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# Suppression of energy disorder by incorporating a small-molecule acceptor into all-polymer solar cells

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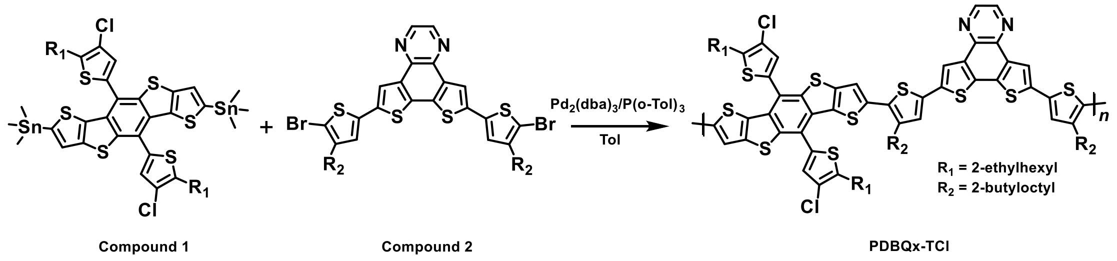
## *Materials and Methods*

### Materials

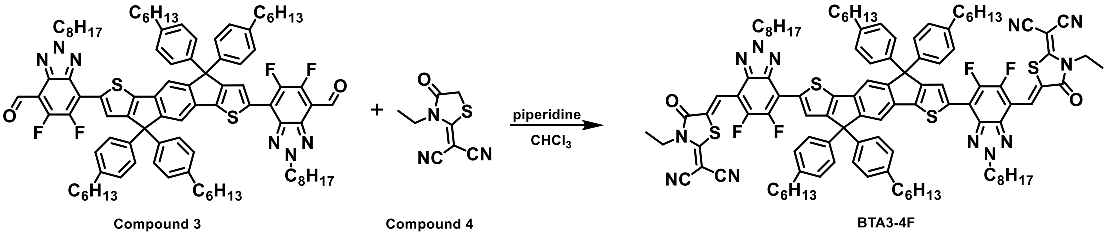
The non-fullerene polymer acceptor PY-IT is purchased from Solarmer (China). The polymer donor PDBQx-TCl is synthesized via the procedures shown in Scheme S1. The BTA3-4F was synthesized by the reaction given in Scheme S2. All the raw materials are purchased from commercial sources and directly used without further purification.

*Synthesis of PDBQx-TCl.* Compound 1 (0.2 mmol), Compound2 (0.2 mmol), $Pd_2(dba)_3$ (1.5mg), and $P(o\text{-Tol})_3$ (15mg) were added to 8 mL toluene and heated at 110 °C for 12 hours. After cooling to room temperature, the polymer material was precipitated in methanol (60 mL). The precipitates were dried and purified by Soxhlet extraction with methanol, hexanes, and chloroform. The polymer was recovered from the chloroform fraction. The solid (151 mg, yield 50 %) was dried under vacuum for 24 h before use. Anal. calcd for $C_{82}H_{94}Cl_2N_2S_{10}$ (%): C 67.29, H 7.09, N 1.75; found: C 67.05, H 7.17, N 1.67. The $M_n$ and PDI of PBQx-TCl estimated by HT-GPC are 44 kDa and 2.9, respectively.



**Scheme S1.** Synthesis procedure of the polymer PDBQx-TCl.

*Synthesis of BTA3-4F.* Compound 3 (200 mg) and Compound 4 (200 mg) were dissolved in 10 mL chloroform and then 0.3 mL piperidine was added. The reaction was carried on at room temperature for 24 hours. After the reaction, the mixed solution was directly subjected to silica gel column chromatography with pure chloroform as eluent. The product was obtained as black solid ((160 mg, yiled 65%).$^1$H NMR (300 MHz, Chloroform-d) $\delta$ = 8.32 (d, 4H), 7.60 (s, 2H),8.20 (s, 2H), 7.23 (d, 8H), 7.12 (d, 8H), 4.80 (t, *J*=6.9, 4H), 4.36(m, 4H), 2.57 (t, *J*=7.8, 8H), 2.23 (t, *J*=6.9, 4H), 1.62-0.84 (m). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ = 166.91, 166.62, 157.21, 154.56, 147.32, 147.24, 141.91, 141.54, 141.34, 137.20, 137.11, 137.06, 136.99, 135.81, 134.75, 128.52, 127.91, 124.00, 120.98, 120.95, 118.48, 117.15, 117.02, 113.07, 112.44, 107.59, 107.47, 63.17, 57.45, 55.43, 40.65, 35.60, 31.72, 31.36, 29.62, 29.18, 29.08, 28.86, 26.51, 22.60, 14.16, 14.09. Anal. calcd for $C_{110}H_{118}F_4N_{12}O_2S_4$ (%): C 71.41, H 6.43, N 8.7; found: C 71.28, H 6.43, N 8.69.



