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Tuning Terminal Aromatics of Electron Acceptors to Achieve High-Efficiency Organic Solar Cells

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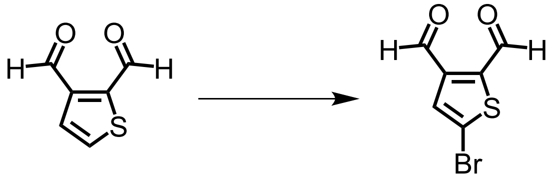
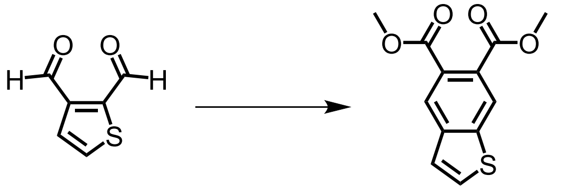
Synthetic Routes


1a 1b

5-Bromothiophene-2,3-dicarbaldehyde (1b)

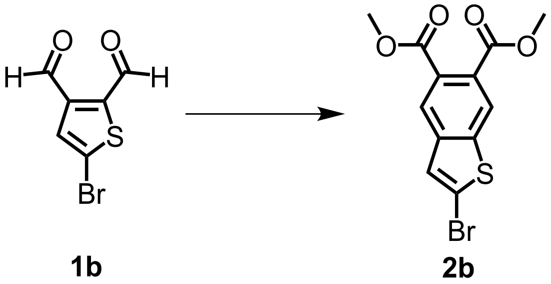
Bromine (9.10 mL, 178.00 mmol) was added dropwise at room temperature to a solution of compound **1a** (7.79 g, 55.60 mmol) in 100 mL of $CHCl_3$. The reaction mixture was stirred overnight and then excess bromine was quenched with a saturated solution of $Na_2S_2O_3$. The organic layer was extracted with $CHCI_3$, dried over Na_2SO_4 and volatiles were removed under reduced pressure to obtain product. The crude material was purified by flash chromatography (4:1 DCM: hexanes) to yield a brown solid. (7.45 g, 61.2 % yield). ^1H NMR (400 MHz, $CDCl_3$, δ): 10.38 (s, 1H), 10.26 (s, 1H), 7.60 (s, 1H).


1a 2a

Dimethyl benzo[b]thiophene-5,6-dicarboxylate (2a)

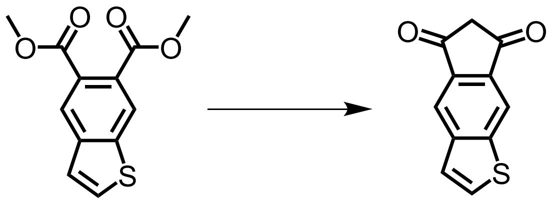
Compound **1a** (10.85 g, 77.41 mmol), dimethyl maleate (16.74 g, 116.12 mmol) and dry DCM (80 mL) were combined in a 250 mL flask and chilled to 0 °C. Triethylphosphine (21.73 g, 107.4 mmol) and diazabicycloundecene (1.09 g, 7.16 mmol) were combined with dry DCM (20 mL), and then the mixture was added to the reaction flask. After stirring for

4 h at room temperature, volatiles were removed from the reaction under reduced pressure. The crude material was purified by flash chromatography (4:5:1 DCM: hexanes: ethyl acetate) to yield a yellow oil (14 g, 72.6 % yield). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.28 (s, 1H), 8.17 (s, 1H), 7.66 (d, *J* = 5.5 Hz, 1H), 7.42 (d, *J* = 5.5 Hz, 1H), 3.93 (s, 6H).



Dimethyl 2-bromobenzo[b]thiophene-5,6-dicarboxylate (2b)

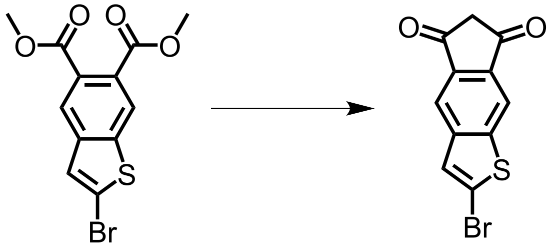
Compound **1b** (5.50 g, 25.10 mmol), dimethyl maleate (5.43 g, 37.66 mmol) and dry DCM (30 mL) were combined in a 100 mL flask and chilled to 0 °C. Triethylphosphine (7.62 g, 37.66 mmol) and diazabicycloundecene (0.38 g, 2.51 mmol) were combined with dry DCM (10 mL), and then the mixture was added to the reaction flask. After stirring for 4 h at room temperature, volatiles were removed from the reaction under reduced pressure. The crude material was purified by flash chromatography (4:5:1 DCM: hexanes: ethyl acetate) to yield a yellow oil (5.69 g, 68.9 % yield). ^{1}H NMR (400 MHz, CDCl$_3$, δ): 8.14 (s, 1H), 8.03 (s, 1H), 7.42 (s, 1H), 3.94 (d, J = 1.8 Hz, 6H).



2a **3a**

5H-indeno[5,6-b]thiophene-5,7(6H)-dione (3a)

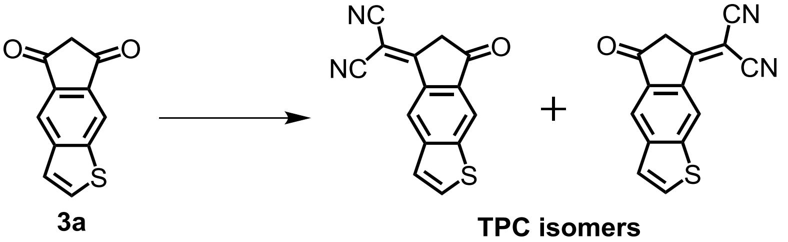
Under the protection of nitrogen, compound **2a** (5.02 g, 20.06 mmol) was dissolved in anhydrous ethyl acetate (20 ml). Then 60% dispersion of NaH in mineral oil (4.01 g, 100.30 mmol of NaH) was added and the mixture was refluxed at 100 °C for 12 hours. After cooling to room temperature, the solids were filtered and washed with a small amount of mixed ethanol and diethyl ether (1:1, v/v) solution. Then they were treated with the hot solution of concentrated HCI (5 ml) in water (50 ml) for about 30 minutes to give the product as an orange solid. (1.66 g, 40.8 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.50 (s, 1 H), 8.41 (s, 1 H), 7.84 (d, J = 5.5 Hz, 1H), 7.60 (d, J = 5.5 Hz, 1H), 3.37 (s, 2 H).



2b **3b**

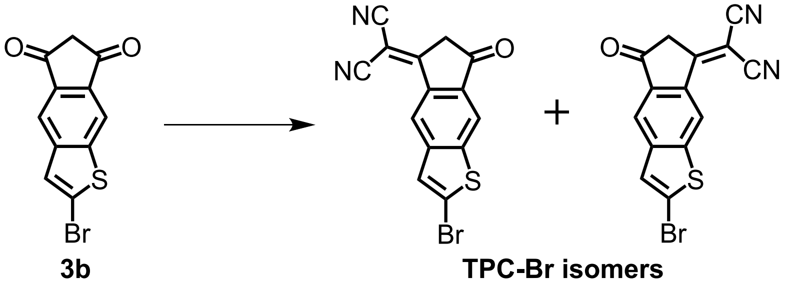
2-Bromo-5H-indeno[5,6-b]thiophene-5,7(6H)-dione (3b)

Under the protection of nitrogen, compound **2b** (2.28 g, 6.92 mmol) was dissolved in anhydrous ethyl acetate (8 ml). Then 60% dispersion of NaH in mineral oil (0.42 g, 10.39 mmol of NaH) was added and the mixture was refluxed at 100 °C for 12 hours. After cooling to room temperature, the solids were filtered and washed with a small amount of mixed ethanol and diethyl ether (1:1, v/v) solution. Then they were treated with the hot solution of concentrated HCI (3 ml) in water (30 ml) for about 30 minutes to give the product as an orange solid. (693 mg, 35.6 % yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.35 (s, 1H), 8.27 (s, 1H), 7.60 (s, 1H), 3.35 (s, 2H).



