.17, 155.64, 152.03, 150.98, 148.32, 146.47, 145.01, 142.58, 142.49, 138.52, 138.02, 137.73, 135.65, 133.29, 132.88, 128.85, 128.51, 128.40, 127.97, 127.84, 127.60, 126.05, 125.99, 120.57, 120.33, 118.74, 118.12, 114.69, 114.48, 113.74, 113.63, 73.69, 35.60, 35.52, 31.71, 31.70, 31.40, 31.34, 31.32, 31.25, 29.59, 29.32, 29.16, 29.10, 25.45, 24.79, 22.59, 14.11, 14.09. MS (MALDI-TOF): *m/z* Calcd. for C<sub>100</sub>H<sub>100</sub>Br<sub>2</sub>N<sub>4</sub>O<sub>4</sub>S<sub>5</sub>: 1741.47 [M], Found 1741.66 [M]<sup>+</sup>.

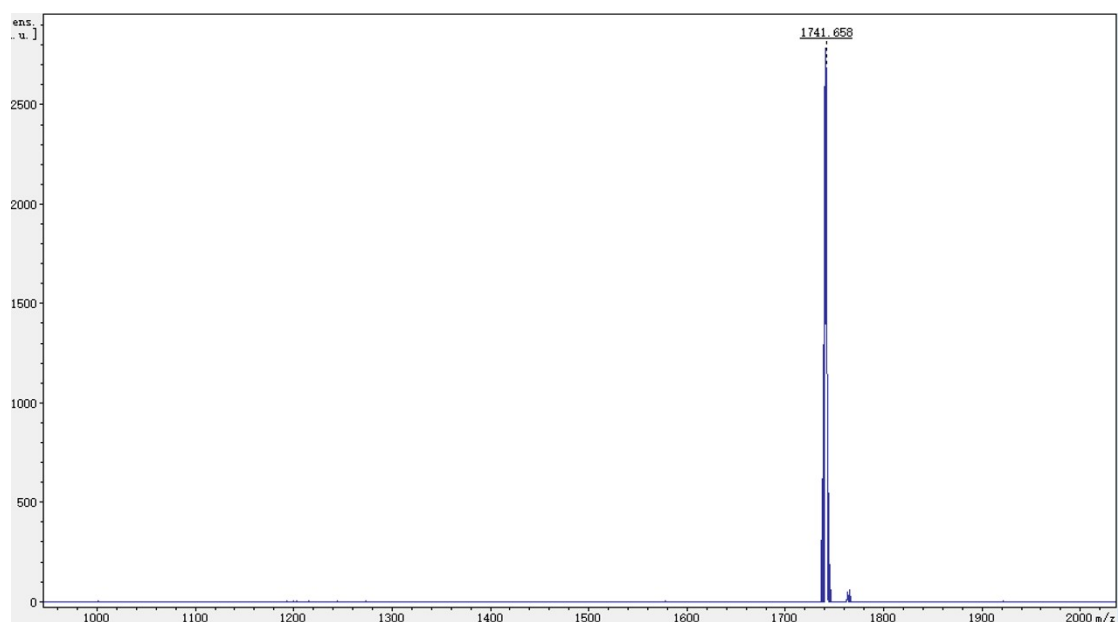


Chemical structure of compound 10 is shown above the  $^{13}\text{C}$  NMR spectrum. The structure is a complex organic molecule featuring a central benzene ring substituted with two phenyl groups and two 4-cyano-2-bromothiophenyl groups. The thiophene rings are also substituted with a 4-cyano-2-bromothiophenyl group. The molecule contains several  $\text{C}_6\text{H}_{13}$  groups and a central  $\text{C}_6\text{H}_5$  group.

