Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

## Supporting Information

# A new non-fullerene acceptor based on the combination of Heptacyclic Benzothiadiazole Unit and thiophene-fused end group achieving over 13% efficiency

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## 1. Characterizations

$^{1}H$ NMR and $^{13}C$ NMR were recorded using Bruker DMX-400 spectrometer with deuterated chloroform as solvent at 298 K. Chemical shifts were reported as *ä*values (ppm) with tetramethylsilane(TMS) as the internal reference. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA-7 with a heating rate of 10 K/min under nitrogen. UV-Vis absorption spectra were recorded on the Shimadzu UV-2600 spectrophotometer. Cyclic voltammetry (CV) was recorded with a computer controlled CHI660E electrochemical workstation using Y10 film on platinum electrode (1.0 cm$^2$) as the working electrode, a platinum wire as the counter electrode and Ag/AgCl (0.1 M) was used as reference electrode in an anhydrous and argon-saturated solution of 0.1 M of tetrabutylammonium hexafluorophosphate ($Bu_4NPF_6$) in acetonitrile at a scan rate of 50 mV s$^{-1}$. The morphologies of the J11:Y10 blend films were investigated by atomic force microscopy (AFM, Agilent Technologies, 5500 AFM/SPM System, USA) in contacting mode with a 5 μm scanner. Transmission electron microscope (TEM) measurements were performed in a JEM-2100F.

## 2. Fabrication and measurement of devices

Solar cells were fabricated in the configuration of the traditional structure with an indium tin oxide (ITO) glass positive electrode and a metal Al negative electrode. The ITO glass was cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone and isopropanol, and UV-treated in ultraviolet–ozone chamber (Jelight Company, USA) for 15 min. The PEDOT:PSS(poly(3,4-ethylene dioxythiophene): poly(styrene sulfonate)) (Baytron PVP Al 4083, Germany) was filtered through a 0.45 μm filter and spin coated at 3000 rpm for 40 s on the ITO substrate. Subsequently, the PEDOT: PSS film was baked at 150 ºC for 20 min in the air, and the thickness of the PEDOT: PSS layer is about 30 nm. TheJ11:Y10 blend was dissolved in chloroform (CF) and 1-chloronaphthalene (CN) (0.8 %, v/v) and spin-cast at 3000 rpm for 30s onto the PEDOT: PSS layer. After cooling to room temperature, methanol solution of PDINO at a concentration of 1.0 mg/mL was deposited atop the active layer at 3000 rpm for 30 s to afford a thickness of 15 nm. Finally, top Al electrode was deposited in vacuum onto the cathode buffer layer at a pressure of ca. $10^{-5}$ Pa. The active area of the device was 5 $mm^2$. Device characterization was carried out under AM 1.5G irradiation with the intensity of 100 mW $cm^{-2}$ (Oriel 67005, 500 W) calibrated by a standard silicon cell. *J-V* curves were recorded with a Keithley 236 digital source meter. The EQE measurements of OSCs were performedby Stanford Systems model SR830 DSP lock-in amplifier coupled withWDG3 monochromator and 500 W xenon lamp. A calibrated silicon detector was used to determine the absolute photosensitivity at different wavelengths. All of these fabrications and characterizations were conducted in a glove box.

The configurations of the hole-only or electron-only diodes were using the ITO/PEDOT:PSS/J11:Y10/Au for holes and ITO/ZnO/J11:Y10/PDINO/Al for electrons. The hole and electron mobilities were extracted by fitting the plots of the current density–voltage curves using the space-charge-limited current (SCLC) model. The SCLC is described by modified Mott-Gurney law.

## 3. Materials

Compound was prepared previously from our lab. All other reagents and solvents such as anhydrous tetrahydrofuran (THF), pyridine, chloroform, o-dichlorobenzene (o-DCB), N, N-dimethylformamide (DMF) and methanol were dried and distilled before use. Compound TPBT was synthesized according to literature procedures.[1]

## 4. The specific synthesis steps

Synthesis of 12, 13-bis(2-ethylhexyl)-3, 9-diundecyl-12, 13-dihydro[1, 2, 5]thiadiazole[3, 4-e]thieno[2”, 3”:4, 5]thieno[2’, 3’:4, 5]pyrrolo[3, 2-g]thieno[2’, 3’:4, 5]thieno[3, 2-b]indole-2, 10-dicarbaldehyde (TPBT-CHO)