**Scheme S2.** Synthesis procedure of the polymer BTA3-4F.

*Fabrication and characterization of the OSC devices*

ITO-coated glass substrates were cleaned by a surfactant scrub and washed with water, acetone, and isopropanol, successively. Then, substrates were treated under UV-ozone for 15 minutes. A 10 nm thick layer of PEDOT:PSS was spin-coated on top of the ITO as an anode interlayer, and annealed for 15 min at 150 °C. The donor (D) PDBQx-TCl and acceptor (A) BTA3-4F were fully dissolved in chlorobenzene at a polymer weight concentration of 6 mg/mL with a D: A mass ratio of 1:1, and 0.5% (v/v) 1,8-iodooctane (DIO) was used as solvent additive. For the PDBQx-TCl:PY-IT based device, the D:A weight ratio is 1:1.2. For the ternary device, the weight ratio is PDBQx-TCl:BTA3-4F:PY-IT = 1:0.2:1. All the other conditions are as the PDBQx-TCl:BTA3-4F based binary device. The thickness of the active layers was about 110 nm as measured by a Bruker Dektak XT profilometer. Active layer films were thermally annealed at 100 °C for 10 min, and then PDINN was spin-coated on the top. Finally, about 80 nm Al was thermally evaporated onto the active layer under a high vacuum, giving an area of 3.70 mm$^2$. Except for the spin-coating of anode interlayer PEDOT:PSS, the other preparation processes were all carried out in a nitrogen-filled glove box.

_Instruments and Measurements_

A Bruker 300 spectrometer was used to measure the $^1$H and $^{13}$C NMR spectra of compounds at room temperature. Elemental analysis results of polymers were measured by a FLASH EA1112 elemental analyzer. Absorption spectra and molecular energy levels of the polymer and small molecular acceptors were measured on a Hitachi UH4150 UV-Vis spectrophotometer and a CHI650D Electrochemical Workstation, respectively. For the molecular energy level measurements, a glassy carbon disk, Pt wire, and a Ag/Ag$^+$ electrode as the working electrode, counter electrode, and reference electrode, respectively. 0.1 M $Bu_4NPF_6$ acetonitrile solution was used as an electrolyte, and ferrocene/ferrocenium was used as an external standard and measured in parallel. The HOMO and LUMO levels were calculated according to the equation, HOMO/LUMO = –e (φox/φred + 4.80–φFc/Fc+) (eV). Standard AM1.5 G solar simulator (100 mW·cm$^{-2}$) was used in the measurements of the photovoltaic performance of the PSC devices, and a NIM (National Institute of Metrology, China) calibrated cell was used as a reference. An integrated quantum efficiency measurement system named QE-R3011 (Enli Technology Co. Ltd., Taiwan) was used to record the EQE spectra of the devices, which was calibrated with a crystal silicon photovoltaic cell before use. The photo-CELIV measurements reported were performed by the all-in-one characterization platform Paios developed and commercialized by Fluxim AG, Switzerland. To reflect the true information, all of the devices are prepared for photoinduced charge extraction by linearly increasing voltage (photo-CELIV) measurements according to the corresponding device fabrication conditions. Highly sensitive EQE was measured using an integrated system (PECT-600, Enlitech), where the photocurrent was amplified and modulated by a lock-in instrument. $EQE_{EL}$ measurements were performed by applying external voltage/current sources through the devices (ELCT-3010, Enlitech). All the devices were prepared for $EQE_{EL}$ measurements according to the optimal device fabrication conditions. The AFM height and phase images were acquired on a Bruker Nanoscope V AF microscope in tapping mode. GIWAXS measurements were carried out by beamline BL02U2, Shanghai Synchrotron Radiation Facility (SSRF). The GIWAXS samples were deposited on the silicon substrate directly with the conditions which are same as that of device fabrication. Femtosecond transient absorption spectroscopy measurements were performed on an Ultrafast Helios pump-probe system in collaboration with a regenerative amplified laser system from Coherent. An 800 nm pulse with a repetition rate of 1 kHz, a length of 100 fs, and an energy of 7 mJ/pulse, was generated by a Ti:sapphire amplifier (Astrella, Coherent). Then the 800 nm pulse was 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 400 nm. The other part was focused onto a YAG plate to generate white light supercontinuum as the probe beams with spectra covering 400-800 nm and 750-1400 nm. The time delay between the 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 are 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 the pump pulse was measured and calibrated by a power meter (PM400, Thorlabs).