The  $^{13}\text{C}$  NMR spectrum (CDCl<sub>3</sub>) shows peaks at the following chemical shifts (ppm):

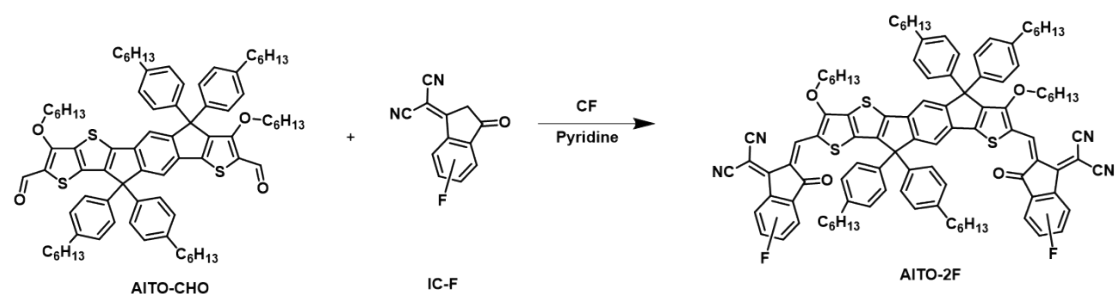
- 180.41, 180.37, 162.62, 160.67, 158.46, 156.20, 151.00, 150.98, 148.32, 147.69, 147.33, 146.47, 142.58, 142.49, 138.52, 138.02, 128.95, 128.85, 128.51, 128.40, 127.97, 127.84, 127.60, 126.05, 120.57, 120.33, 119.67, 77.20, 77.02, 76.84, 73.69, 68.80, 68.19, 35.60, 35.52, 31.71, 31.70, 31.40, 31.34, 31.32, 31.25, 29.59, 29.32, 29.16, 29.10, 25.45, 24.79, 22.59, 14.11, 14.09

 $^{13}\text{C}$ -NMR spectrum of AITO-Br in  $\text{CDCl}_3$ .



MALDI-TOF spectrum of AITO-Br.