To a solution of compound TPBT (490 mg, 0.500mmol) in DMF (20 mL) at 0 °C was added phosphorus oxychloride (1.20 mL, 12.9mmol) dropwise slowly under nitrogen. The mixture was stirred at 0 °C for 2 h, and then the solution was heated to 80 °C and stirred overnight. The reaction mixture was poured into ice water (150 mL), and then extracted with dichloromethane twice. The combined organic layer was washed with water and brine, dried over $MgSO_4$, and evaporated under reduced pressure. The crude product was purified with column chromatography on silica gel using dichloromethane/petroleum ether(2/1, *v*/*v*) as the eluent to obtain compound TPBT-CHO(411 mg, 80%) as a yellow solid.$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 10.07 (s, 2H), 4.57 (d, *J* = 7.3 Hz, 4H), 3.13 (t, *J* = 7.6 Hz, 4H), 1.97-1.81 (m, 6H), 1.44-1.36 (m, 4H), 1.32-1.16 (m, 32H), 0.81 (dd, *J* = 17.4, 10.8 Hz, 18H), 0.61-0.49 (m, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 181.78, 147.54, 146.89, 143.18, 137.04, 136.80, 132.74, 129.60, 127.22, 112.38, 55.12, 40.13, 31.92, 30.35, 29.75-29.20, 28.18, 27.55, 23.07, 22.70, 14.14, 13.68, 10.03.

**Synthesis of Y10**

Compound TPBT-CHO(0.150g, 0.150mmol), 2-(6-oxo-5, 6-dihydro-4*H*-cyclopenta[c]thiophen-4-ylidene) malononitrile (300 mg,1.50mmol), pyridine (1.2 mL) and chloroform (50 mL) were dissolved in a round bottom flask under nitrogen. The mixture was stirred at 65 °C overnight. After cooling to room temperature, the mixture was poured into methanol and filtered. The residue was purified with column chromatography on silica gel using dichloromethane/petroleum ether(2/1, *v*/*v*) as the eluent to give a dark-red solidY10(160 mg, 77% yield).$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.04 (s, 2H), 8.36 (d, *J* = 1.8 Hz, 2H), 7.97 (d, *J* = 1.9 Hz, 2H), 4.78 (d, *J* = 7.6 Hz, 4H), 3.20 (t, *J* = 7.3 Hz, 4H), 2.24-2.09 (m, 2H), 1.97-1.78 (m, 4H), 1.50 (dt, *J* = 14.9, 7.3 Hz, 4H), 1.25 (s, 32H), 1.08 (dd, *J* = 13.9, 6.9 Hz, 12H), 0.83 (dt, *J* = 14.5, 6.9 Hz, 12H), 0.74-0.60 (m, 6H).

$^{13}$C NMR (100MHz, $CDCl_3$) $\delta$ 181.72, 156.78, 153.10, 147.39, 145.08, 142.69, 142.33, 137.94, 136.21, 135.80, 133.47, 133.27, 129.91, 127.37, 127.04, 125.23, 115.32, 115.03, 113.61, 66.51, 55.68, 40.31, 31.91, 31.15, 29.82, 29.64, 29.62, 29.52, 29.50, 29.34, 27.56, 23.28, 22.83, 22.68, 14.11, 13.71.