*DFT calculation*

The molecular geometries were optimized by Gaussian 09 with a functional of B3LYP and a basis set of 6-31G(d,p). The long alkyl chains were replaced by methyl or ethyl to save computation time. The density of states were obtained from a wavefunction-analysis software Multiwfn (J. Comput. Chem., 33: 580-592).

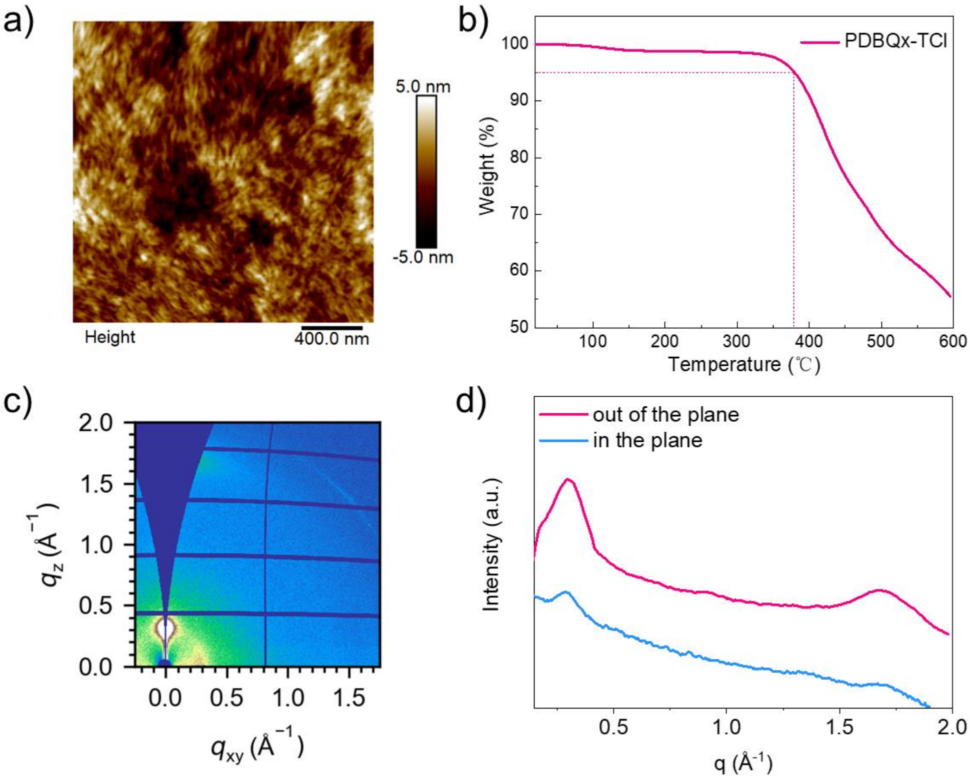


**Figure S1.** a) AFM height image, b) thermogravimetric analysis diagram, c) 2D-GIWAXS, and d) 1D-profile of the polymer PDBQx-TCl.

