

Supplementary Information

Molecular design of a non-fullerene acceptor enables P3HT-based organic solar cell with 9.46% efficiency

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1. Experimental Section

1.1 Materials and synthesis

IO-4H, IO-4Cl and ZY-4Cl were synthesized according to the same method in previous works.¹ P3HT ($M_w = 50$ -70k; PDI = 2.0-2.5; Regioregularity = 91-94%), ITIC, IT-4Cl and BTP-4Cl were purchased from Solarmer Material Inc. in Beijing.

The synthesis routes of TT-O and TT-CN are shown in Scheme S1. Here, 5,6-dichloro-1H-indene-1,3(2H)-dione (**2**) and 2-(5,6-dichloro-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile (**3**) were purchased from Solarmer Materials Inc.. 5-hexylthieno[3,2-b]thiophene-2-carbaldehyde (**1**) was synthesized following the reported procedures.²

Compound **1** (210 mg, 0.83 mmol) and **2** (270 mg, 1.25 mmol) were dissolved in 10 mL of CHCl_3 under nitrogen protection, and 0.3 mL of pyridine was added into the solution dropwise. Then, the reaction was stirred overnight at room temperature. The mixture was directly purified by silica gel column chromatography using dichloromethane as the eluent to yield the product as a yellow solid (306 mg, yield 82%). ^1H NMR (CDCl_3 , 400 MHz), δ (ppm): 8.36 (s, 1H, Ar H), 8.03 (s, 1H, Ar H), 7.58 (s, 2H, Ar H), 7.05 (s, 1H, Ar H), 2.95 (t, 2H, CH_2), 1.76 (m, 2H, CH_2), 1.42-1.33 (m, 6H, CH_2), 0.92 (t, 3H, CH_3) (Fig. S7). The synthetic process of TT-CN is the same as that of TT-O, and a red solid was obtained as last. ^1H NMR (CDCl_3 , 400 MHz), δ (ppm): 8.94 (s, 1H, Ar H), 8.76 (s, 1H, Ar H), 8.05 (s, 1H, Ar H), 7.95 (s, 1H, Ar H), 7.09 (s, 1H, Ar H), 2.97 (t, 2H, CH_2), 1.77 (m, 2H, CH_2), 1.42 (m, 2H, CH_2), 1.34 (m, 4H, CH_2), 0.90 (t, 3H, CH_3) (Fig. S8).

1.2 Device fabrication

The Indium tin oxide (ITO)-coated glass substrates were pre-cleaned by sequential ultrasonication in deionized water, acetone and isopropanol for 30 min each. After 20 min of ultraviolet-ozone treatment, a thin layer of 15 nm thick PEDOT:PSS was spin-coated onto the substrates as the anode interlayer and annealed at 150 °C for 15 min. Subsequently, the substrates were transferred into the nitrogen-filled glove box. Then the active layer solution was spin-coated on the PEDOT:PSS layer to form the 100 nm thick active layer, followed with thermal annealing at 130 °C for 10 min. P3HT:ITIC, P3HT:IO-4H, P3HT:IT-4Cl and P3HT:IO-4Cl solution were prepared with a donor/acceptor (D/A) weight ratio of 1:0.6 in chloroform at a concentration of 8 mg mL^{-1} , and 0.5% vol chloronaphthalene was added in P3HT:IT-4Cl and P3HT:IO-4Cl solution. For P3HT:BTP-4Cl and P3HT:ZY-4Cl, the D/A ratio is 1:1, and the solution was prepared in tetrahydrofuran at a concentration of 7 mg mL^{-1} . Then PFN-Br methanol solution (0.5 mg mL^{-1}) was spin-coated on the active layer to give a 5 nm thick cathode interlayer. Finally, about 100 nm thick of Al was deposited onto the active layer under high vacuum, giving an effective cell area of 3.90 mm^2 .