## 5. $^1$H NMR and $^{13}$C NMR

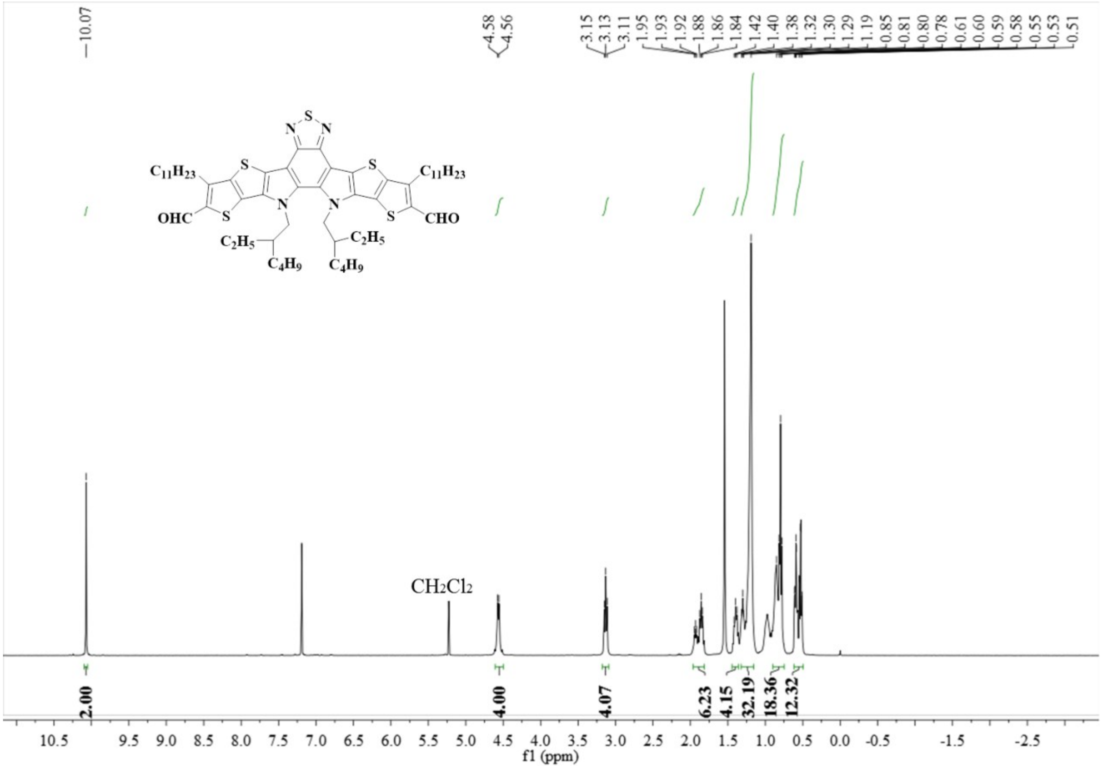


**Figure S1**. $^{1}H$ NMR spectrum of **TPBT-CHO** in $CDCl_3$

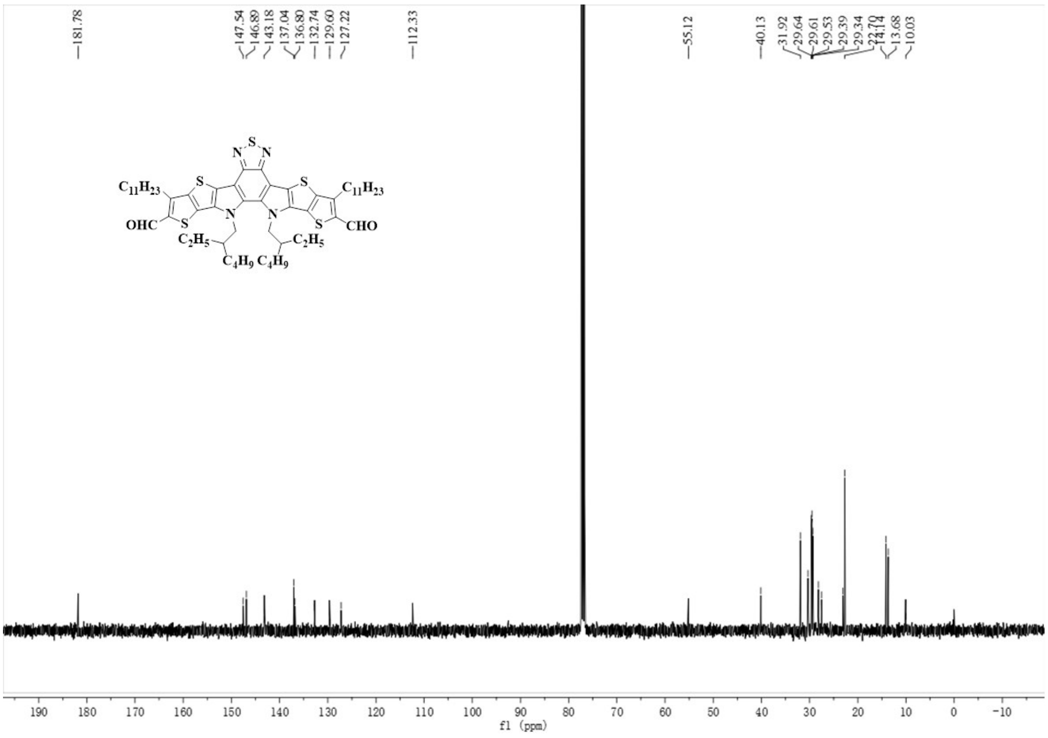


**Figure S2**. $^{13}C$ NMR spectrum of **TPBT-CHO** in $CDCl_3$

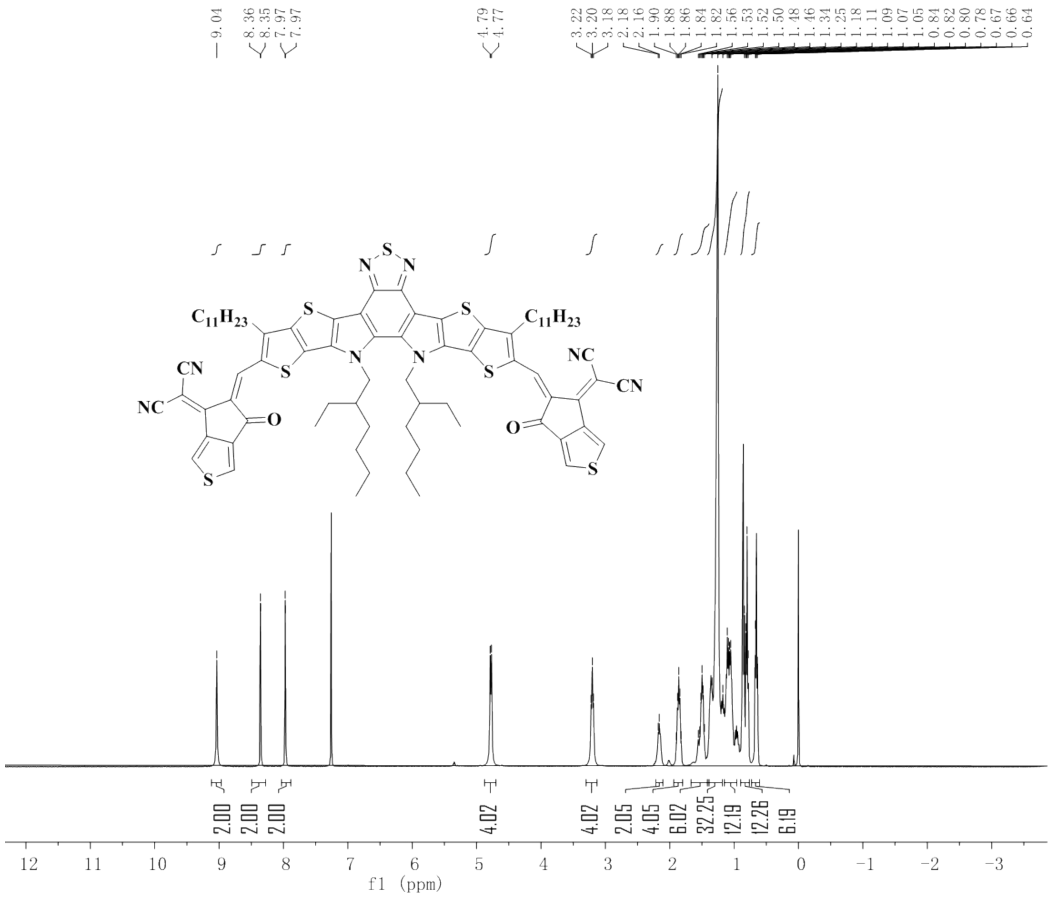


**Figure S3**. $^1$H NMR spectrum of **Y10** in CDCl$_3$

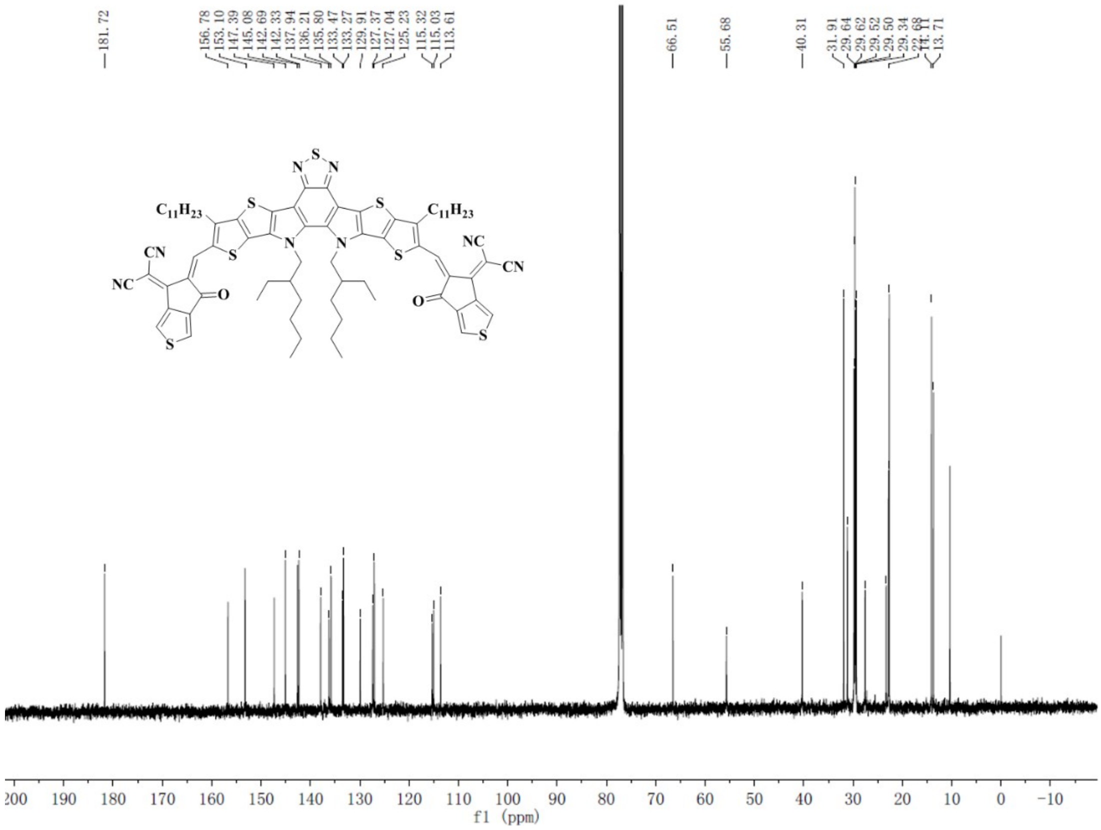


**Figure S4**. $^{13}$C NMR spectrum of **Y10** in $CDCl_3$

## 6. TGA curve and corresponding energy level

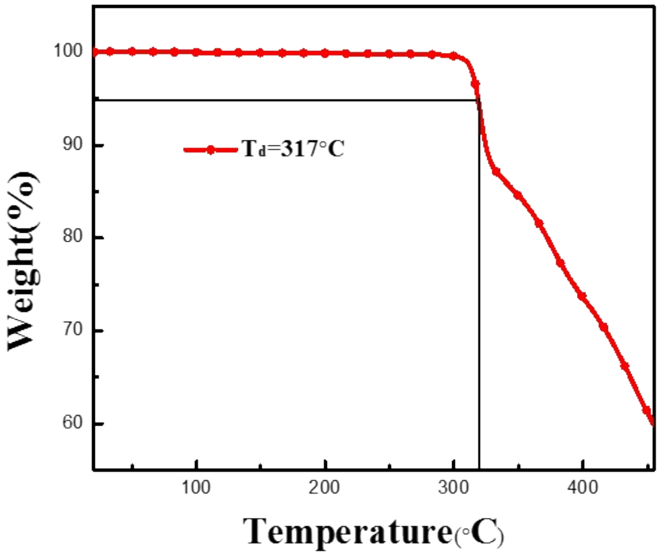