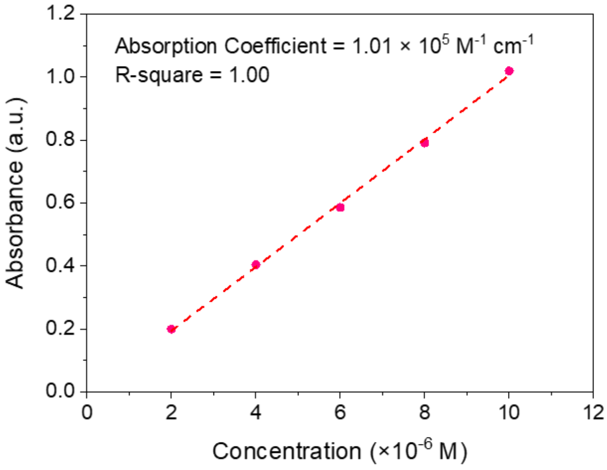


**Figure S2.** Absorption coefficient of the polymer PDBQx-TCl

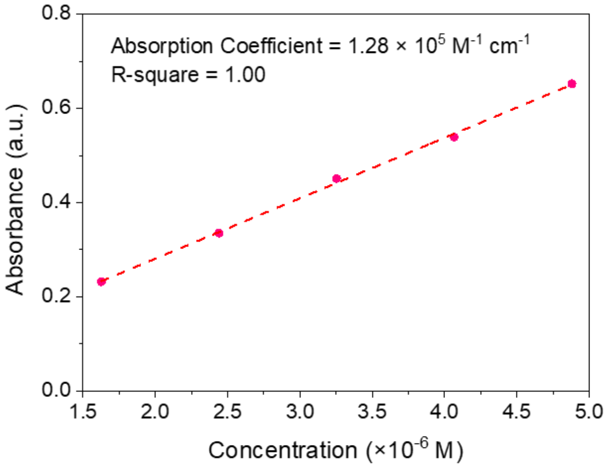


**Figure S3.** Absorption coefficient of the acceptor BTA3-4F.

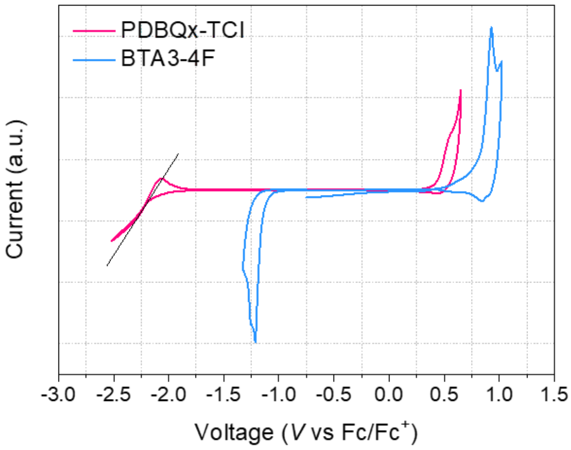


**Figure S4.** Cyclic voltammetry data of the polymer PDBQx-TCl and the acceptor BTA3-4F.

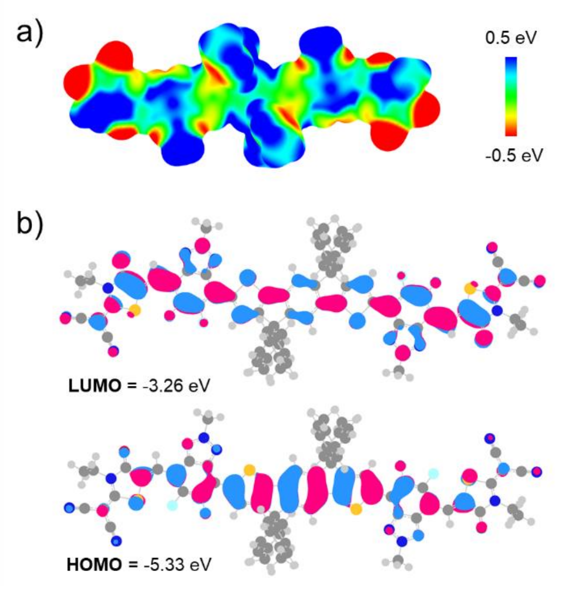


**Figure S5.** a) ESP distribution and b) molecular orbitals of the BTA3-4F.

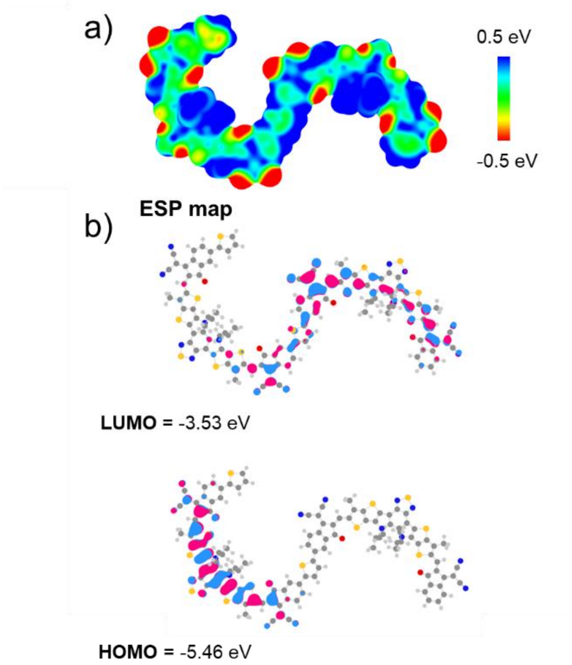


**Figure S6.** a) ESP distribution and b) molecular orbitals of the PY-IT.

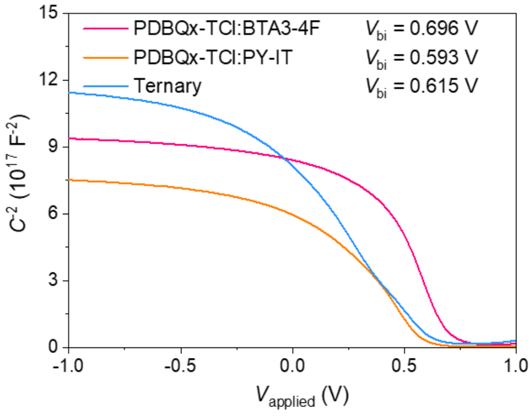


**Figure S7.** Capacitance-frequency characteristics of the three devices.

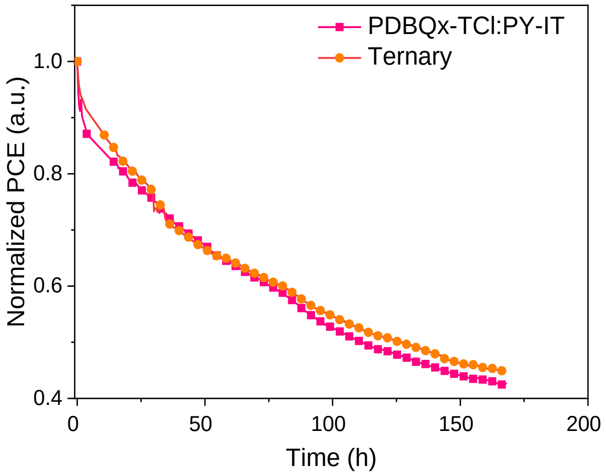