1.3 Instruments and measurements

Flory-Huggins interaction parameters (χ) were estimated by the following equation:

$$\chi = \alpha \frac{V_{ref}}{RT} \left[(\delta_{d1} - \delta_{d2})^2 + \frac{1}{4}(\delta_{p1} - \delta_{p2})^2 + \frac{1}{4}(\delta_{h1} - \delta_{h2})^2 \right]$$

Where δ_d , δ_p and δ_h respectively represent the dispersive, polar and hydrogen bonding forces of Hansen solubility parameters (HSPs), and their values for P3HT and acceptors are listed in Table S1; α is a correction coefficient (~ 0.5); V_{ref} is a reference molar volume (geometric mean of polymer and SMAs); the $1/4$ prefactor associates with the polar and hydrogen-bonding contribution relates to the shape of the “solubility spheroid” defined in the three-dimensional (d, p, h)-space.

Differential scanning calorimetry measurements were performed using a TA Instruments differential scanning calorimeter (Q2000) under nitrogen at a heating rate of 10 °C min^{-1} . It should be noted that the weight ratio of 1:0.6 in DSC measurements for the P3HT:TT-CN and P3HT:TT-O blends is derived from the weight ratio of 1:1 for donor and acceptor used in P3HT:BTP-4Cl- and P3HT:ZY-4Cl-based devices, respectively.

Atomic force microscopy images were acquired on a Nanoscope V AFM (Bruker) by tapping mode.

Cyclic voltammetry measurements were conducted on a CHI650D electrochemical workstation. The acceptor neat films were coated on the glassy-carbon electrode (working electrode) and measured in 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution at a potential scan rate of 0.1 V s⁻¹. Platinum-wire and Ag/Ag⁺ electrode was respectively used as counter electrode and reference electrode to measure the onset of oxidation and reduction potentials of the materials. Ferrocene/ferrocenium (Fc/Fc⁺) was measured as an internal standard with an absolute energy level of 4.8 eV below vacuum. The HOMO and LUMO levels can be calculated by the equation of $E_{\text{HOMO}}/E_{\text{LUMO}} = -e (\phi_{\text{ox}}/\phi_{\text{red}} + 4.8 - \phi_{\text{Fc/Fc}^+})$ (eV).

UV-visible absorption spectra were recorded on a Hitachi UH4150 spectrophotometer.

J-V measurements were performed via solar simulator (SS-F5-3A) under 100 mW cm⁻² of the standard AM 1.5G spectrum, which is calibrated by a certified standard silicon solar cell (SRC-2020, Enlitech).

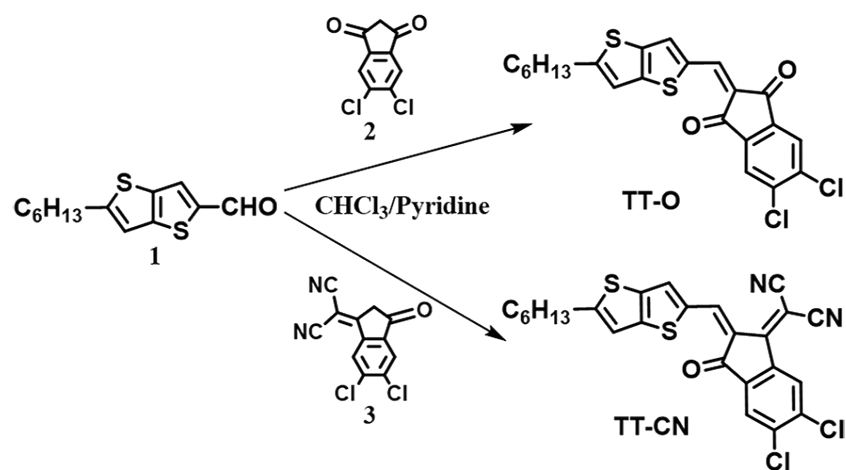
External quantum efficiency was measured by solar cell spectral response measurement system QE-R3011 (Enlitech Co, Ltd.).

