Supplementary Information (SI) for ChemComm.

Supporting Information

for

A Linear Non-halogenated Polymer Donor via Suzuki-Miyaura Coupling for Organic Solar Cells

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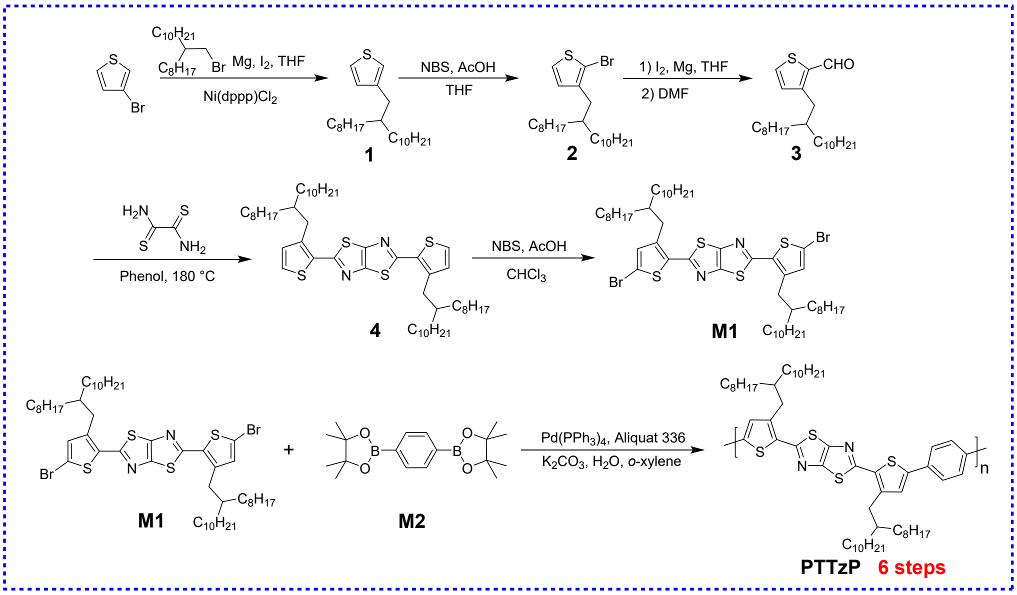
1. Synthesis

The synthesis routes of polymer PTTzP and its intermediates are shown in Scheme S1. The compounds 3-(2-octyldodecyl)thiophene (1), 2-bromo-3-(2-octyldodecyl)-thiophene (2), 3-(2-octyldodecyl)thiophene-2-carbaldehyde (3), 2,5-bis(3-(2-octyldodecyl)thiophen-2-yl)thiazolo[5,4-d]thiazole (4) and 2,5-bis(5-bromo-3-(2-octyldodecyl)thiophen-2-yl)thiazolo[5,4-d]thiazole (M1) were synthesized according to the procedures reported in literature.[1] The monomer 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (M2) was purchased from Suna Tech Inc. The non-fullerene acceptor Y6-BO was purchased from Solarmer organic photoelectric Technology (Beijing) Co., LTD. The other reagents and chemicals were purchased from commercial suppliers (Innochem, Energy-Chemical, Sigma-Aldrich and *J&K*) and used as received without further purification unless specifically mentioned.



Scheme S1. The synthetic route of PTTzP.

Synthesis of PTTzP: Monomer M1 (153.80 mg, 0.15 mmol), M2 (49.51 mg, 0.15 mmol) and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh$_3$)$_4$) (3.47 mg, 3 μmol) were dissolved in o-xylene (3 mL) under nitrogen atmosphere. Then 1M K_2CO_3 aqueous solution (1.5 mL) and Aliquat 336 (2 drops) were added to the mixture. The reaction mixture was stirred at 95 °C for 48 hours. After cooling to room temperature, the reaction mixture was precipitated in methanol and filtered through a Soxhlet thimble. The precipitation was subjected to Soxhlet extraction with methanol, acetone, hexane, dichloromethane, chloroform and chlorobenzene sequentially under argon protection. The chlorobenzene fraction was concentrated under reduced pressure and precipitated in methanol to obtain the polymer PTTzP (133 mg, yield = 91%). M_n = 52.3 kDa, $Đ_M$ = 2.1.