2-(7-Oxo-6,7-dihydro-5H-indeno[5,6-b]thiophen-5-ylidene)malononitrile and **2-(5-Oxo-5,6-dihydro-7H-indeno[5,6-b]thiophen-7-ylidene)malononitrile (TPC isomers)**

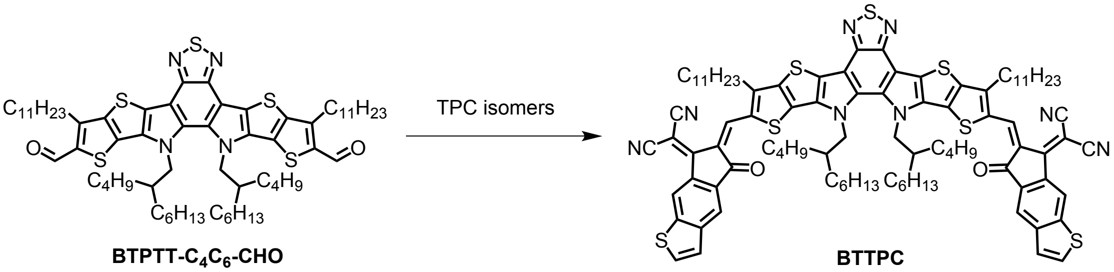
Compound **3a** (680 mg, 3.36 mmol) and malononitrile (444 mg, 6.72 mmol) were suspended in absolute ethanol (15 ml) in a 100 ml flask at room temperature. Anhydrous sodium acetate (367 mg, 4.48 mmol) was further added and then the reaction was heated to 50 °C. After 3 hours, the reaction mass was dissolved in ethanol and the mixture was diluted with water (50 ml) and acidified to PH 1-2 with HCl. The suspension was stirred for another 15 minutes. Then the solid was filtered off and washed thoroughly with water. The obtained crude product was further purified by column chromatography with dichloromethane to obtain the product as the yellow solid. (616 mg, 73.3 % yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ) 9.19 (s, 0.45H), 9.09 (s, 0.55H), 8.49 (s, 0.55H), 8.40 (s, 0.45H), 7.94 (d, *J* = 5.5 Hz, 0.45H), 7.90 (d, *J* = 5.5 Hz, 0.55H), 7.64 (d, *J* = 5.5 Hz, 0.55H), 7.61 (d, *J* = 5.5 Hz, 0.45H), 3.84 (d, *J* = 1.6 Hz, 2H).



2-(2-Bromo-7-oxo-6,7-dihydro-5H-indeno[5,6-b]thiophen-5-ylidene)malononitrile and **2-(2-Bromo-5-oxo-5,6-dihydro-7H-indeno[5,6-b]thiophen-7-ylidene)malononitrile (TPC-Br isomers)**

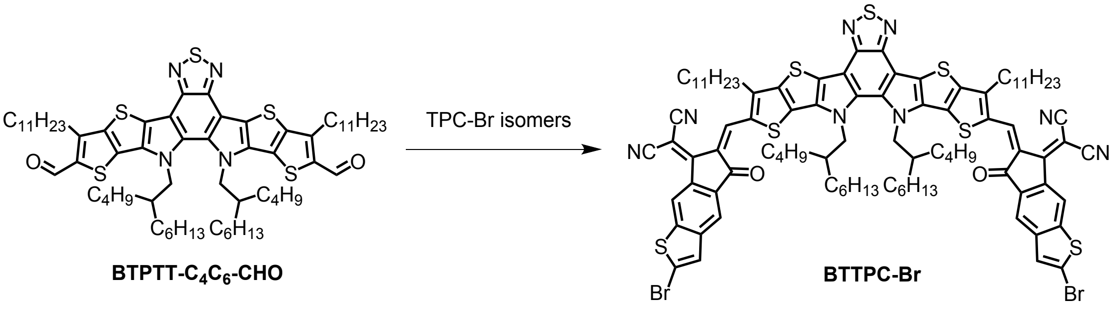
Compound **3b** (150 mg, 0.53 mmol) and malononitrile (71 mg, 1.07 mmol) were suspended in absolute ethanol (10 ml) in a 50 ml flask at room temperature. Anhydrous sodium acetate (58 mg, 0.71 mmol) was further added and then the reaction was heated to 50 °C. After 3 hours, the reaction mass was dissolved in ethanol and the mixture was diluted with water (20 ml) and acidified to PH 1-2 with HCl. The suspension was stirred for another 15 minutes. Then the solid was filtered off and washed thoroughly with water. The obtained crude product was further purified by column chromatography with dichloromethane to obtain the product as the yellow solid. (137 mg, 78.6 % yield). ^{1}H NMR (500 MHz, $CDCl_3$, δ) 9.03 (s, 0.40H), 8.94 (s, 0.60H), 8.34 (s, 0.60H), 8.25 (s, 0.40H), 7.64 (s, 0.60H), 7.61 (s, 0.40H), 3.82 (s, 2H).

BTPTT-C_4C_6 and **BTPTT-C_4C_6-CHO** were synthesized according to literature while 2-ethylhexyl bromide were substituted with 5-(bromomethyl)undecane.[1]



BTTPC

To a solution of **BTPTT-C_4C_6-CHO** (100 mg, 0.09mmol) and **TPC** (88 mg, 0.35 mmol) in dried $CHCl_3$ (10 mL), pyridine (0.1 mL) was added under the protection of nitrogen. The mixture was stirred at 65 °C for 12 h. After cooling to room temperature, the mixture was extracted with chloroform and the organic phase was washed with water, dried over anhydrous $MgSO_4$. The solvent was removed by vacuum evaporation and the obtained product was purified by column chromatography on silica gel with the mixture of hexane/dichloromethane (1:2). The refined product was brown solid. (88 mg, 62.3%) ^1H NMR (600 MHz, $CDCl_3$, δ) 9.11 (s, 2H), 9.09 (s, 0.95H), 9.04 (s, 1.05H), 8.42 (s, 1.05H), 8.33 (s, 0.95H), 7.80 (d, J = 5.2 Hz, 0.95H), 7.77 (d, J = 5.2 Hz, 1.05H), 7.60 – 7.56 (m, 1.05H), 7.52 – 7.50 (m, 0.95H), 4.89 – 4.80 (m, 4H), 3.22 – 3.12 (m, 4H), 2.25 (s, 2H), 1.86 (s, 4H), 1.49 (s, 4H), 1.35 (s, 4H), 1.31 – 0.93 (m, 54H), 0.85 (t, J = 6.7 Hz, 8H), 0.77 – 0.66 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$, δ) 150.02, 148.68, 147.64, 146.99, 145.96, 138.24, 137.55, 136.46, 136.20, 135.80, 135.35, 135.10, 132.74, 128.07, 127.73, 123.37, 122.63, 121.27, 120.98, 118.36, 118.12, 116.11, 58.48, 41.86, 34.56, 34.27, 33.80, 33.20, 33.11, 32.48, 32.32, 32.27, 32.18, 31.98, 30.72, 30.59, 28.20, 28.05, 25.58, 25.54, 25.32, 25.19, 16.75, 16.71, 16.49, 16.45, 2.64. MS (MALDI-TOF): Calcd for $C_{94}H_{106}N_8O_2S_7$ (M^+): 1604.36, Found: 1604.16.