SCLC charge mobility measurement was conducted with the device structure of ITO/PEDOT:PSS/neat or blend film/Au for hole and ITO/ZnO/neat or blend film/Al for electron. The charge mobilities were calculated by the equation $J = (9/8)\epsilon\epsilon_0\mu_0 V^2 \exp(0.89\sqrt{V/EE_0})/L^3$, where ϵ is the dielectric constant of the polymer; ϵ_0 is the permittivity of the vacuum; μ_0 is the zero-field mobility; E_0 is the characteristic field; J is the current density; L is the thickness of the blended films layer; $V = V_{\text{appl}} - V_{\text{bi}}$, V_{appl} is the applied potential, and V_{bi} is the built-in potential which results from the difference in the work function of the anode and the cathode (in this contribution, $V_{\text{bi}} = 0.2$ V).

¹H NMR spectra were recorded on a BRUKER Fourier 300 spectrometer.

GIWAXS measurements were conducted on a Xeuss 2.0 SAXS/WAXS system (Xenocs SA, France). with X-ray wavelength of 1.5418 Å. The film samples were irradiated at a fixed angle of 0.3°.

2. Results and Discussion



Scheme S1 The synthesis routes of TT-O and TT-CN.

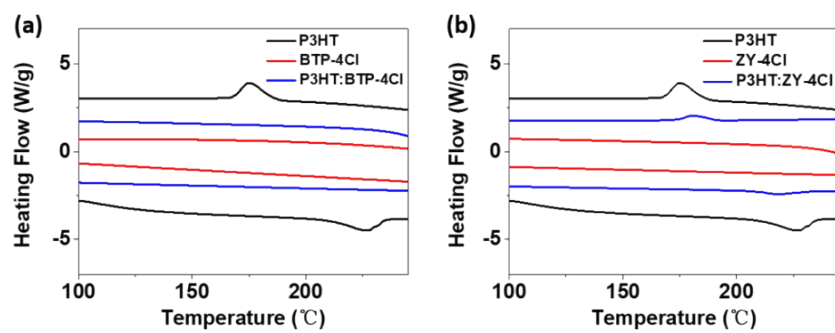


Fig. S1 DSC curves (exo up) of P3HT, BTP-4Cl, ZY-4Cl and their blends.

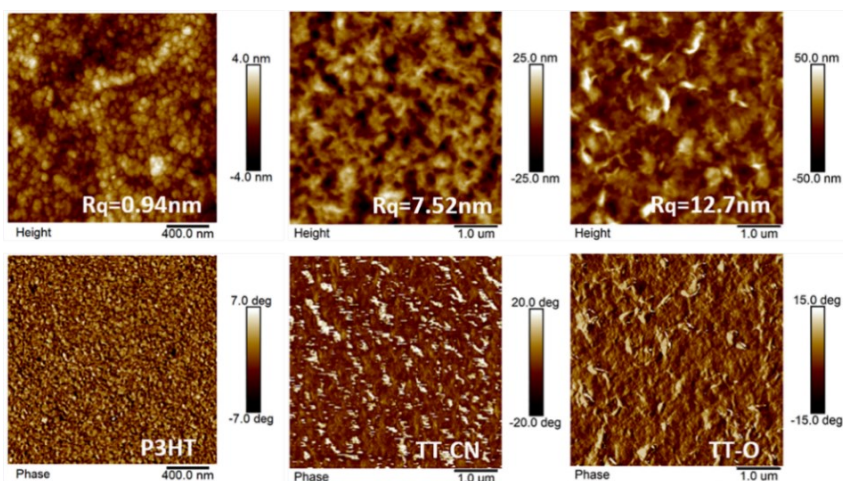


Fig. S2 AFM images of P3HT, TT-CN and TT-O.