**Figure S8.** Photostability for encapsulated inverted devices measured under continuous LED illumination in the air.

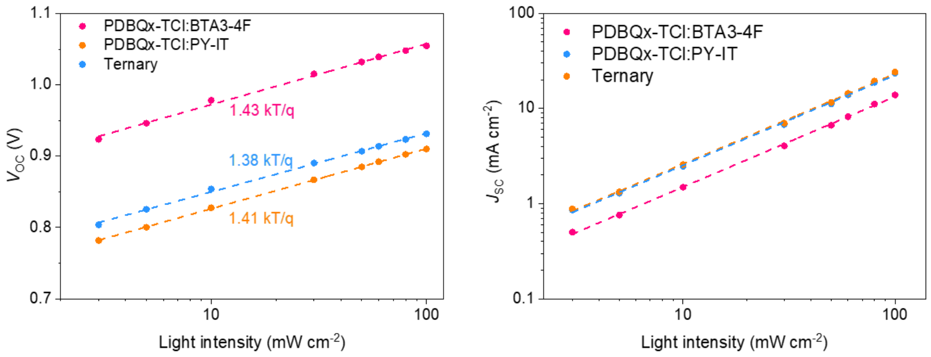


**Figure S9.** a) Voltage and b) Current densities versus light intensities of the devices.

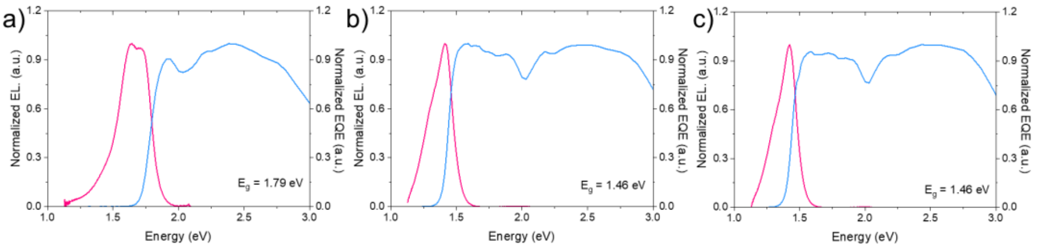


**Figure S10.** Normalized Electroluminescence (EL) counts and normalized EQE curves of **a)** PDBQx-TCl:BTA3-4F, **b)** PDBQx-TCl:PY-IT and **c)** PDBQx-TCl:BTA3-4F:PY-IT for determining bandgaps.

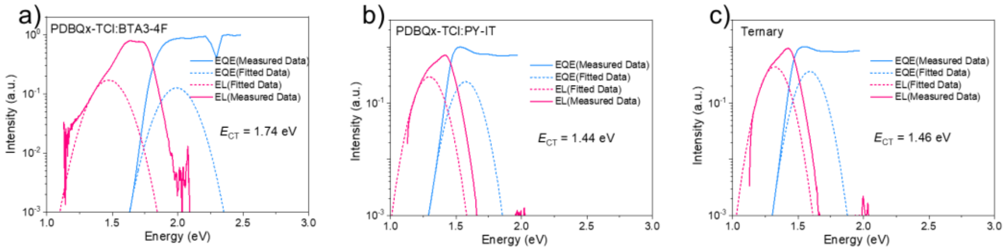


**Figure S11.** Reduced EL and s-EQE and their fitted curves of **a)** PDBQx-TCl:BTA3-4F, **b)** PDBQx-TCl:PY-IT and **c)** PDBQx-TCl:BTA3-4F:PY-IT.