**Figure S5**. Thermogravimetric analysis curve of Y10

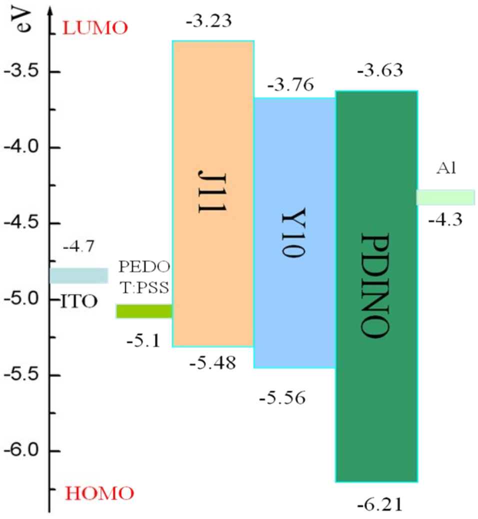


**Figure. S6.** Estimated energy levels of J11 and Y10 from electrochemical voltammetry

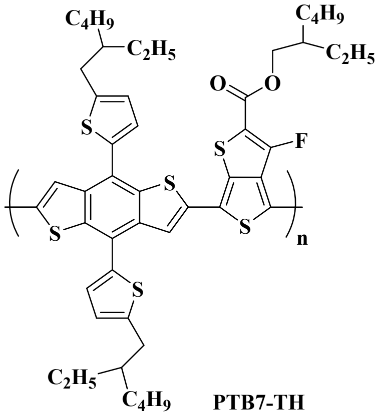
## 7. Photovoltaic data

**Table S1.** The photovoltaic characteristics of the J11:Y10 blend films

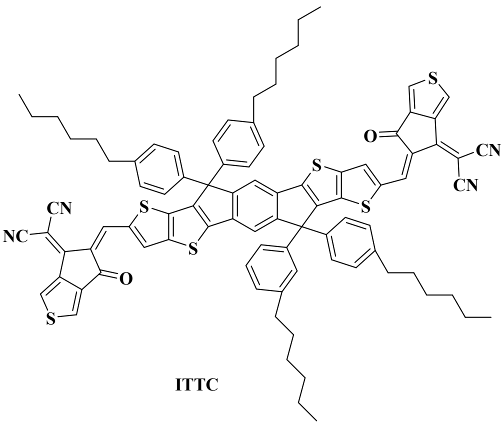
| J11:Y10 Ratio | Additive[a] (%) | Annealing (°C) | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF (%) | PCE (%) |
|---|---|---|---|---|---|---|
| 1:1.2 | 0 | 0 | 0.92 | 19.76 | 62.57 | 11.37 |
| | 0.3 | 100 | 0.90 | 18.86 | 66.90 | 11.40 |
| | 0.5 | 100 | 0.90 | 21.47 | 67.79 | 13.01 |
| | 0.8 | 100 | 0.89 | 21.21 | 71.55 | 13.46 |
| 1:1 | 0 | 0 | 0.91 | 18.37 | 62.64 | 10.47 |
| | 0.5 | 100 | 0.90 | 21.18 | 65.37 | 12.52 |
| 1:1.5 | 0 | 0 | 0.90 | 17.85 | 64.62 | 10.38 |
| | 0.5 | 100 | 0.90 | 19.96 | 66.81 | 12.05 |

[a] The additive is 1-Chloronaphthalene (CN).