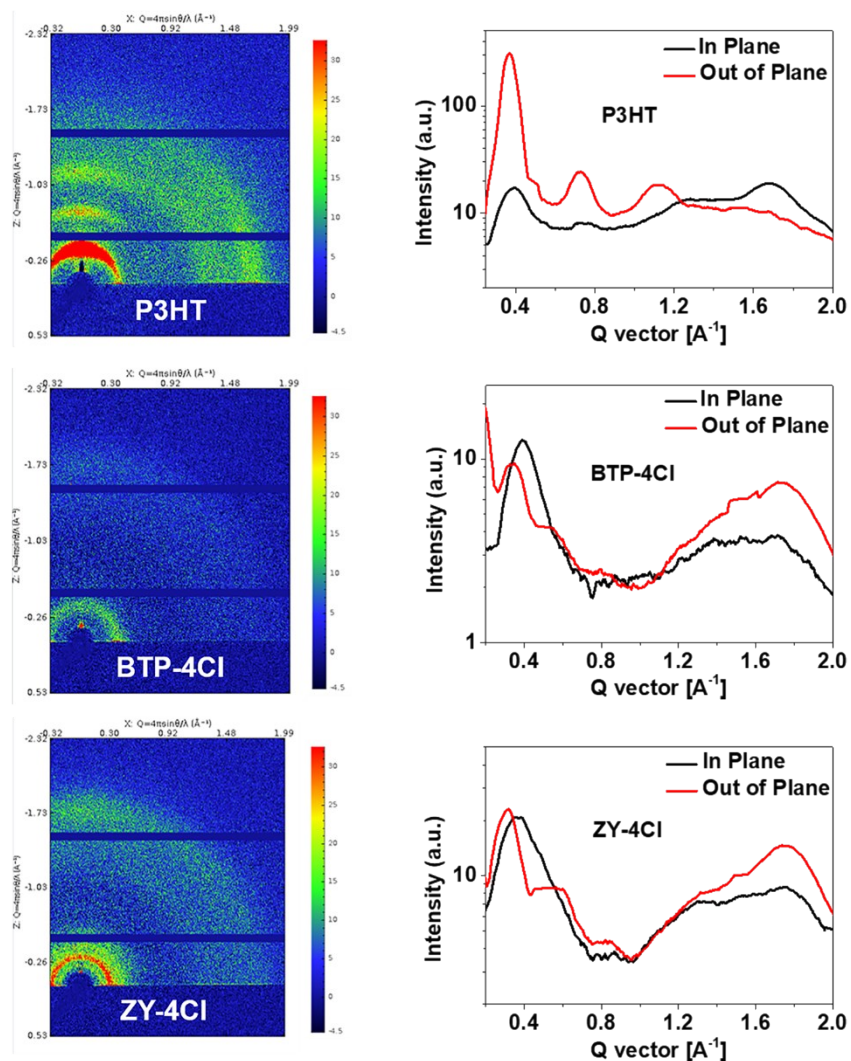


Fig. S3 GIWAXS images and intensity profiles of P3HT, BTP-4Cl and ZY-4Cl neat films.

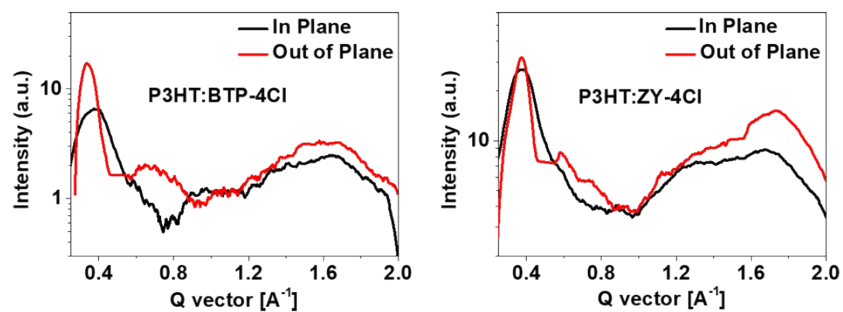


Fig. S4 1D profiles of GIWAXS for P3HT:BTP-4Cl and P3HT:ZY-4Cl blend films.