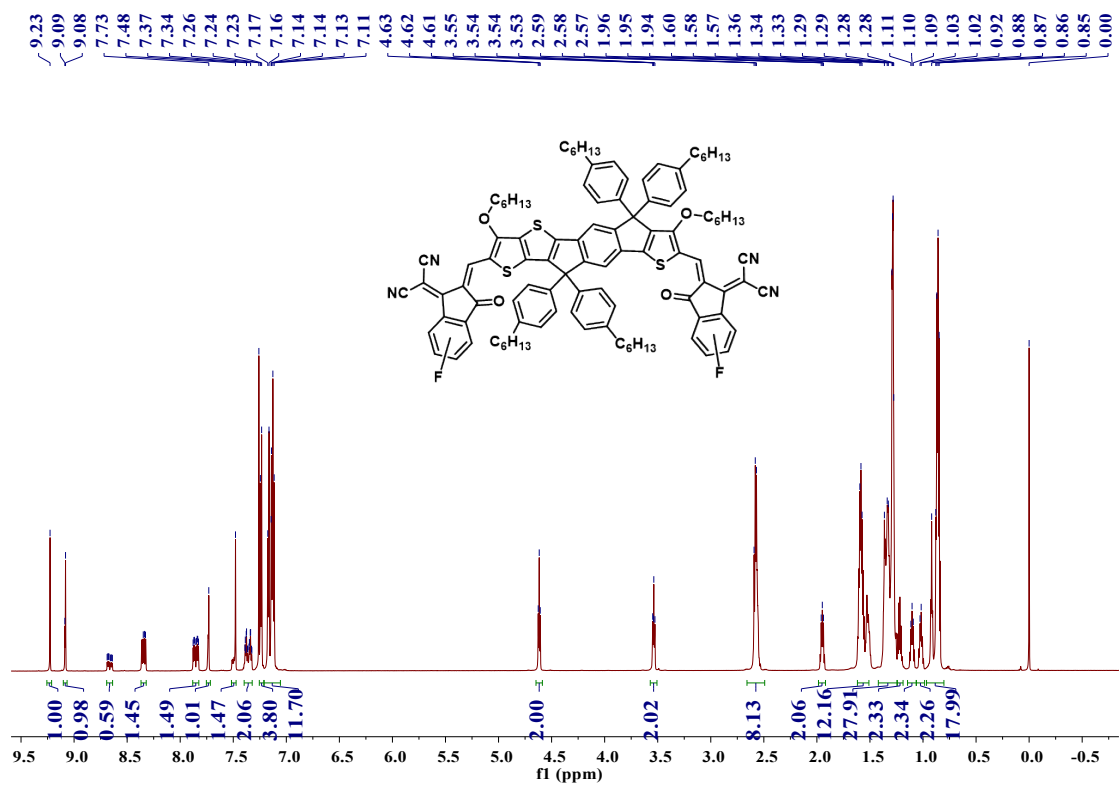
## AITO-2F



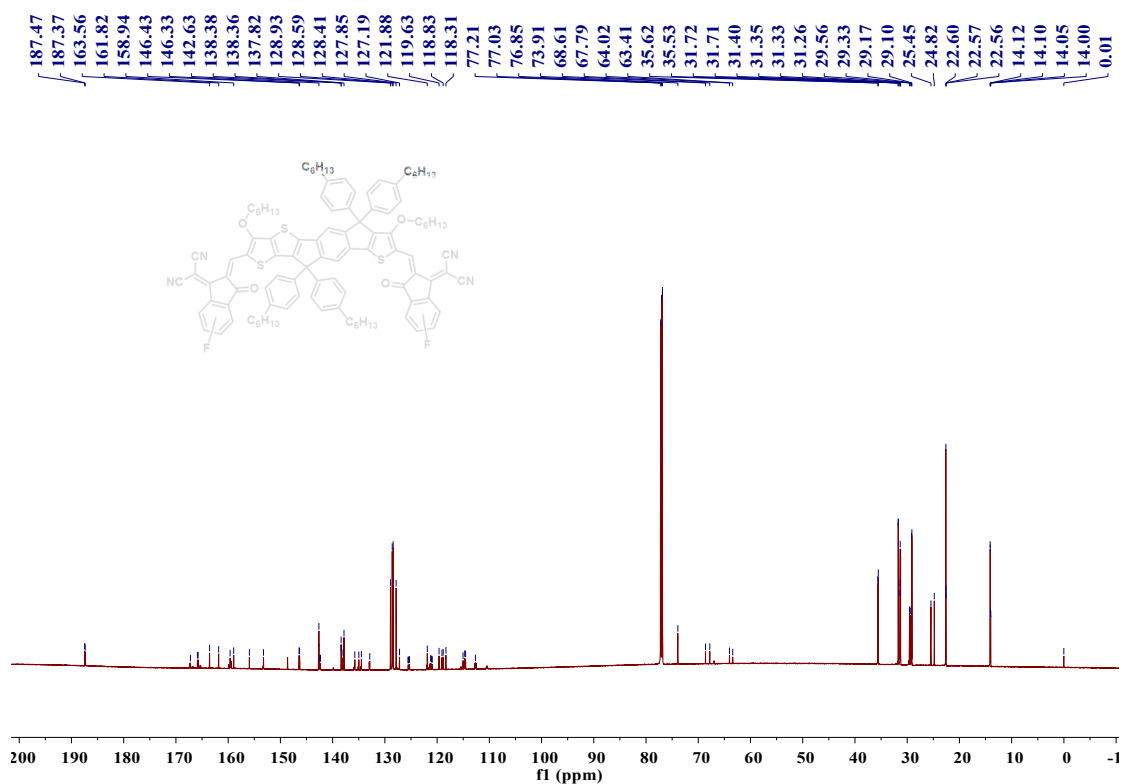
In a 50 mL of two-neck round bottom flask, AITO-CHO (140 mg, 0.115 mmol) and IC-F (97.4 mg, 0.459 mmol) were dissolved in 5 mL of  $\text{CHCl}_3$ , and then 0.20 mL of pyridine was added into the mixture by syringe. The reaction was stirred at room temperature overnight. The solvent was removed under vacuum and the residue was purified by silica gel column using  $\text{CHCl}_3$  as eluent. The product AITO-2F was obtained as blue black solid (148.0 mg, 80%).