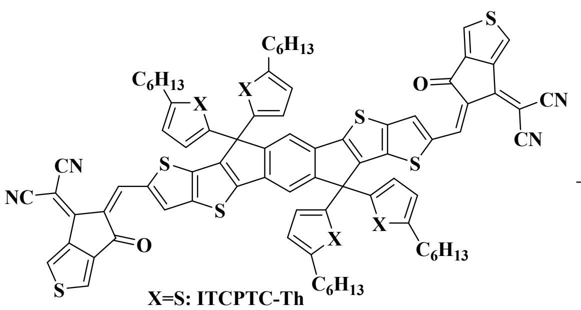
## 8. The names of compounds



**PTB7-TH**

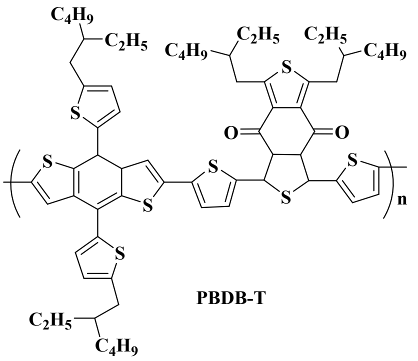


**ITTC**

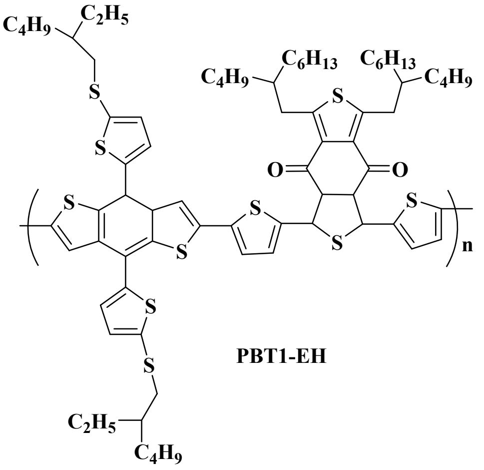


**X=S: ITCPTC-Th**

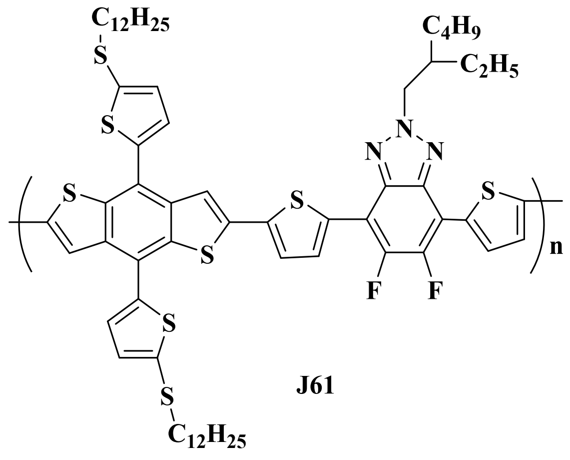
**X=Se:ITCPTC-Se**



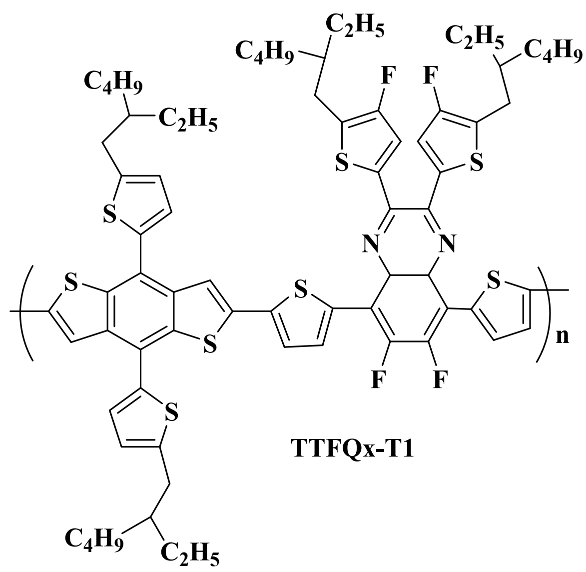
**PBDB-T**



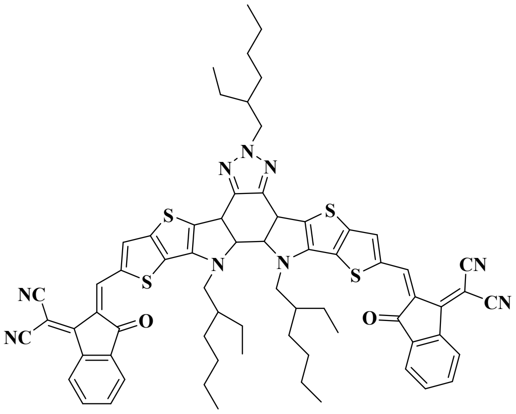
**PBT1-EH**



**J61**

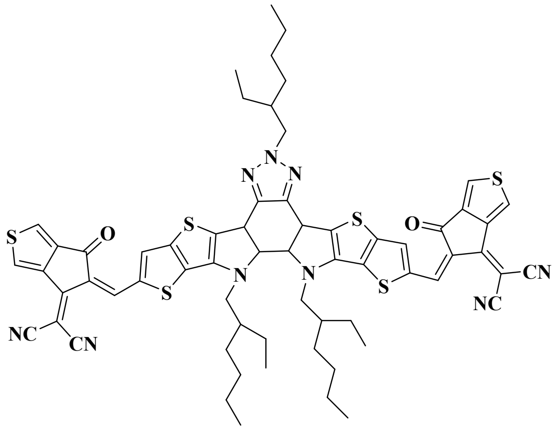


**TTFQx-T1**



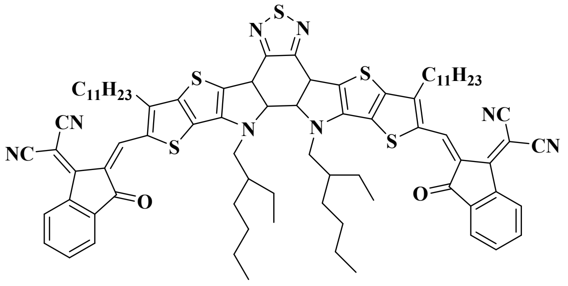
**Y1**

**2,2'-((2*Z*,2'*Z*)-((6,12,13-tris(2-ethylhexyl)-4b,7b,12,12a,12b,13-hexahydro-6*H*-thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[2',3':4,5]thieno[3,2-*b*][1,2,3]triazolo[4,5-*e*]indole-2,10-diyl)bis(methanylylidene))bis(3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile**



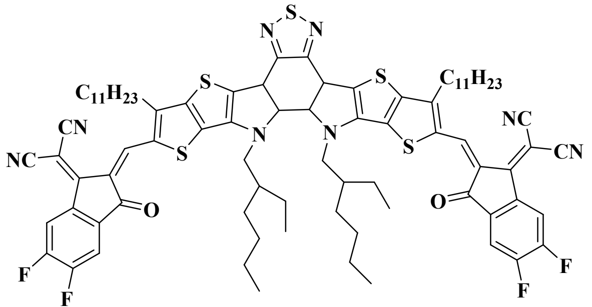