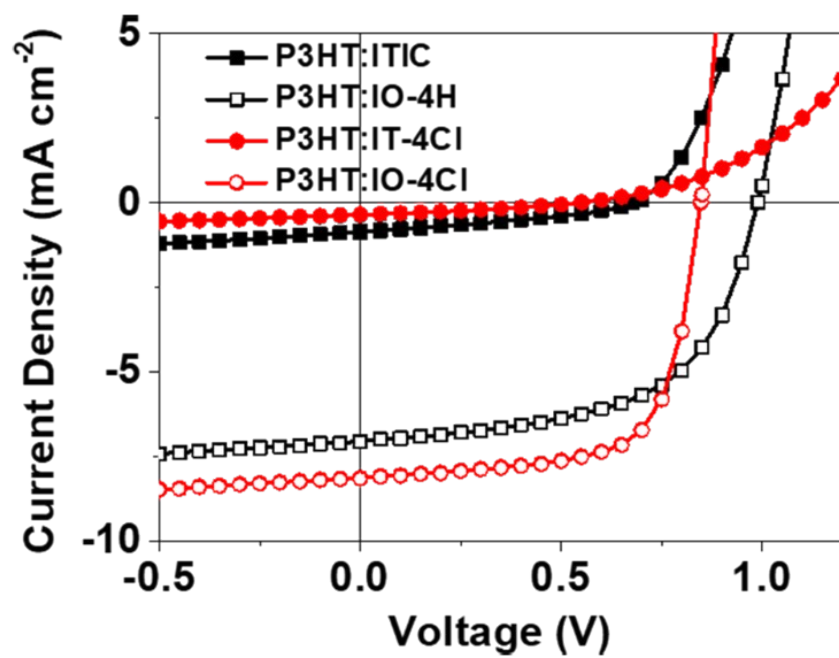


Fig. S5 J - V curves of P3HT-based devices.

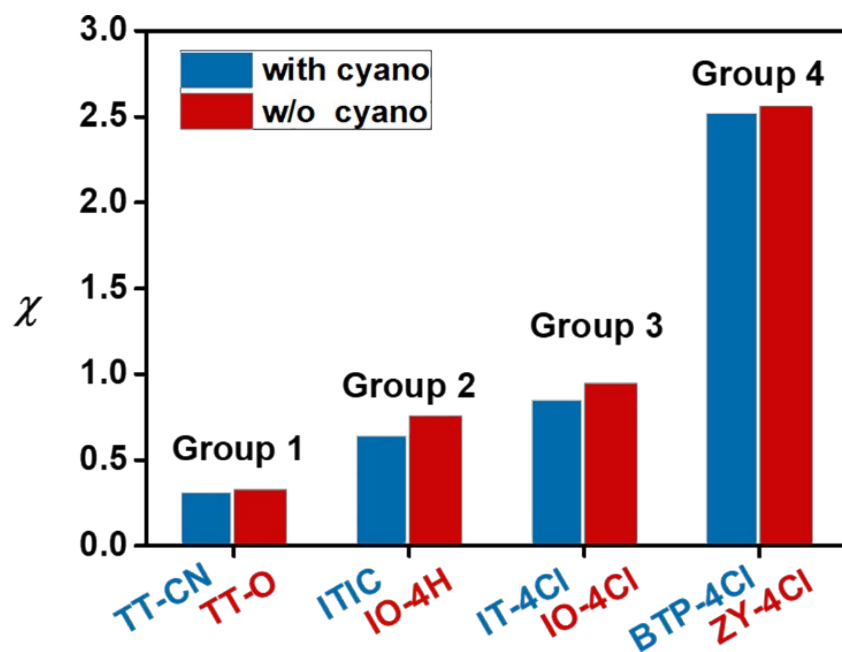


Fig. S6 χ parameters of P3HT-based blend films.