$^1\text{H}$  NMR (700 MHz, Chloroform-*d*)  $\delta$  9.23 (s, 1H), 9.08 (d,  $J = 4.3$  Hz, 1H), 8.66 (ddd,  $J = 21.6$ , 8.7, 4.2 Hz, 1H), 8.37 – 8.32 (m, 1H), 7.85 (ddd,  $J = 21.8$ , 8.3, 5.1 Hz, 1H), 7.73 (s, 1H), 7.48 (s, 2H), 7.36 (dtd,  $J = 26.7$ , 8.2, 2.1 Hz, 2H), 7.24 (d,  $J = 8.2$  Hz, 4H), 7.21 – 7.06 (m, 12H), 4.62 (t,  $J = 6.7$  Hz, 2H), 3.54 (t,  $J = 7.3$  Hz, 2H), 2.66 – 2.49 (m, 8H), 1.99 – 1.92 (m, 2H), 1.62 – 1.51 (m, 12H), 1.42 – 1.24 (m, 28H), 1.22 (p,  $J = 7.4$  Hz, 2H), 1.10 (t,  $J = 7.9$  Hz, 2H), 1.02 (d,  $J = 7.5$  Hz, 2H), 0.97 – 0.80 (m, 18H).  $^{13}\text{C}$  NMR (176 MHz, Chloroform-*d*)  $\delta$  187.37, 161.82, 158.94, 155.94, 146.43, 146.33, 142.63, 138.38, 138.36, 138.01, 137.82, 134.98, 134.50, 132.89, 128.93, 128.59,

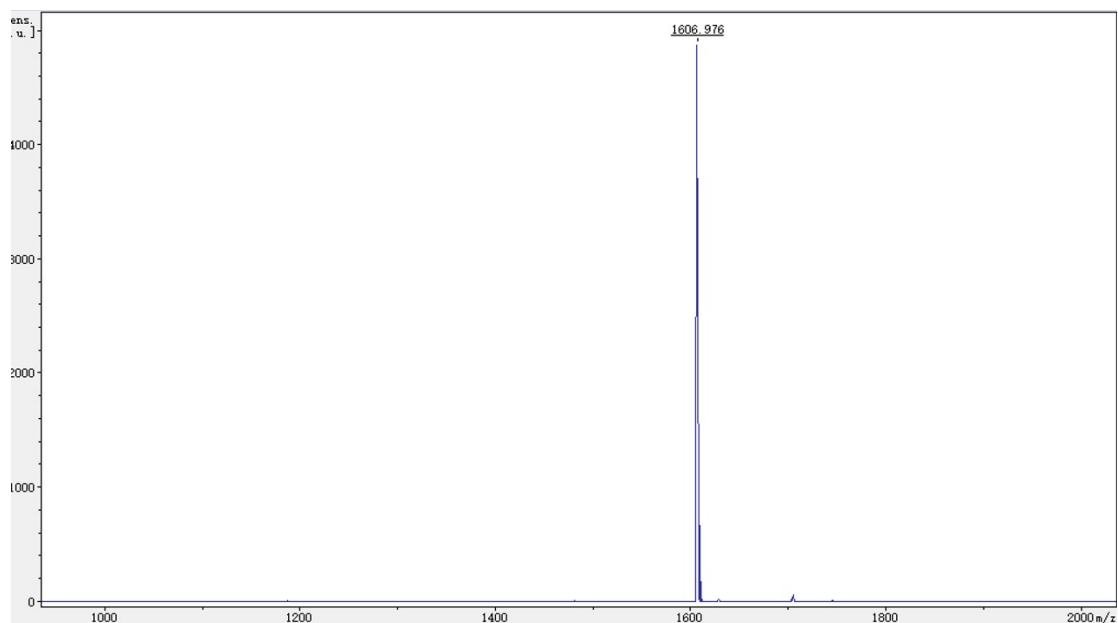
128.41, 127.85, 121.88, 119.63, 119.07, 118.83, 118.31, 115.04, 114.72, 114.55, 73.91, 67.79, 35.62, 35.53, 31.72, 31.71, 31.40, 31.35, 31.33, 31.26, 29.56, 29.33, 29.17, 29.10, 25.45, 24.82, 22.60, 22.57, 22.56, 14.12, 14.10, 14.05, 14.00. MS (MALDI-TOF):  $m/z$  Calcd. for  $C_{104}H_{104}F_2N_4O_4S_3$ : 1607.72 [M], Found 1606.98 [M]<sup>+</sup>.