2. Measurements and Characterization

Gel permeation chromatography (GPC): The molecular weight of PTTzP was determined by Agilent Technologies PL-GPC 220 high-temperature chromatography in 1,2,4-trichlorobenzene (TCB) at 150 °C using a calibration curve of polystyrene standards.

Thermogravimetric analyses (TGA): TGA measurements were carried out with a NETZSCH (TG209F3) apparatus at a heating rate of 20 °C min^{-1} under nitrogen atmosphere.

Differential scanning calorimetry (DSC): DSC measurements were performed on a NETZSCH (DSC200F3) apparatus under a nitrogen atmosphere with a heating/cooling rate of 10/20 °C min^{-1} for the first cycle and a heating/cooling rate of 10/40 °C min^{-1} for the second cycle, respectively.

UV-Vis absorption spectra: UV-Vis absorption spectra of the polymer in chlorobenzene solutions and in films were recorded on a SHIMADZU UV-3600 spectrophotometer. The solution concentration was 0.02 mg mL^{-1}, and the films were spin-coated on glass substrates.

Cyclic voltammetry (CV): Cyclic voltammetry measurements were conducted on a CHI660A electrochemical workstation in a solution of tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) in acetonitrile. A glassy carbon, a platinum wire, and an Ag/AgCl electrode were used as working electrode, counter electrode, and reference electrode, respectively. A ferrocene/ferrocenium (Fc/Fc$^+$) redox couple was used as internal standard and was assigned an absolute energy of –4.80 eV versus vacuum. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of materials were determined according to the equation: $E_{\mathrm{HOMO}} = -e\,(E_{\mathrm{ox\ onset}} + 4.80 - E_{1/2}^{\mathrm{Fc/Fc+}})$ and $E_{\mathrm{LUMO}} = -e\,(E_{\mathrm{re,\ onset}} + 4.80 - E_{1/2}^{\mathrm{Fc/Fc+}})$, where $E_{\mathrm{ox,\ onset}}$ and $E_{\mathrm{re,\ onset}}$ are the onsets of oxidation and reduction potential relative to the measured Fc/Fc$^+$ redox couple, respectively. $E_{1/2}^{\mathrm{Fc/Fc+}}$ was measured as 0.42 V.

Steady-state photoluminescence (PL): The PL quenching measurements were performed at different excitation wavelengths for the corresponding films on a Shimadzu RF-6000 spectrometer.

Atomic force microscopy (AFM): Patterned glass substrates were pre-cleaned through sonication in a detergent bath, followed by rinsing with deionized water and sonication in an isopropanol bath, with each step lasting for 15 minutes. The donor and acceptor materials were dissolved in chloroform (CF) or tetrahydrofuran (THF) with a donor-to-acceptor ratio of 1:1.2. The solutions were stirred at 60 °C for 2 hours before being spin-coated at speed of 2500 rpm for 30 seconds, forming a thin active layer with an approximate thickness of 100 nm. Subsequently, the active layers were thermally annealed at 100 °C for 10 minutes. AFM images were obtained by Bruker Multimode 8 Microscope AFM in tapping mode.

Transmission electron microscopy (TEM): Patterned ITO glass substrates were pre-cleaned through sonication in a detergent bath, followed by rinsing with deionized water and sonication in an isopropanol bath, with each step lasting for 15 minutes. The prepared substrates were then subjected to oxygen plasma treatment for 5 minutes. Subsequently, PEDOT:PSS (CLEVIOSTM P VP AI 4083, supplied by Heraeus) was spin-coated on the ITO glass substrates at 3000 rpm for 30 seconds, resulting in a thickness of 40 nm. This was followed by baking at 150 °C for 15 minutes. After the baking process, the substrates were then transferred to a nitrogen-filled glove box. The donor and acceptor materials were dissolved in CF or THF with a donor-to-acceptor ratio of 1:1.2. The solutions were stirred at 60 °C for 2 hours before being spin-coated at speed of 2500 rpm for 30 seconds, forming a thin active layer with an approximate thickness of 100 nm. Subsequently, the active layers were thermally annealed at 100 °C for 10 minutes. The ITO glass coated with the active layer was then placed in a Petri dish filled with deionized water. Owing to the hydrophilic property of PEDOT:PSS, the active layer detached from the PEDOT:PSS. After that the active layer was collected by a copper grid and then vacuum dried overnight. TEM images were collected from JEM-2100F transmission electron microscope operated at 200 kV.