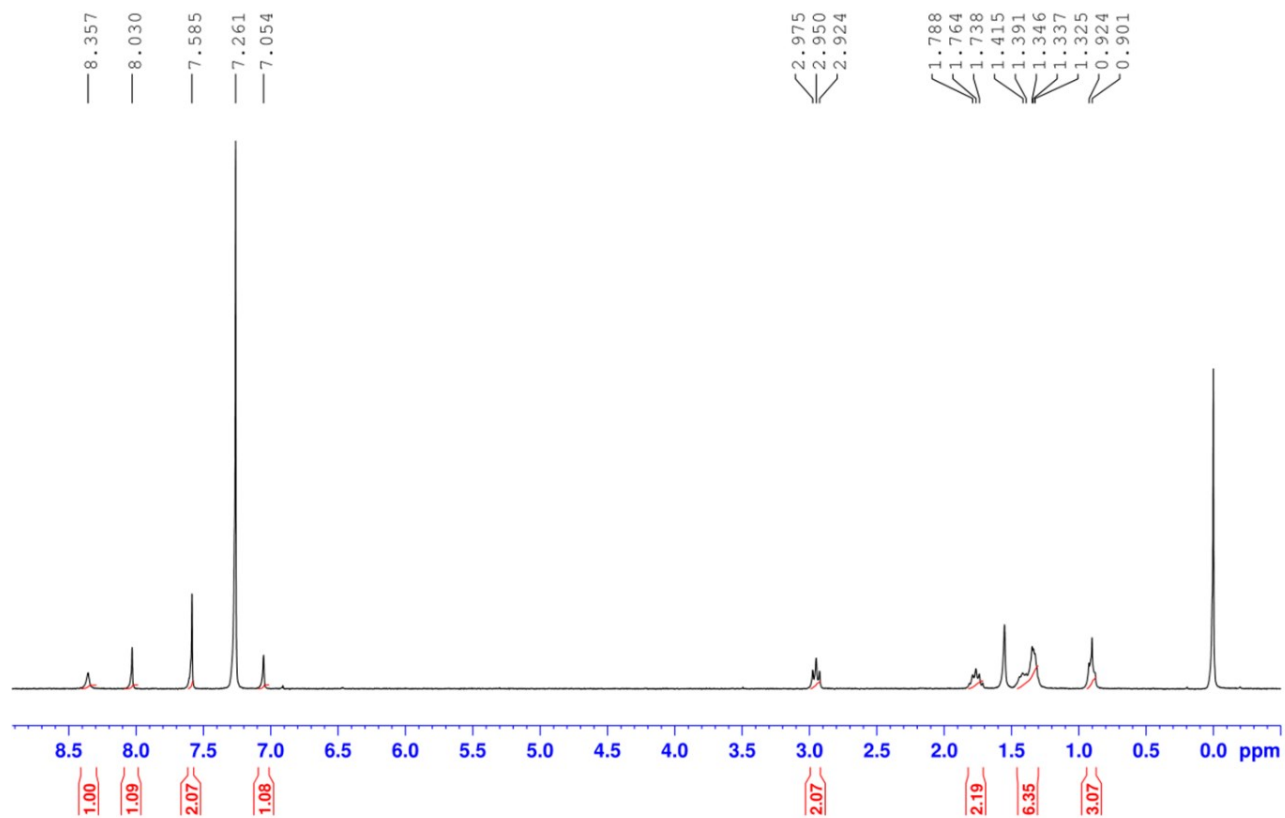


Fig. S7 ¹H NMR spectrum of TT-O.