**Y2**

**2,2'-((5*Z*,5'*Z*)-((6,12,13-tris(2-ethylhexyl)-4b,7b,12,12a,12b,13-hexahydro-6*H*-thieno[2'',3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[2',3':4,5]thieno[3,2-*b*][1,2,3]triazolo[4,5-*e*]indole-2,10-diyl)bis(methanylylidene))bis(6-oxo-5,6-dihydro-4*H*-cyclopenta[*c*]thiophene-5,4-diylidene))dimalononitrile**



**Y5**

**2,2'-((2*Z*,2'*Z*)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-4b,7b,12,12a,12b,13-hexahydro-[1,2,5]thiadiazolo[3,4-*e*]thieno[2",3":4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[2',3':4,5]thieno[3,2-*b*]indole-2,10-diyl)bis(methanylylidene))bis(3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile**



**Y6**

**2,2'-((2*Z*,2'*Z*)-((12,13-bis(2-ethylhexyl)-3,9-diundecyl-4b,7b,12,12a,12b,13-hexahydro-[1,2,5]thiadiazolo[3,4-*e*]thieno[2",3":4',5']thieno[2',3':4,5]pyrrolo[3,2-*g*]thieno[2',3':4,5]thieno[3,2-*b*]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1*H*-indene-2,1-diylidene))dimalononitrile**