<sup>1</sup>H-NMR spectrum of AITO-2F in CDCl<sub>3</sub>.

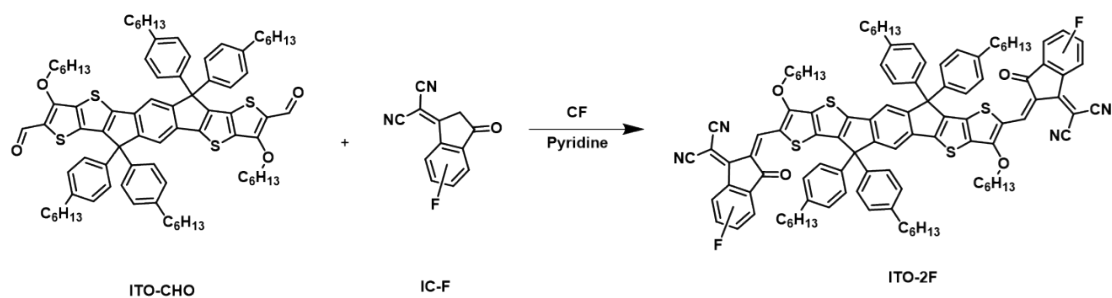


<sup>13</sup>C-NMR spectrum of AITO-2F in CDCl<sub>3</sub>.



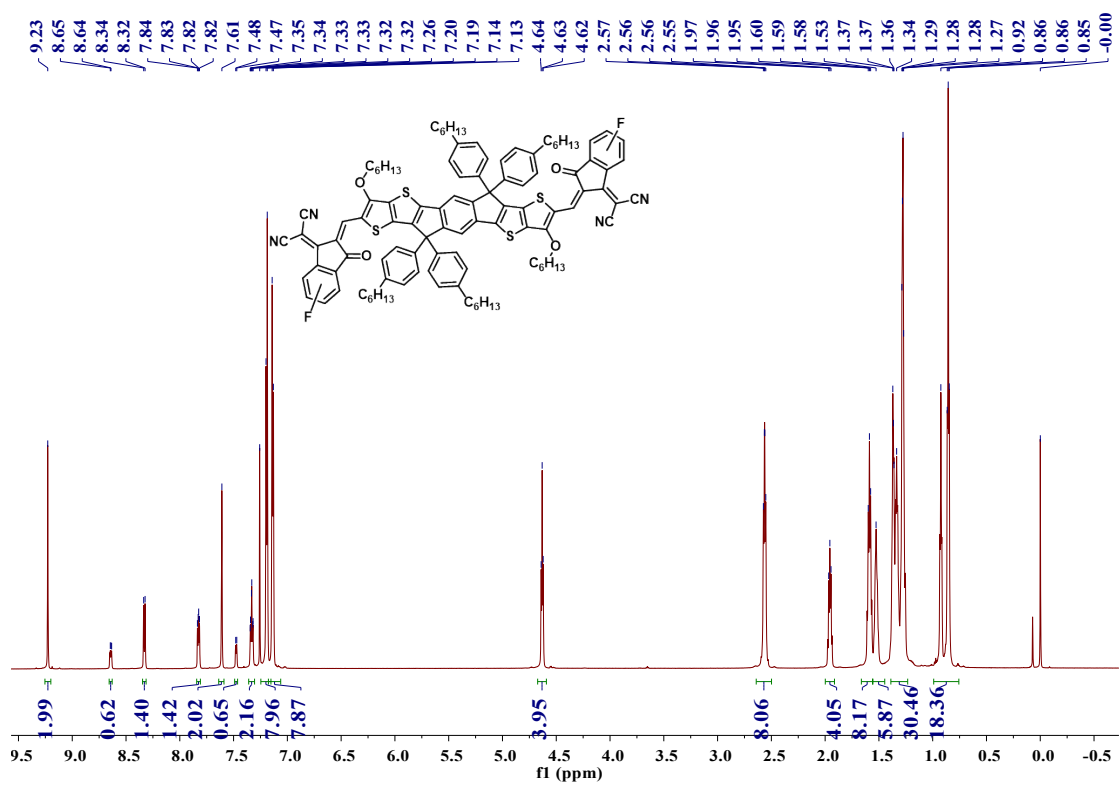
MALDI-TOF spectrum of AITO-2F.