BTTPC-Br

To a solution of **BTPTT-C_4C_6-CHO** (80 mg, 0.07mmol) and **TPC-Br** (92 mg, 0.28 mmol) in dried $CHCl_3$ (10 mL), pyridine (0.1 mL) was added under the protection of nitrogen. The mixture was stirred at 65 °C for 12 h. After cooling to room temperature, the mixture was extracted with chloroform and the organic phase was washed with water, dried over anhydrous $MgSO_4$. The solvent was removed by vacuum evaporation and the obtained product was purified by column chromatography on silica gel with the mixture of hexane/dichloromethane (1:2). The refined product was brown solid. (92 mg, 74.6%) ^1H NMR (600 MHz, $CDCl_3$, δ) 9.28 (s, 2H), 9.01 (s, 0.92H), 8.94 (s, 1.08H), 8.23 (s, 1.08H), 8.16 (s, 0.92H), 7.55 (s, 0.92H), 7.50 (s, 1.08H), 4.80 (s, 4H), 3.07 (s, 4H), 2.22 (s, 2H), 1.87 (s, 4H), 1.49 (s, 4H), 1.35 (s, 4H), 1.32-0.90 (m, 54H), 0.86 (t, J = 6.5 Hz, 8H), 0.76 – 0.65 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$, δ) 149.65, 148.86, 148.51, 146.84, 145.75, 138.94, 137.86, 136.50, 136.18, 135.21, 132.95, 130.51, 130.25, 127.72, 127.30, 125.35, 124.47, 121.90, 121.27, 119.98, 119.81, 117.85, 58.62, 41.79, 34.56, 34.27, 33.24, 33.14, 32.49, 32.32, 32.27, 32.18, 32.14, 31.99, 30.76, 30.61, 28.21, 28.05, 25.57, 25.53, 25.33, 25.18, 16.76, 16.72, 16.50, 16.46, 2.64. MS (MALDI-TOF): Calcd for $C_{94}H_{106}Br_2N_8O_2S_7$ (M^+): 1762.15, Found: 1762.61.

Materials and Methods

Materials

All reagents and solvents, unless otherwise specified, were purchased from J&K Scientific, Suna Tech, HWRK Chem Co, Derthon and Energy Chemical Ltd. and were used without further purification. PBDB-T and PFN-Br were purchased from Solarmer Materials Inc.

Instruments

^{1}H NMR spectra and ^{13}C NMR spectra of BTTPC and BTTPC-Br were obtained on Agilent 600 MHz DD2 NMR spectroscope. ^{1}H NMR spectra of TPC and TPC-Br were obtained on Bruker Advance III 500 (500 MHz) NMR spectroscope. ^{1}H NMR spectra of other molecules were obtained on Bruker Advance III 400 (400 MHz) NMR spectroscope. MALDI-TOF MS spectra were measured on a Walters Maldi Q-TOF Premier mass spectrometry. UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a WCT-2 thermal balance under protection of nitrogen at a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) was recorded on a Pekin-Elmer Pyris 1 differential scanning calorimeter. Cyclic voltammetry (CV) curves were measured on a CHI600A electrochemical workstation with Pt disk, Pt plate, and standard calomel electrode (SCE) as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammoniumhexafluorophosphate (Bu_4NPF_6) acetonitrile solution. The morphologies of films were characterized by a VeecoMultiMode atomic force microscopy (AFM) in the tapping mode using an etched silicon cantilever at a nominal load of ~2 nN, and the scanning rate for a 10 μm×10 μm image size was 1.5 Hz.

Device Fabrication and Characterization

Organic solar cells were fabricated on indium tin oxides (ITO) glass substrates with the inverted structure of ITO/PEDOT: PSS/active layer/PFN-Br/Ag. The ITO/glass substrates were cleaned by sonication using detergent, deionized water, acetone, and isopropanol sequentially for 30 min before fabrication. The pre-cleaned ITO substrates were then treated in an ultraviolet generator for 20 min, followed by deposition of PEDOT: PSS thin film by spin coating precursor solution onto the substrates at 4,000 rpm for 50s and then annealing at 140℃ for 30 min. Then the substrates were transferred into a glovebox. The PBDB-T: BTTPC active layer was then spin coated from 16 mg/mL solution (PBDB-T: BTTPC = 1:0.9 and PBDB-T:

BTTPC-Br = 1:1.1 by wt., dissolved in chloroform with 0.5vol.% 1-chloronaphthalene) at 4000 rpm for 40 s. And then devices were annealed at 130 ^{o}C (PBDB-T: BTTPC) and 140 ^{o}C (PBDB-T: BTTPC-Br) for 10 min. Finally, a layer of PFN-Br was deposited by spin coating onto the substrates at 3,000 rpm for 50s and the Ag (100 nm) electrode were deposited by thermal evaporation under a background pressure of approximately 2×10^{-4} Pa.

The current density-voltage (*J*-*V*) curves of the devices were measured in glovebox with Keithley 2400 measurement source units under 1 sun, AM 1.5 G spectra from a solar simulator (Taiwan, Enlitech), and the light intensity was calibrated with a standard silicon photovoltaic reference cell. The external quantum efficiency (EQE) spectra were measured by a Solar Cell Spectral Response Measurement System QE-R3011 (Enlitech, Taiwan).

The charge carrier mobilities of the PBDB-T: BTTPC and PBDB-T: BTTPC-Br films were measured using the space-charge-limited current (SCLC) method. Hole-only devices were fabricated in a structure of ITO/PEDOT: PSS/active layer/MoO_3/Ag, electron-only devices were fabricated in a structure of ITO/ZnO/active layer/PFN-Br/Ag. The device characteristics were extracted by modelling the dark current under forward bias using the SCLC expression described by the Mott-Gurney law:

$$J = \frac{9}{8}\varepsilon_r \varepsilon_0 \mu \frac{V^2}{L^3} \qquad (1)$$

Here, $\varepsilon_r \approx 3$ is the average dielectric constant of the blend film, ε_0 is the permittivity of the free space, μ is the carrier mobility, $L \approx 100$ nm is the thickness of the film, and V is the applied voltage.

GIWAXS and GISAXS Measurements

Grazing-incidence wide-angle and small angle X-ray scattering (GIWAXS/GISAXS) measurements were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05k eV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle is 0.2°.

Transient Absorption Spectroscopy

For femtosecond transient absorption spectroscopy, the fundamental output from Yb:KGW laser (1030 nm, 220 fs Gaussian fit, 100 kHz, Light Conversion Ltd) was separated to two light beam. One was introduced to NOPA (ORPHEUS-N, Light Conversion Ltd) to produce a certain wavelength for pump beam (here we use 750 nm), the other was focused onto a YAG plate to generate white light continuum as probe beam. The pump and probe overlapped on the sample at a small angle less than 10°. The transmitted probe light from sample was collected by a linear CCD array. Then we obtained transient differential transmission signals by equation shown below:

$$\frac{\Delta T}{T} = \frac{T_{pump-on} - T_{pump-off}}{T_{pump-off}} \qquad (2)$$

Time-resolved Photoluminescence Spectroscopy

The optically pumped lasing measurements were taken on a home-build far-field microfluorescence system (Olympus, IX73 inverted microscope). The crystal sample was immersed by diethylether and then dispersed onto a glass substrate. The excitation light (515 nm) was generated from the second harmonic of the fundamental output that was seeded by a mode-locked Ti:sapphire laser (Light Conversion Pharos, 1030 nm, < 300 fs, 1 MHz). The excitation light was filtered with a 515 nm band-pass filter and then diverged with a convex lens (f = 500 mm), finally focused down to a 140 μm diameter spot through an objective lens (Olympus MplanFLN, 20x, NA = 0.45). The emission light was collected by the same objective and focused into a spectrograph (Princeton Instruments, Acton SpectraPro, SP-2300i) with a 600 mm^{-1} grating and detected by a liquid-N_2-cooled CCD (PyLon 100B excelon). The instrument resolution (FWHM) was ~0.1 nm. All measurements were taken at room temperature with pulse picker = 1000. TRPL decay kinetics were collected using a TCSPC module (PicoHarp 300) and a SPAD detector (IDQ, id100) with an instrument response function ~100 ps. The two-photon pumped lasing performance was measured upon excitation at 1030 nm.