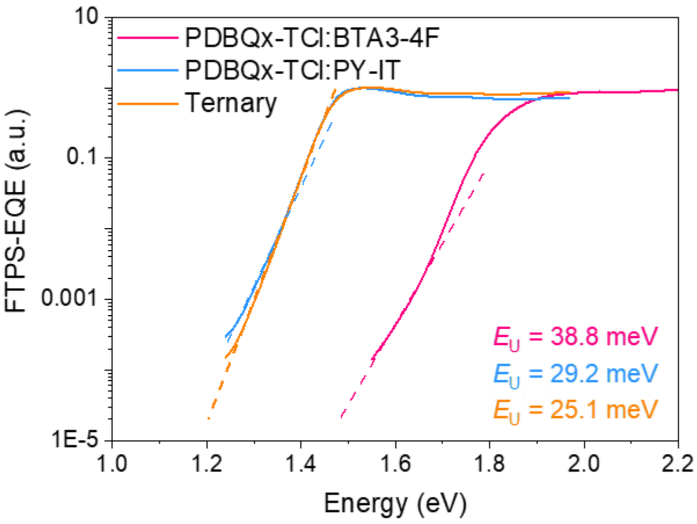


**Figure S12**. Highly sensitive EQE curves of the devices

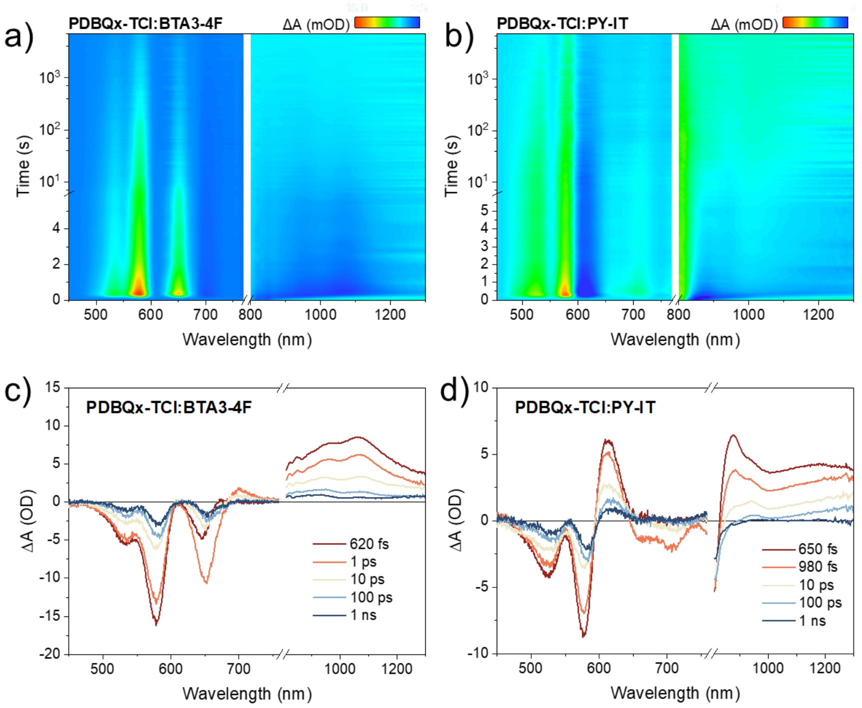


**Figure S13.** 2D TA profiles of a) PDBQx-TCl:BTA3-4F and b) PDBQx-TCl:PY-IT. TA spectra at different time delays of a) PDBQx-TCl:BTA3-4F and b) PDBQx-TCl:PY-IT.