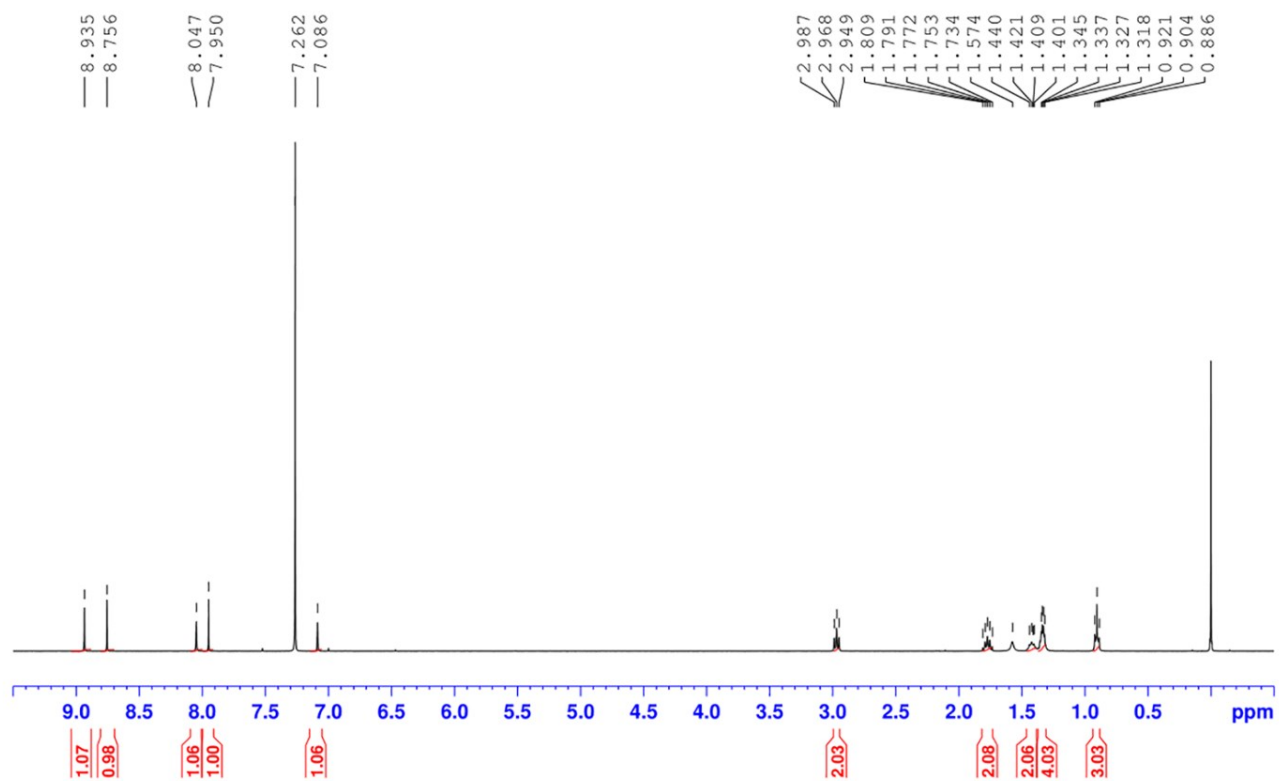


Fig. S8 ¹H NMR spectrum of TT-CN.

Table S1 δ_d , δ_p , δ_h of P3HT and acceptors.

HSPs	P3HT ^a	BTP-4Cl	ZY-4Cl	TT-CN	TT-O
δ_d	18.50	21.73	21.80	19.80	20.16
δ_p	4.10	2.79	2.40	5.51	4.59
δ_h	4.20	5.93	5.65	5.37	4.82

^a δ_d , δ_p , δ_h of P3HT sourced from Leman, D et al. *Macromolecules*, 2015, **48**, 383-392.³

Table S2. Photovoltaic results of the device optimization process for P3HT:ZY-4Cl-based OSCs.

D/A	Solvent	TA ^a	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%)
1:0.6	CF	130 °C	0.82	9.10	0.44	3.31
1:1	CF	130 °C	0.79	14.28	0.50	5.60
1:1.5	CF	130 °C	0.75	13.19	0.43	4.28
1:1	CB	130 °C	0.86	10.56	0.57	5.14
1:1	<i>o</i> -xylene	130 °C	0.88	12.86	0.61	6.90
1:1	THF	130 °C	0.88	16.49	0.65	9.46
1:1	THF	110 °C	0.87	16.47	0.59	8.42
1:1	THF	150 °C	0.86	14.51	0.60	7.48

^a Annealing time is 10 min.

Table S3. Photovoltaic parameters of the P3HT-based OSCs.

Acceptors	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF	PCE (%) ^a
ITIC	0.68	0.85	0.35	0.20 (0.19±0.02)
IO-4H	0.99	7.05	0.58	4.04 (3.87±0.13)
IT-4Cl	0.55	0.38	0.31	0.06 (0.06±0.01)
IO-4Cl	0.85	8.14	0.68	4.70 (4.50±0.19)

^a Average value ± SD from more than ten devices.

3. References

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