Supporting Figures and Tables

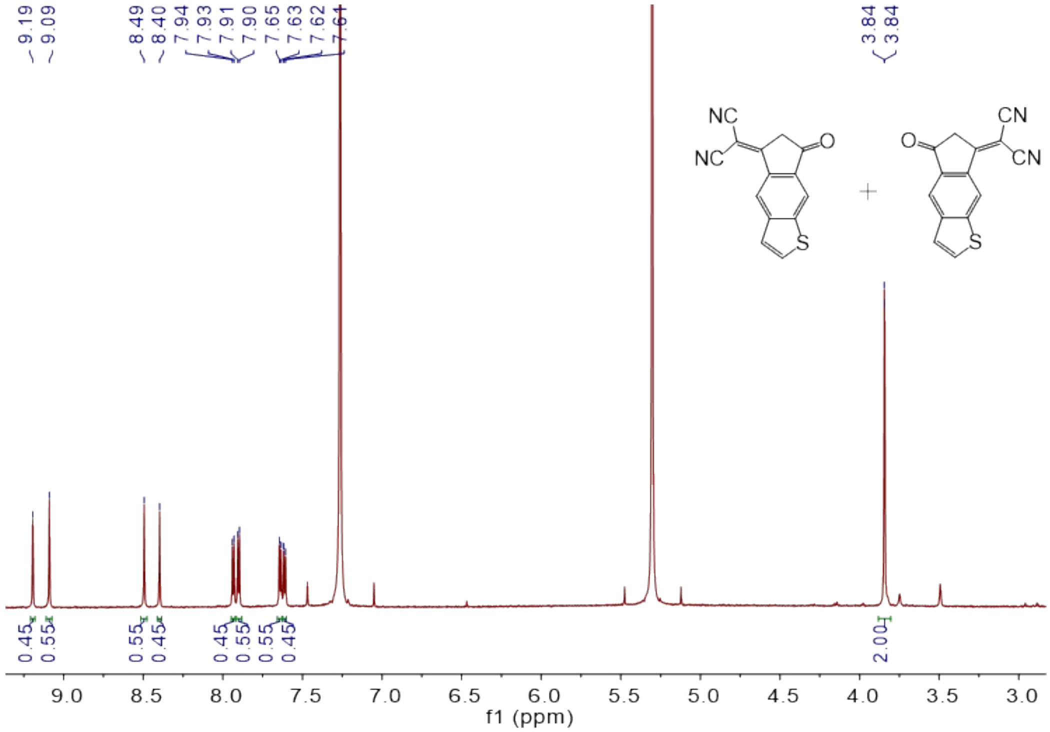


Figure S1. ^{1}H NMR spectrum of TPC isomers in CDCl$_3$ solution.

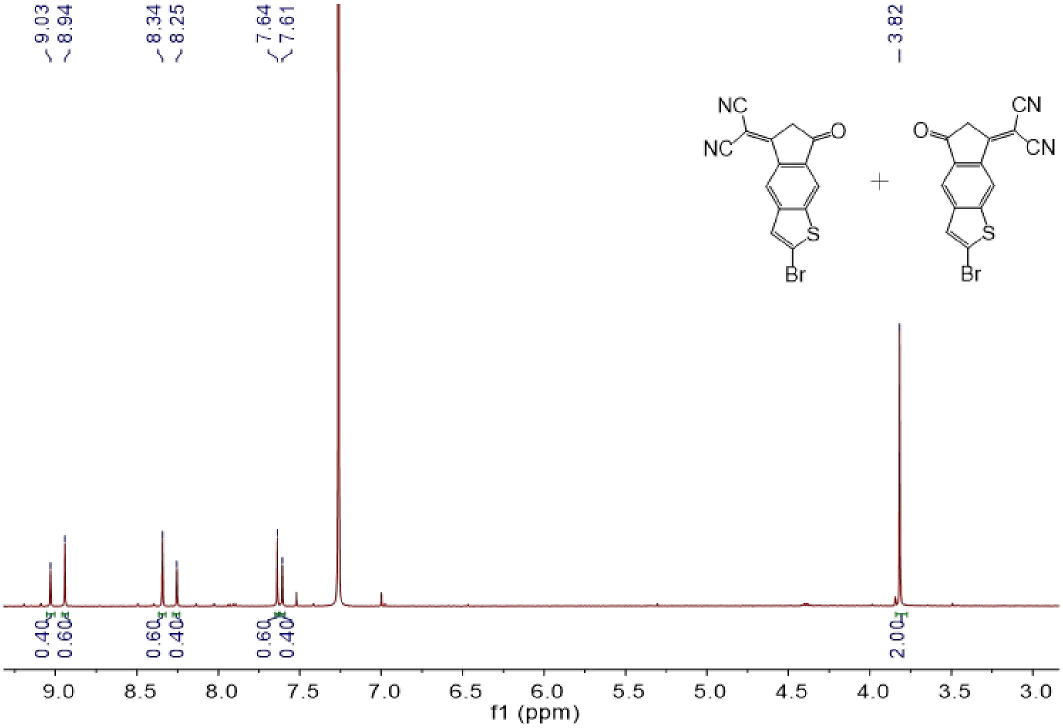


Figure S2. ^{1}H NMR spectrum of TPC-Br isomers in CDCl$_3$ solution.

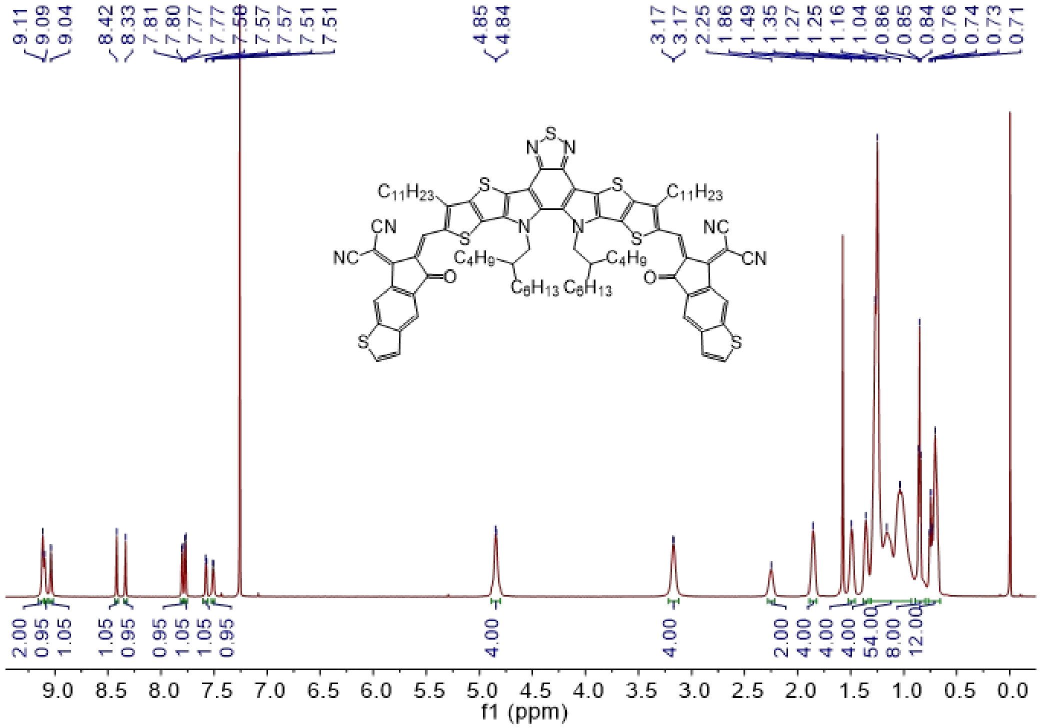


Figure S3. ^{1}H NMR spectrum of BTTPC in $CDCl_3$ solution.