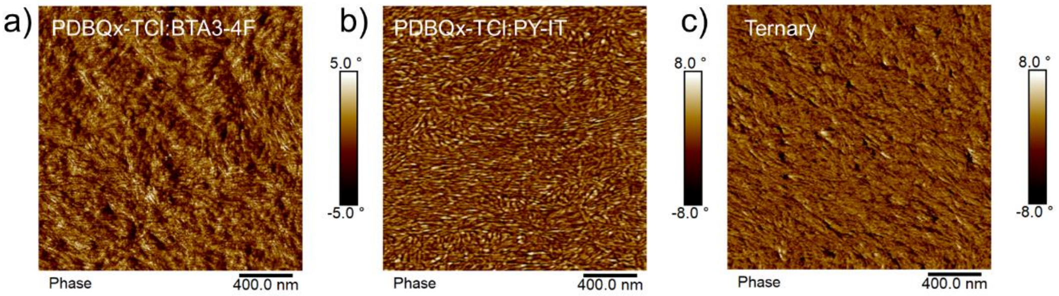
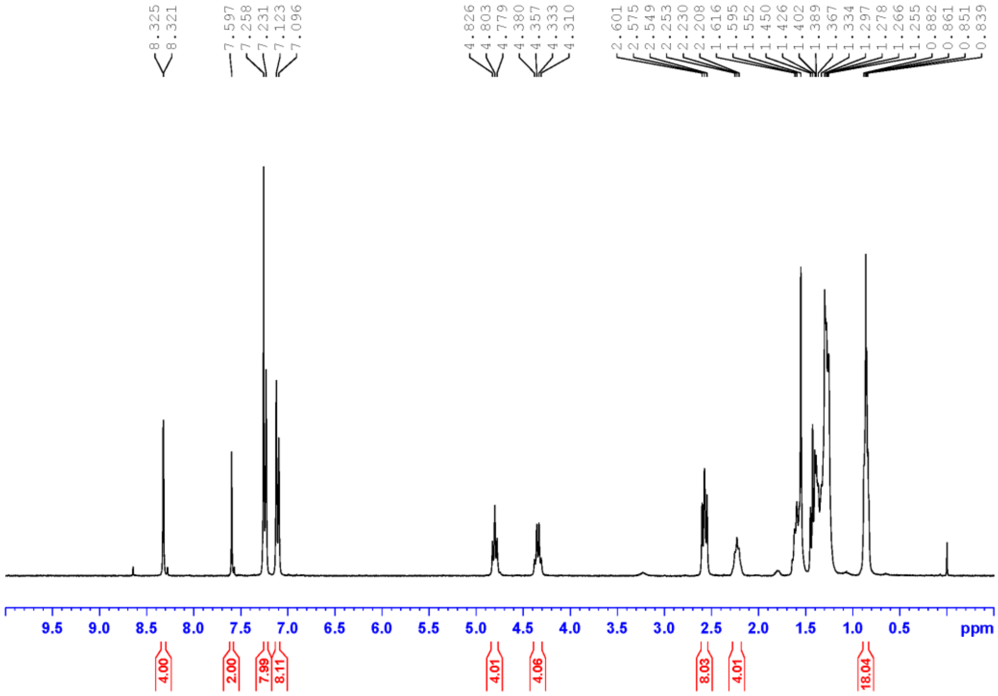
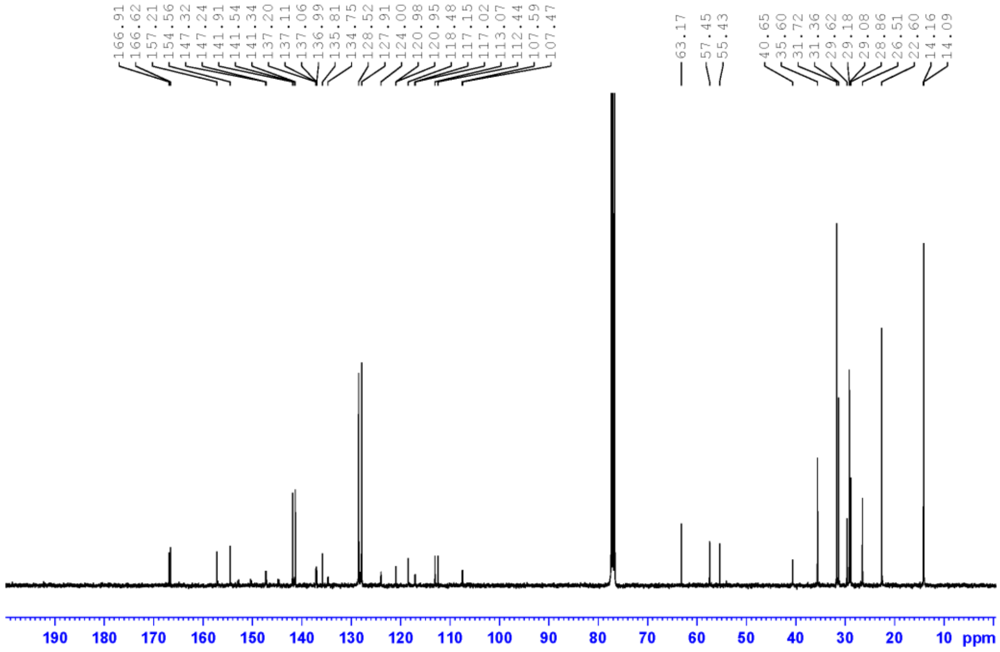