Grazing incidence wide-angle X-ray scattering (GIWAXS): GIWAXS measurements were carried out on the Xeuss 3.0 UHR system from Xenocs. The instrument is equipped with a Eiger 1M detector with a pixel size of 75um × 75um. The X-ray source is a Microfocus Sealed Tube X-ray Cu-source with the wavelength of $\lambda = 1.54$ Å. The sample was placed horizontally on the goniometer at a grazing angle of 0.2° relative to the incident beam.

3. Device Fabrication and Characterization

Fabrication of organic solar cells (OSCs): Patterned ITO glass substrates were pre-cleaned through sonication in a detergent bath, followed by rinsing with deionized water and sonication in an isopropanol bath, with each step lasting for 15 minutes. The prepared substrates were then subjected to oxygen plasma treatment for 5 minutes. Subsequently, PEDOT:PSS (CLEVIOSTM P VP AI 4083, supplied by Heraeus) was spin-coated on the ITO glass substrates at 3000 rpm for 30 seconds, resulting in a thickness of 40 nm. This was followed by baking at 150 °C for 15 minutes. After the baking process, the substrates were then transferred to a nitrogen-filled glove box. The donor and acceptor materials were dissolved in CF or THF with a donor-to-acceptor ratio of 1:1.2. The solutions were stirred at 60 °C for 2 hours before being spin-coated at speed of 2500 rpm for 30 seconds, forming a thin active layer with an approximate thickness of 100 nm. Subsequently, the active layers were thermally annealed at 100 °C for 10 minutes. Following this, a layer of PFN-Br was spin-coated onto the active layer. Finally, a 100 nm-thick layer of silver (Ag) was thermally evaporated onto the structure at a pressure of 5×10^{-6} Torr.

Photovoltaic performance measurements: The photovoltaic performances were measured under AM1.5G irradiation (100 mW $\mathrm{cm^{-2}}$) derived from a class solar simulator (Enlitech, Taiwan), which was calibrated by a China General Certification Center-certified reference single-crystal silicon cell (Enlitech). The current density–voltage (*J*–*V*) curves were recorded with a Keithley 2400 source meter. The device area is 0.0516 $\mathrm{cm^{-2}}$, and the test was performed with a mask aperture which defined an effective area of 0.04 $\mathrm{cm^{-2}}$.

External quantum efficiencies (EQEs): The EQE spectra were measured by a QE system (QE-R3011, Enlitech, Taiwan) with the light intensity calibrated by a standard single-crystal silicon photovoltaic cell (Enlitech).

Light-intensity dependence measurements: The light-intensity dependence measurements were carried out with illumination between 10–100 mW $\mathrm{cm^{-2}}$, which was calibrated by a standard single-crystal silicon solar cell (Enlitech). The current density and voltage were recorded with a Keithley 2400 source meter.

Fabrication and characterization of single-carrier devices: The charge carrier mobilities were measured in single-carrier devices with a structure of ITO/PEDOT:PSS/active layer/MoO_3/Ag for hole-only devices, and a structure of ITO/ZnO/active layer/PFNBr/Ag for electron-only devices. The dark current densities were measured by applying a voltage between 0 and 4 V with a Keithley 2400 source meter.