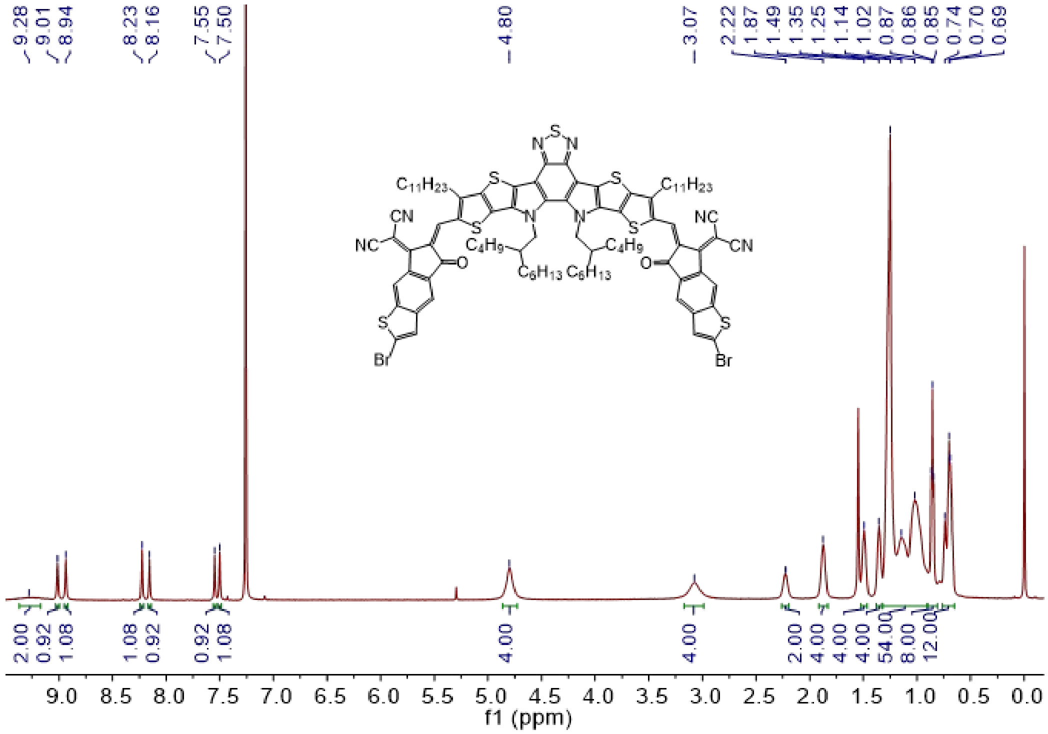


Figure S4. ^{1}H NMR spectrum of BTTPC-Br in $CDCl_3$ solution.

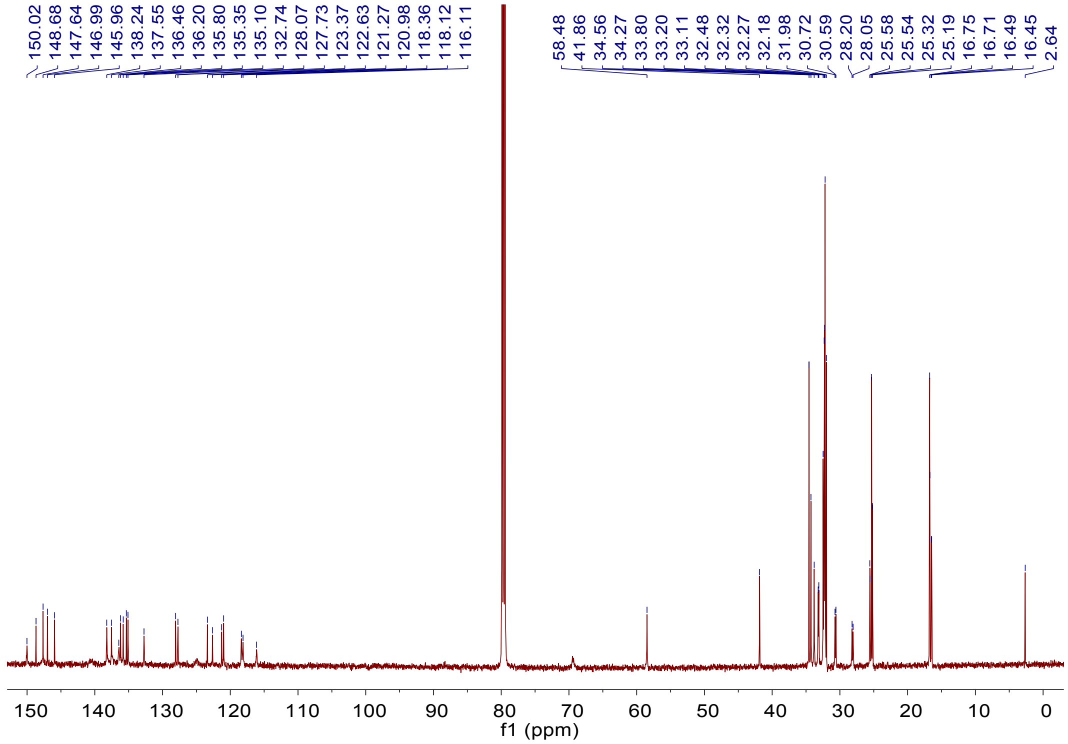


Figure S5. ^{13}C NMR spectrum of BTTPC in $CDCl_3$ solution.

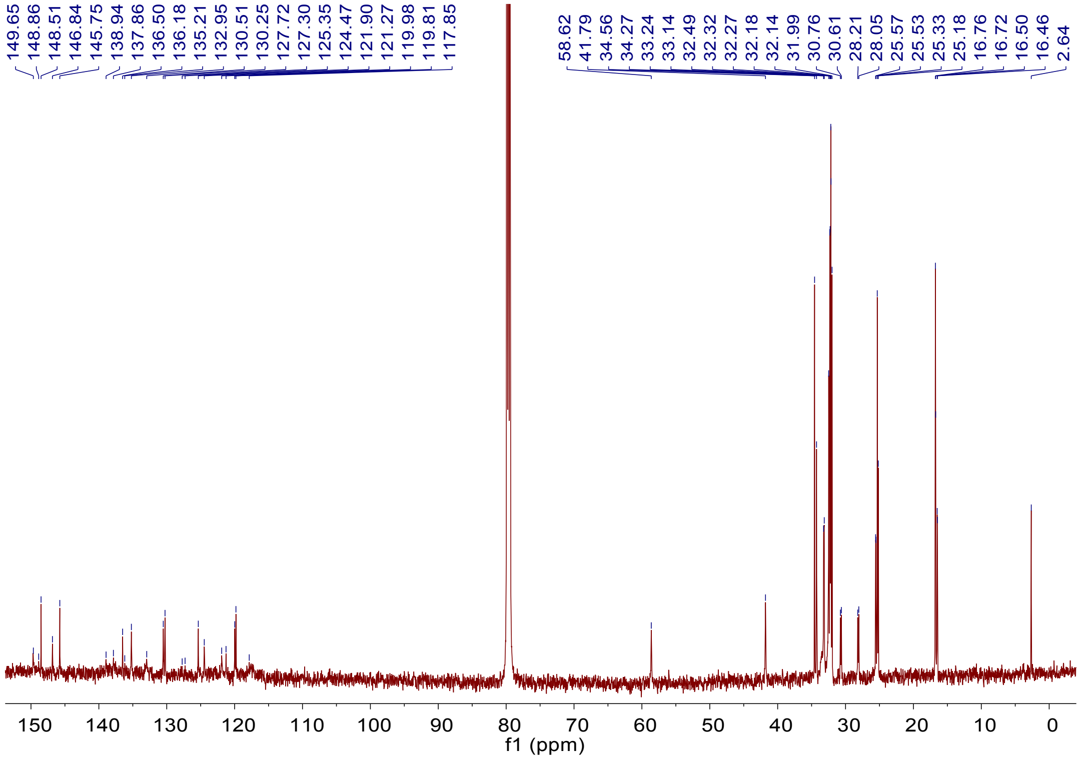


Figure S6. ^{13}C NMR spectrum of BTTPC-Br in $CDCl_3$ solution.