## ITO-2F

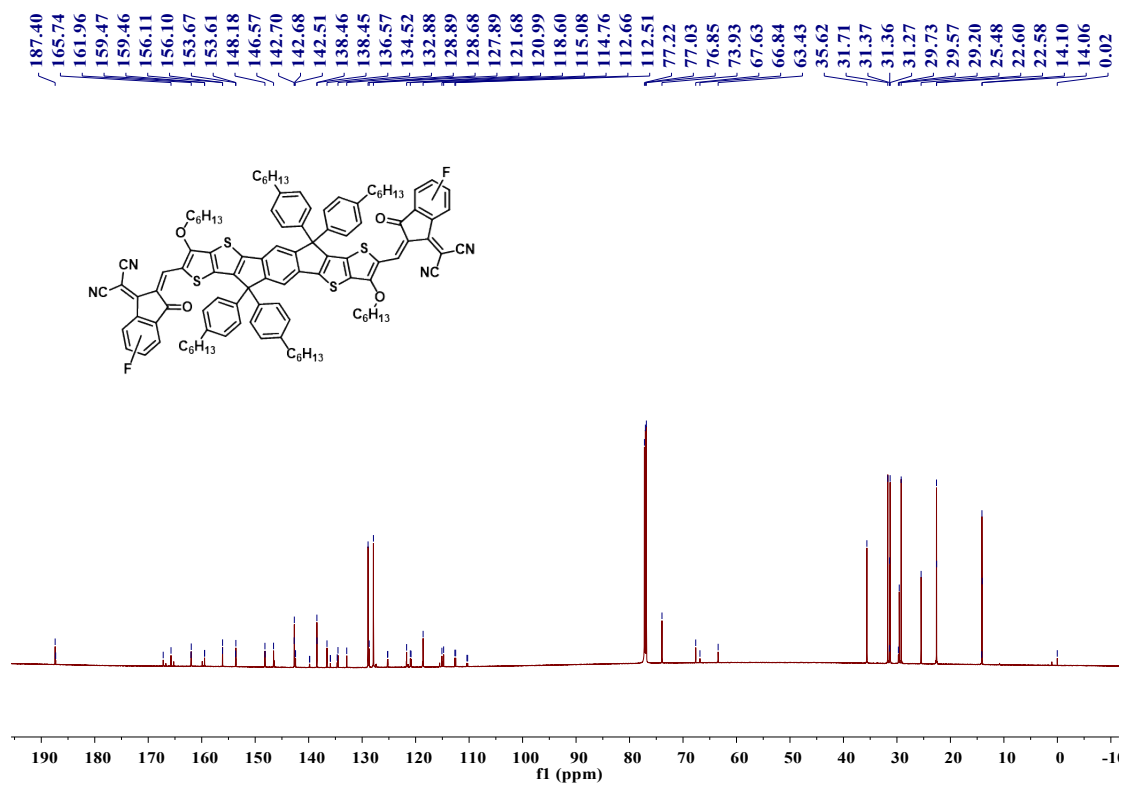


In a 50 mL of two-neck round bottom flask, ITO-CHO (140 mg, 0.115 mmol) and IC-F (97.4 mg, 0.459 mmol) were dissolved in 5 mL of CHCl<sub>3</sub>, and then 0.20 mL of pyridine was added into the mixture by syringe. The reaction was stirred at room temperature overnight. The solvent was removed under vacuum and the residue was purified by silica gel column using CHCl<sub>3</sub> as eluent. The product ITO-2F was obtained as blue black solid (110.9 mg, 85%).