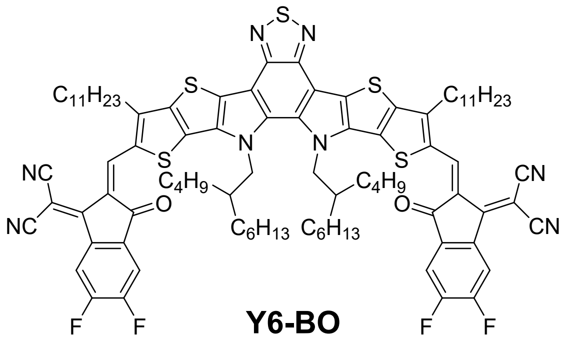
Charge carrier mobility estimation: The charge carrier mobility was estimated by fitting the data acquired from single-carrier devices to a space-charge-limit-current (SCLC) model. The mobility was determined by fitting the dark current according to the Mott-Gurney law that consider a Poole-Frenkel-type dependence of mobility on the electric field, given by the following equation:

$$J = \frac{9}{8}\varepsilon_r\varepsilon_0\mu_0\frac{V^2}{d^3}\exp\left(0.89\gamma\sqrt{V/d}\right) \qquad \text{(S1)}$$

where J is the dark current density, ε_0 is the permittivity of free space, ε_r is the dielectric constant of the polymer which is assumed to be 3 for organic semiconductors, μ_0 is the zero-filed mobility, γ is a parameter that describes the strength of the field-dependence effect, V is voltage drop across the device, and d is the thickness of the active layer. The hole and electron mobilities are extracted with the fit parameters at an electric field (E) of 1.0×10^5 V cm^{-1} by the Murgatroyd equation:

$$\mu = \mu_0\exp\left(\gamma\sqrt{E}\right) \qquad \text{(S2)}$$

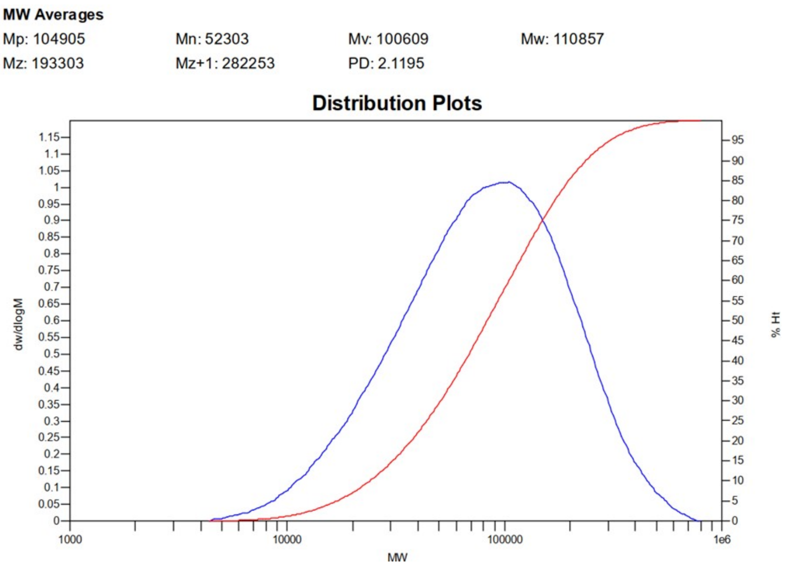
4. Additional Figures and Tables



Y6-BO

5.

Figure S1. The chemical structure of non-fullerene acceptor Y6-BO.



MW Averages

Mp: 104905
Mn: 52303
Mv: 100609
Mw: 110857
Mz: 193303
Mz+1: 282253
PD: 2.1195

Figure S2. GPC traces of PTTzP measured at 150 °C with 1,2,4-trichlorobenzene as the eluent.