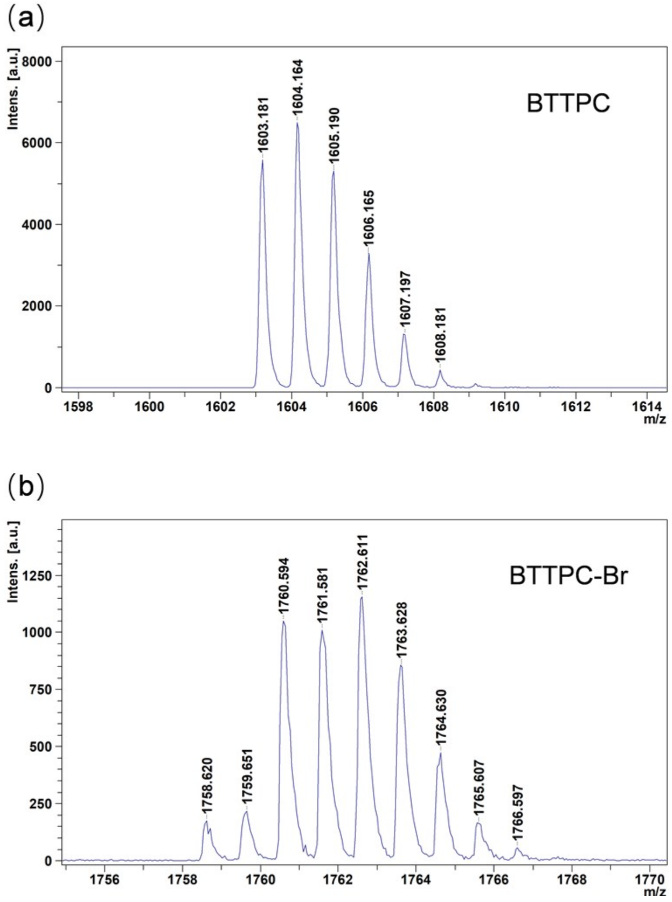


Figure S7. The mass spectra (MALDI-TOF) of (a) BTTPC and (b) BTTPC-Br.

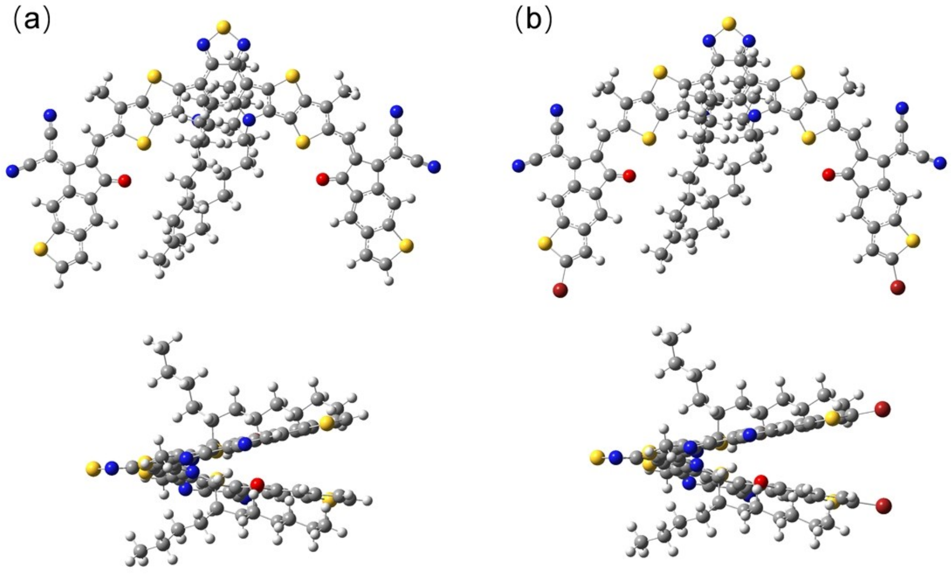


Figure S8. Calculated geometries of (a) BTTPC and (b) BTTPC-Br.

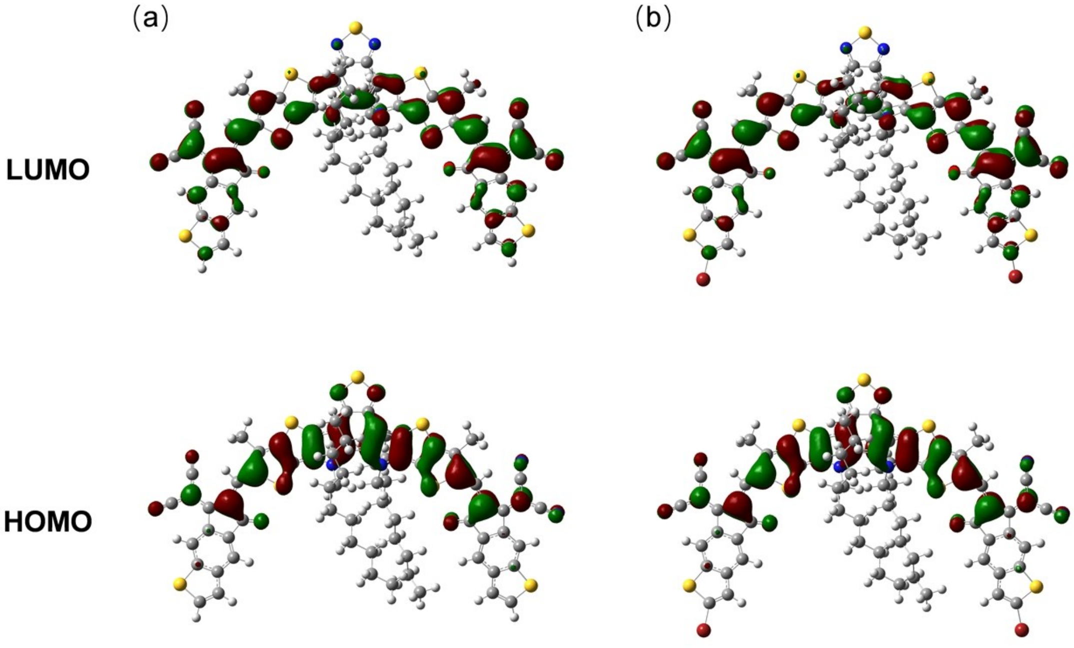


Figure S9. Calculated HOMO/LUMO of (a) BTTPC and (b) BTTPC-Br.

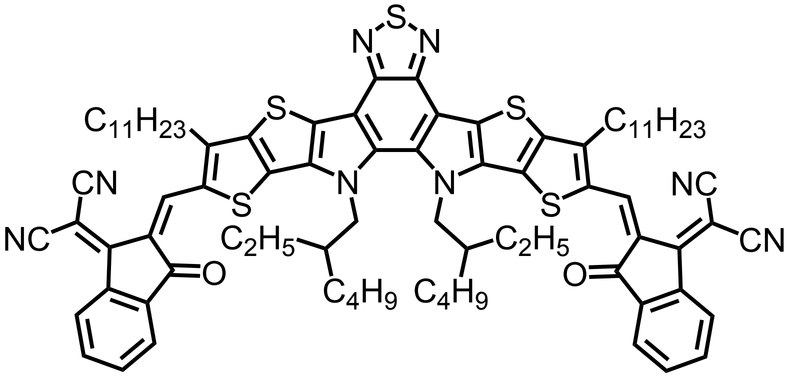


Figure S10. Chemical structure of Y5.

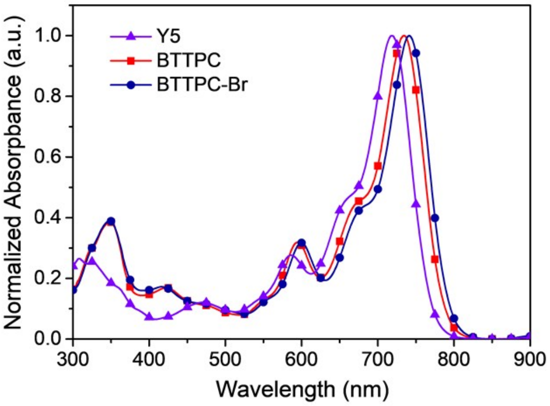


Figure S11. Normalized UV–vis absorption spectra of Y5, BTTPC and BTTPC-Br in chloroform solution.

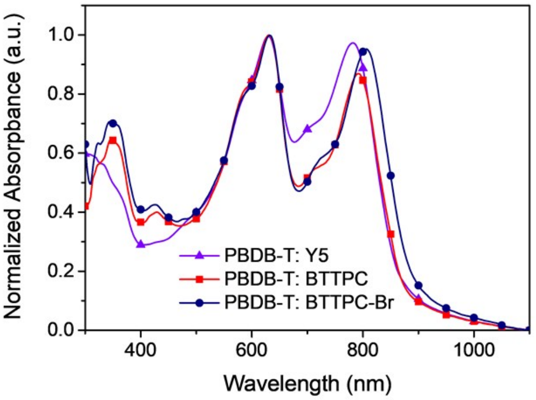


Figure S12. Normalized UV–vis absorption spectra of PBDB-T: Y5, PBDB-T: BTTPC and PBDB-T: BTTPC-Br blend films.