**Figure. S7. The names and structures of abbreviated molecules**

## 9. AFM phase images of J11:Y10 blend films

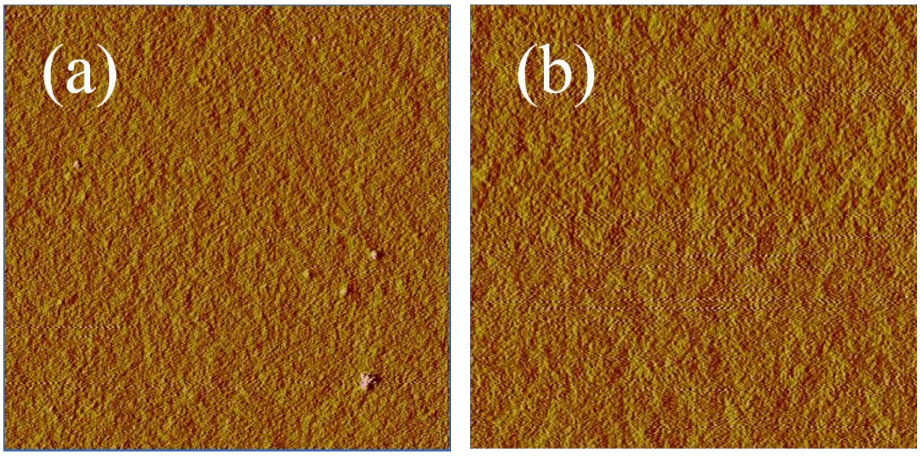
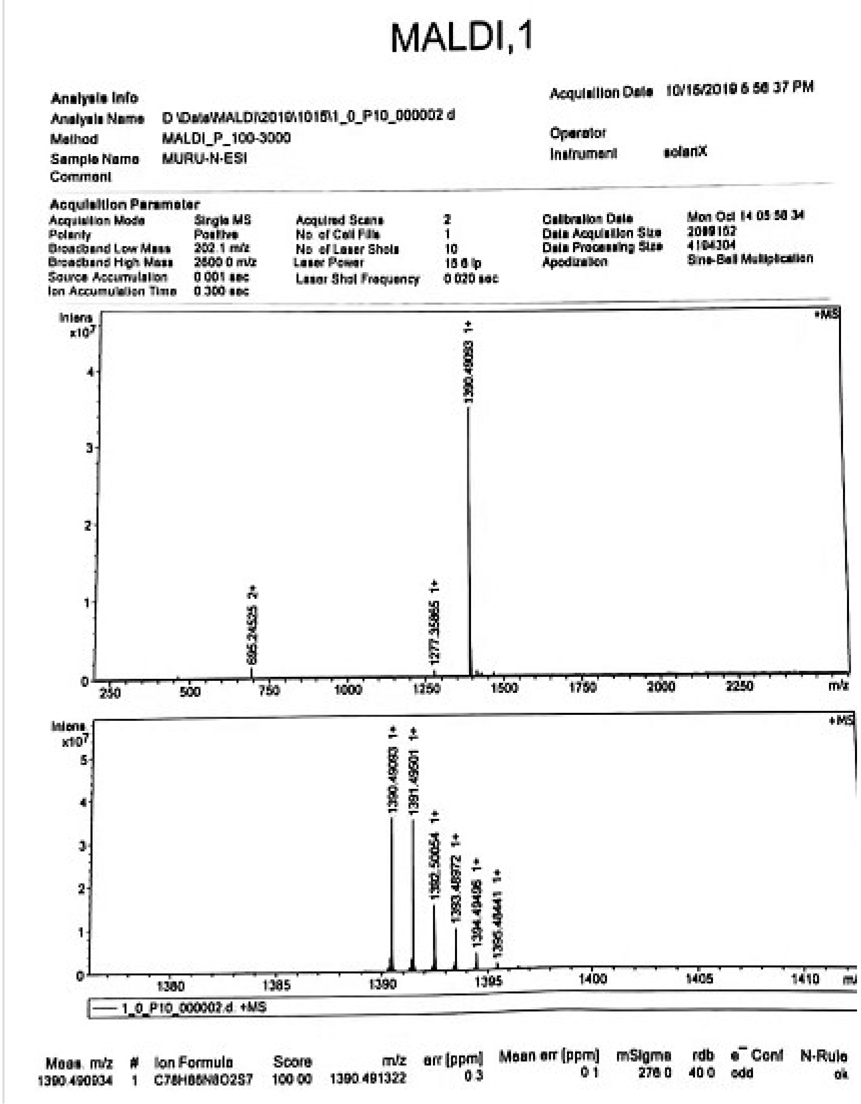


**Figure S8.** AFM phase images of J11:Y10 blend films (a) as cast film, (b) optimized film

## 10.The high-resolution mass data of Y10



MALDI,1

Analysis Info

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Method MALDI_P_100-3000

Sample Name MURU-N-ESI

Comment

Acquisition Date 10/16/2019 6:56:37 PM

Operator

Instrument solariX

Acquisition Parameter

| | | | | | |
|---|---|---|---|---|---|
| Acquisition Mode | Single MS | Acquired Scans | 2 | Calibration Date | Mon Oct 14 05:56:34 |
| Polarity | Positive | No. of Cell Fills | 1 | Data Acquisition Size | 2097152 |
| Broadband Low Mass | 202.1 m/z | No. of Laser Shots | 10 | Data Processing Size | 4194304 |
| Broadband High Mass | 2500.0 m/z | Laser Power | 15.6 lp | Apodization | Sine-Bell Multiplication |
| Source Accumulation | 0.001 sec | Laser Shot Frequency | 0.020 sec | | |
| Ion Accumulation Time | 0.300 sec | | | | |

| Meas. m/z | # | Ion Formula | Score | m/z | err [ppm] | Mean err [ppm] | mSigma | rdb | e⁻ Conf | N-Rule |
|---|---|---|---|---|---|---|---|---|---|---|
| 1390.490934 | 1 | C78H86N8O2S7 | 100.00 | 1390.491322 | 0.3 | 0.1 | 276.0 | 40.0 | odd | ok |

**Figure S9.** The high-resolution mass data of Y10

1. J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H.-L. Yip, T.-K. Lau, X. Lu, C. Zhu, H. Peng and P. A. Johnson, *Joule*, 2019. 3,1140-1151