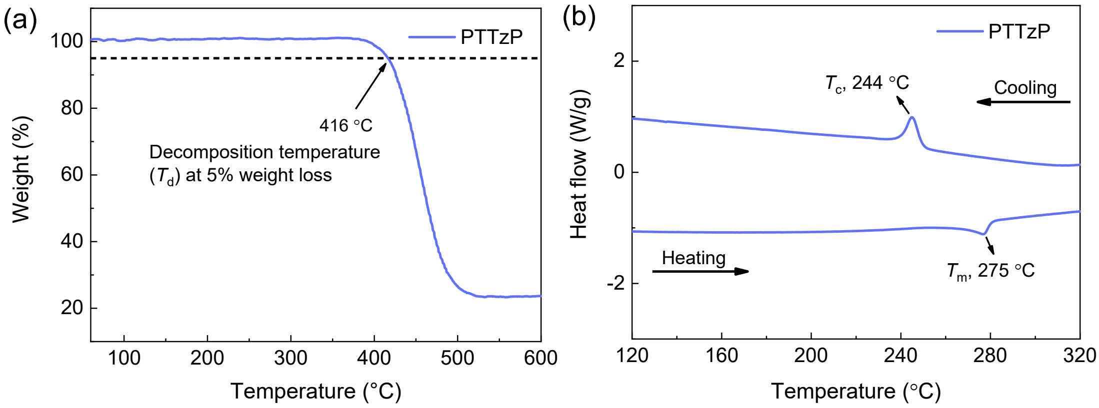


Figure S3. (a) TGA and (b) DSC curves of the polymer PTTzP.

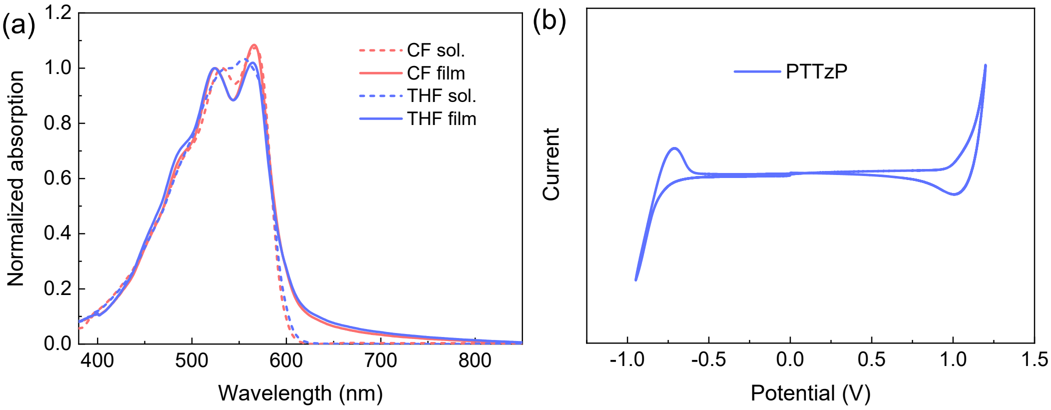


Figure S4. (a) The UV-Vis absorption spectra of PTTzP in CF and THF solution and thin films processed with CF and THF, respectively. (b) cyclic voltammogram of the polymer.

Table S1 Device performance of the OSCs based on PTTzP:Y6-BO processed with CF under different fabrication conditions.

D/A	Conc. (mg mL^{-1})	Solvent	Annealing	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
1:1	9.9	CF+20% CS_2[a]	100 °C, 10 min	0.83	22.24	0.62	11.43
1:1.2		CF	W/O	0.85	20.94	0.55	9.9
			80 °C, 10 min	0.84	22.25	0.58	10.79
			100 °C, 10 min	0.84	24.68	0.60	12.44
			120 °C, 10 min	0.83	23.77	0.60	11.84
1:1.5		CF+20% CS_2[a]	100 °C, 10 min	0.82	22.82	0.46	8.61

[a] CS_2 is carbon disulfide;

Table S2 Device performance of the OSCs based on PTTzP:Y6-BO processed with THF under different fabrication conditions.

D/A	Conc. (mg mL^{-1})	Solvent	Annealing	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%)
1:1	14	THF	100 °C, 10 min	0.84	22.34	0.58	10.75
		THF+0.5% NMP[a]		0.81	17.23	0.54	7.45
		THF+0.5% DPE[b]		0.82	22.29	0.58	10.68
1:1.2		THF		0.85	23.31	0.62	12.28
1:1.5				0.82	17.05	0.57	8.01

[a] NMP is *N*-methylpyrrolidone; [b] DPE is diphenyl ether.