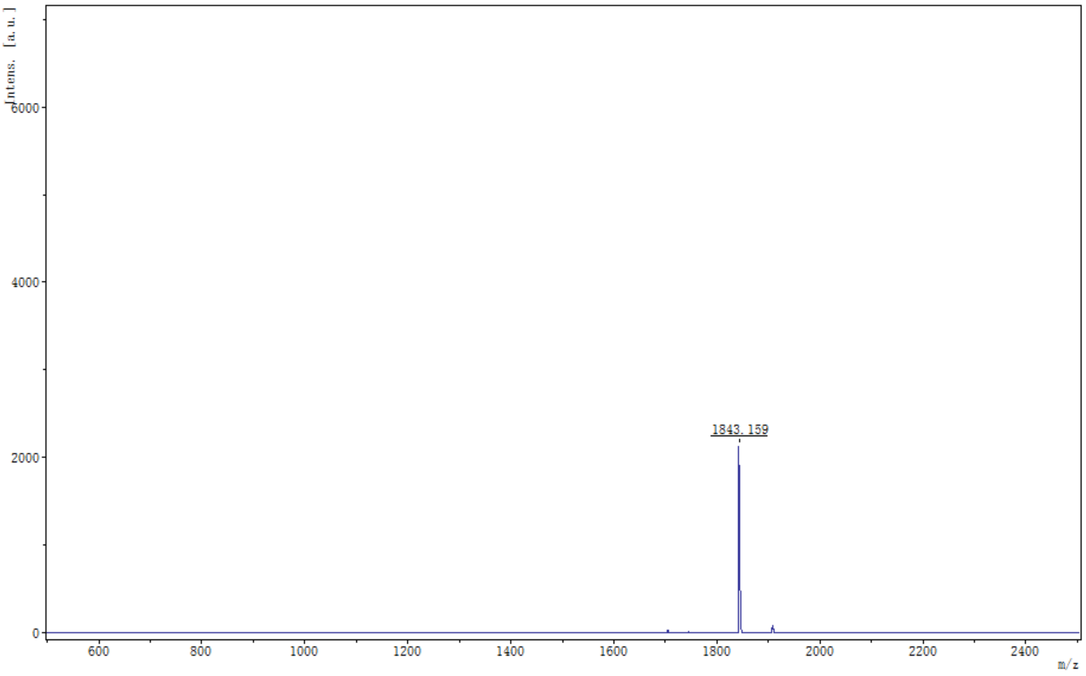
**Figure S14.** AFM height images of **a)** PDBQx-TCl:BTA3-4F, **b)** PDBQx-TCl:PY-IT and **c)** PDBQx-TCl:BTA3-4F:PY-IT.



$^{1}$H NMR of BTA3-4F.



$^{13}$C NMR of BTA3-4F.



MALDI-TOF result of BTA3-4F.

**Figure S15.** Characterizations of BTA3-4F.

**Table S1.** Summary of photovoltaic parameters of the state-of-the-art PSCs mainly based on polymer donor and polymer acceptors.

| Device | $V_{OC}$ (V) | $J_{SC}$ (mA cm$^{-2}$) | FF(%) | PCE(%) | Ref (DOI number) |
|---|---|---|---|---|---|
| PBDB-T:PY-T | 0.91 | 23.07 | 77.0 | 16.05 | 10.1016/j.nanoen.2021.106858 |
| JD40:PJTVT | 0.89 | 23.75 | 76.4 | 16.13 | 10.1002/aenm.202102559 |
| PM6:PYT-1S1Se | 0.926 | 24.1 | 73 | 16.3 | 10.1007/s11426-021-1140-x |
| PM6:PYT:PY2F-T | 0.90 | 25.2 | 76.0 | 17.2 | 10.1016/j.joule.2021.04.007 |
| PQM-Cl:PY-IT | 0.920 | 24.3 | 80.7 | 18.0 | 10.1002/adma.202205009 |
| PM6:PY-82:PY-DT | 0.947 | 24.31 | 78.3 | 18.03 | 10.1002/adma.202208165 |
| PQB-2:PY-IT | 0.942 | 24.2 | 0.795 | 18.1 | 10.1039/D2EE03535A |
| PM6:PY-IT: PYFCl-T | 0.940 | 25.76 | 74.84 | 18.12 | 10.1002/adma.202211296 |
| PY-SSe-V:PY-Cl | 0.910 | 25.88 | 77.04 | 18.14 | 10.1002/adma.202209350 |
| PM6:PY-DT:Y6 (1:1:0.02) | 0.945 | 24.51 | 77.8 | 18.02 | 10.1002/adma.202301906 |
| PDBQx-TCl:BTA3-4F:PY-IT (1:0.2:1, w/w) | 0.934 | 24.9 | 79.8 | 18.6 | this work |