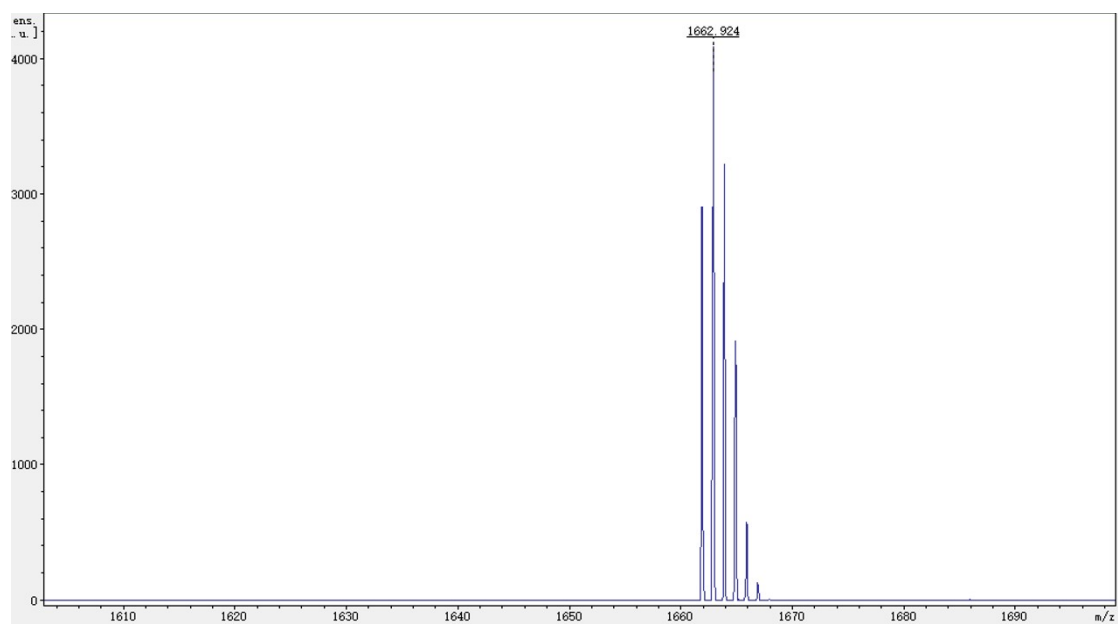
<sup>1</sup>H NMR (700 MHz, Chloroform-*d*) δ 9.23 (s, 2H), 8.66 – 8.63 (m, 1H), 8.33 (d, *J* = 9.0 Hz, 1H), 7.83 (dd, *J* = 8.3, 5.1 Hz, 1H), 7.61 (s, 2H), 7.48 (d, *J* = 6.8 Hz, 1H), 7.33 (td, *J* = 8.3, 2.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 8H), 7.14 (d, *J* = 7.9 Hz, 8H), 4.63 (t, *J* = 6.6 Hz, 4H), 2.56 (dd, *J* = 9.2, 6.5 Hz, 8H), 1.96 (t, *J* = 7.5 Hz, 4H), 1.59 (t, *J* = 7.7 Hz, 8H), 1.53 (s, 6H), 1.39 – 1.23 (m, 30H), 0.99 – 0.76 (m, 18H). <sup>13</sup>C NMR (176 MHz, Chloroform-*d*) δ 187.40, 161.96, 156.10, 153.61, 148.18, 146.57, 142.70, 142.68, 138.46, 136.57, 134.52, 132.88, 128.89, 128.68, 127.89, 125.26, 125.20, 121.68, 120.99, 118.60, 115.08, 114.76, 112.66, 112.51, 73.93, 67.63, 35.62, 31.71, 31.37, 31.27, 29.73, 29.57, 29.20, 25.48, 22.60, 22.58, 14.10, 14.06. MS (MALDI-TOF): *m/z* Calcd. for C<sub>106</sub>H<sub>104</sub>F<sub>2</sub>N<sub>4</sub>O<sub>4</sub>S<sub>4</sub>: 1663.69 [M], Found 1662.92 [M]<sup>+</sup>.



<sup>1</sup>H-NMR spectrum of ITO-2F in CDCl<sub>3</sub>.



<sup>13</sup>C-NMR spectrum of ITO-2F in CDCl<sub>3</sub>.



MALDI-TOF spectrum of ITO-2F.

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