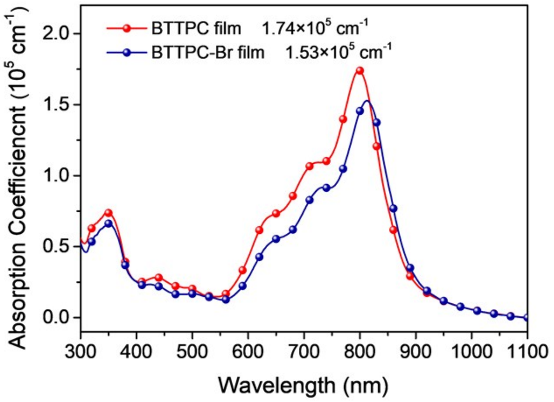


Figure S13. Absorption coefficients of BTTPC and BTTPC-Br films.

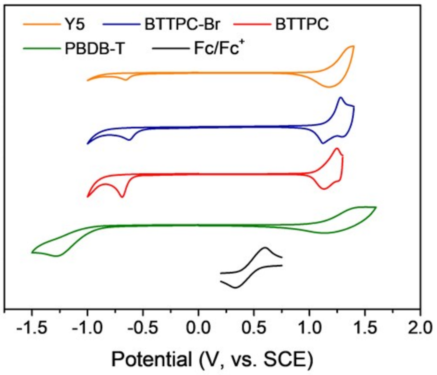


Figure S14. Cyclic voltammograms of Fc/Fc$^+$, Y5, BTTPC, BTTPC-Br and PBDB-T.

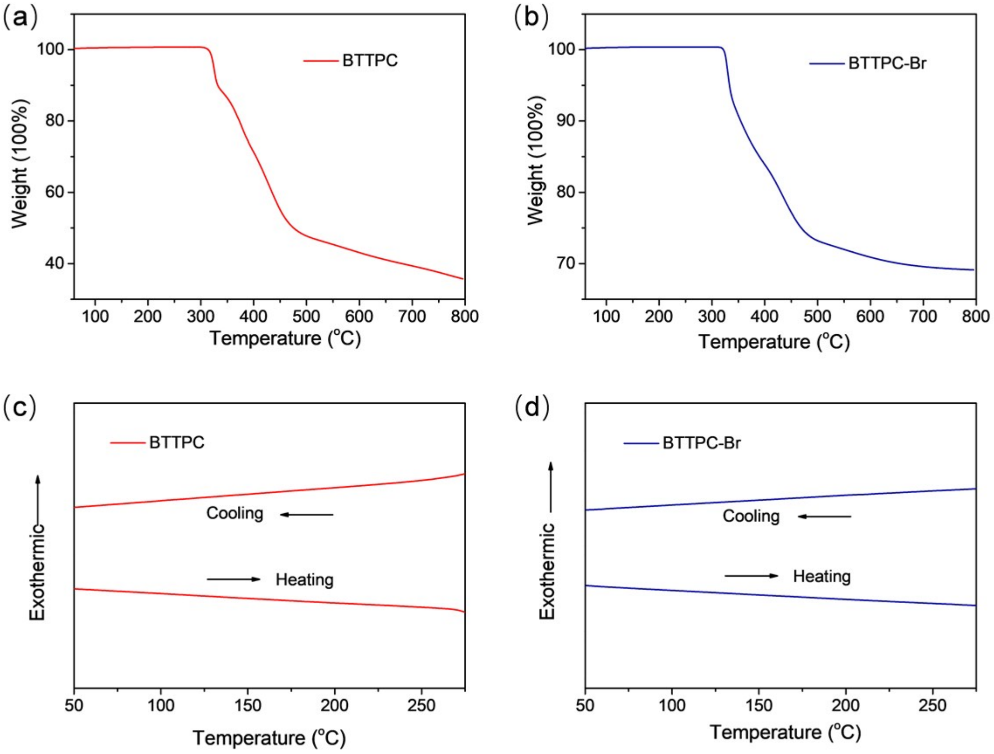


Figure S15. TGA curves of (a) BTTPC and (b) BTTPC-Br. DSC curves of (c) BTTPC and (d) BTTPC-Br.

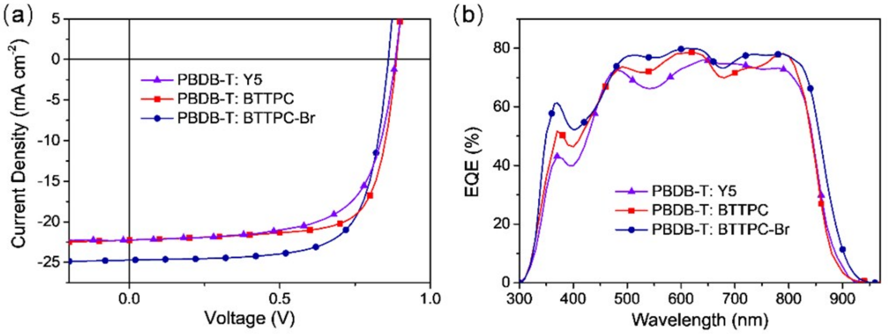


Figure S16. Comparisons of (a) *J–V* curves and (b) EQE spectra in PBDB-T: Y5, PBDB-T: BTTPC and PBDB-T: BTTPC-Br systems.

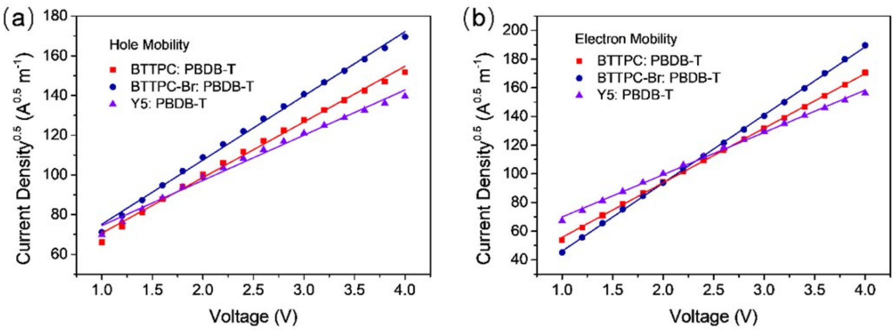


Figure S17. $J^{0.5}$-V curves of (a) hole-only devices and (b) electron-only devices based on Y5: PBDB-T, BTTPC: PBDB-T and BTTPC-Br: PBDB-T films.

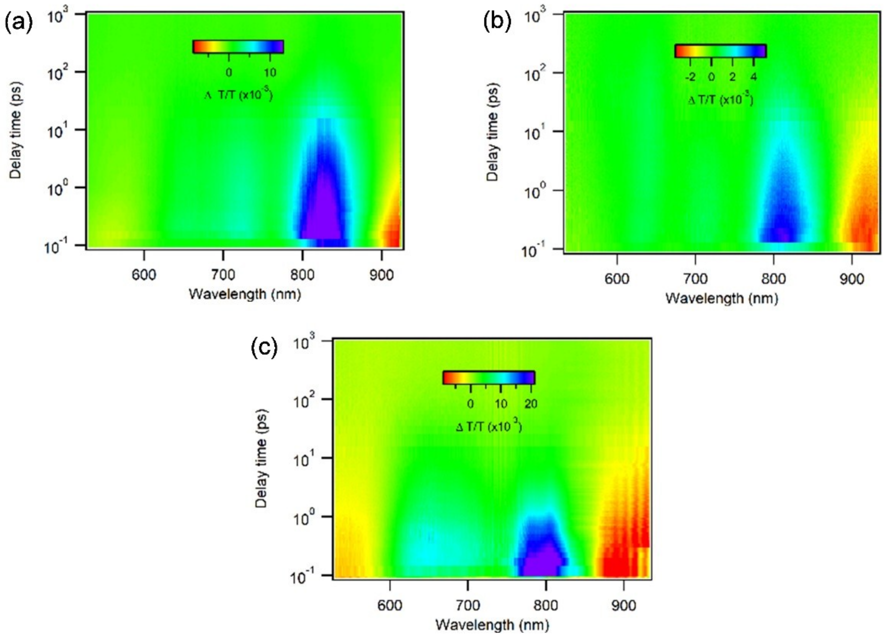


Figure S18. Color plot of fs-TA spectra of neat BTTPC-Br, BTTPC and Y5 film at indicated delay times under 750 nm excitation with a fluence below 10 μJ/cm^2.

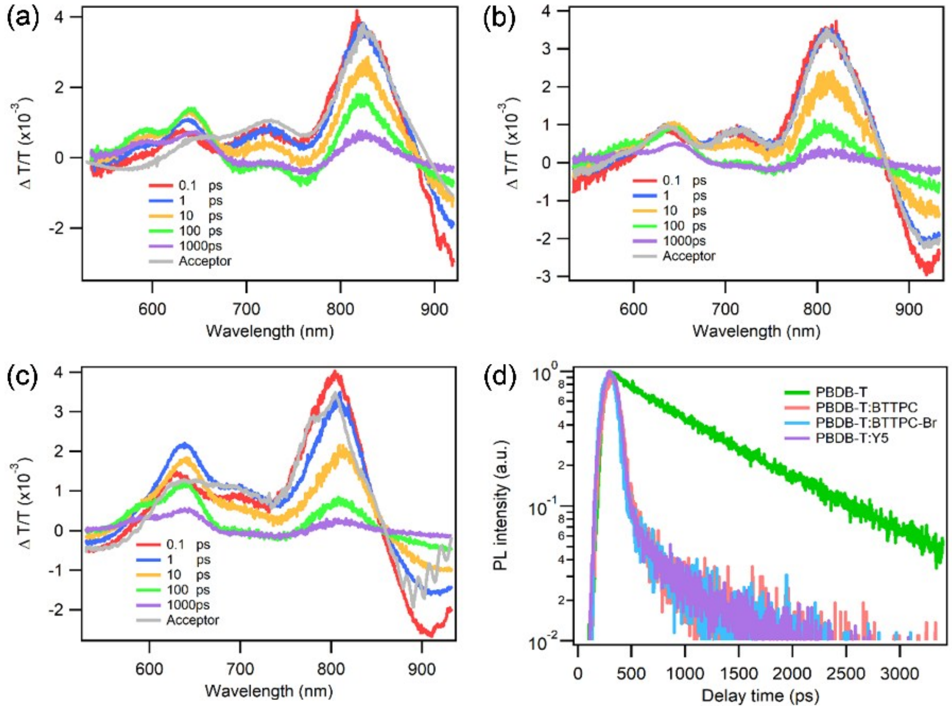


Figure S19. Representative fs-TA spectra of (a) PBDB-T: BTTPC-Br, (b) PBDB-T: BTTPC and (c) PBDB-T: Y5 blend films at indicated delay time. (d) TRPL kinetics of neat PBDB-T film, PBDB-T: BTTPC, PBDB-T: BTTPC-Br and PBDB-T: Y5 blend film.

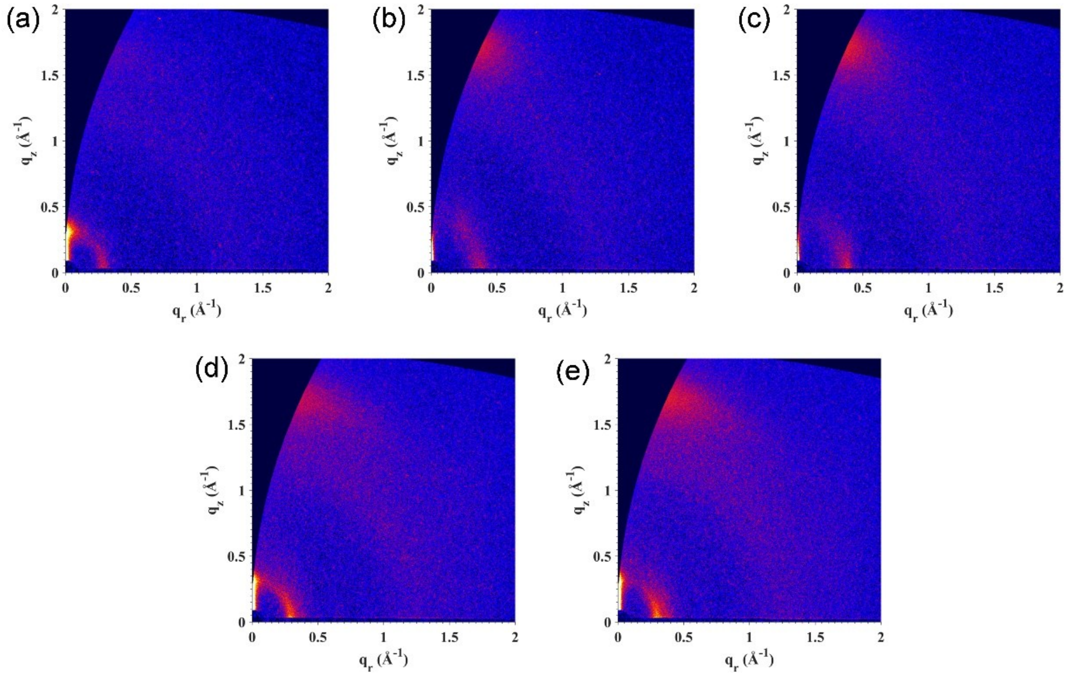


Figure S20. 2D GIWAXS patterns of (a) PBDB-T, (b) BTTPC, (c) BTTPC-Br, (d) PBDB-T: BTTPC and (e) PBDB-T: BTTPC-Br.

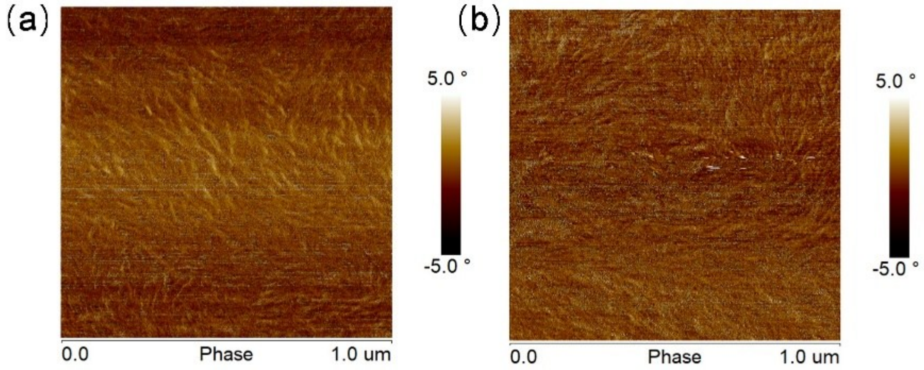


Figure S21. AFM phase images of the optimized blend films based on (a) PBDB-T: BTTPC and (b) PBDB-T: BTTPC-Br.

Table S1. The mobility data of OSCs based on PBDB-T: Y5, PBDB-T: BTTPC and PBDB-T: BTTPC-Br blend films.

Active layer	Hole Mobility (μ_h) (cm^2 V^{-1} s^{-1})	Electron Mobility (μ_e) (cm^2 V^{-1} s^{-1})
PBDB-T: Y5	1.71×10^{-4}	2.73×10^{-4}
PBDB-T: BTTPC	2.77×10^{-4}	5.34×10^{-4}
PBDB-T: BTTPC-Br	3.53×10^{-4}	6.58×10^{-4}

References

1. J. Yuan, Y. Zhang, L. Zhou, C. Zhang, T.-K. Lau, G. Zhang, X. Lu, H.-L. Yip, S. K. So, S. Beaupré, M. Mainville, P. A. Johnson, M. Leclerc, H. Chen, H. Peng, Y. Li and Y. Zou, Adv. Mater., 2019, 31, 1807577.