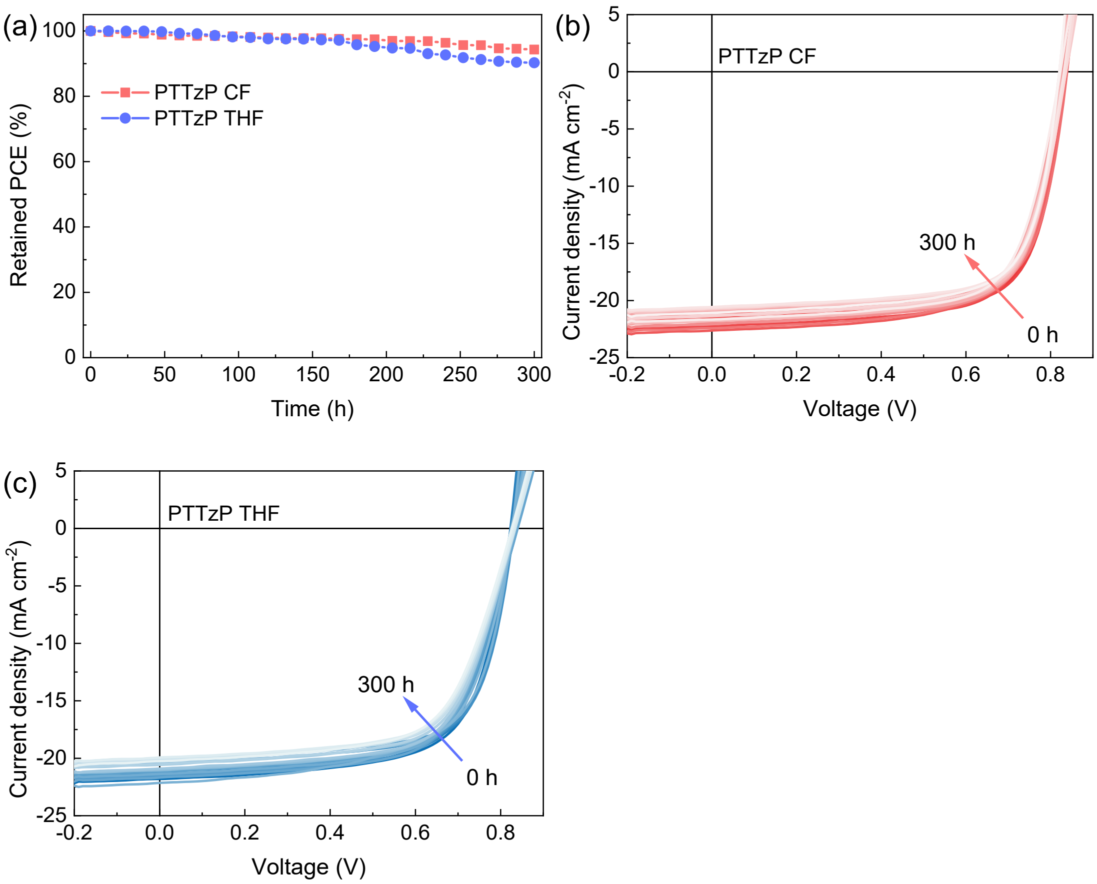


Figure S5. (a) Normalized performance loss of PCE during storage-stability tests, (b-c) devices recorded under AM1.5G illumination storage for 0 to 300 h, with arrows indicating the ageing trend.

Table S3 The device performance of the reported OSCs based on thiazolothiazole-based polymer donors.

Polymer	Acceptor	Synthetic steps	PCE [%]	References
PBT-S-TTz	PC$_{71}$BM	11	8.2	*J. Mater. Chem. A*, 2016, **4**, 9511–9518
PTZ1	PC$_{71}$BM	11	7.7	*J. Mater. Chem. A*, 2016, **4**, 13251–13258
PBTz-2	IT-4F	14	12.4	*Polym. Chem.*, 2020, **11**, 1629–1636
PCTZ-B	Y6	13	12.7	*Chem. Mater.*, 2021, **33**, 580–588
PTTz-3HD	Y6-BO	7	16.1	*Adv. Energy Mater.*, 2022, **12**, 2104050
PTTz-4HD	Y6-BO	6	15.0	*Adv. Energy Mater.*, 2022, **12**, 2104050
PTTzF	Y6	10	17.3	*Energy Environ. Sci.*, 2022, **15**, 4789
PTTz-2FT20	m-BTP-PhC6	12	16.2	*Chem. Eng. J.*, 2023, **474**, 145531.
PTTzP	**Y6-BO**	**6**	**12.4**	***This work***

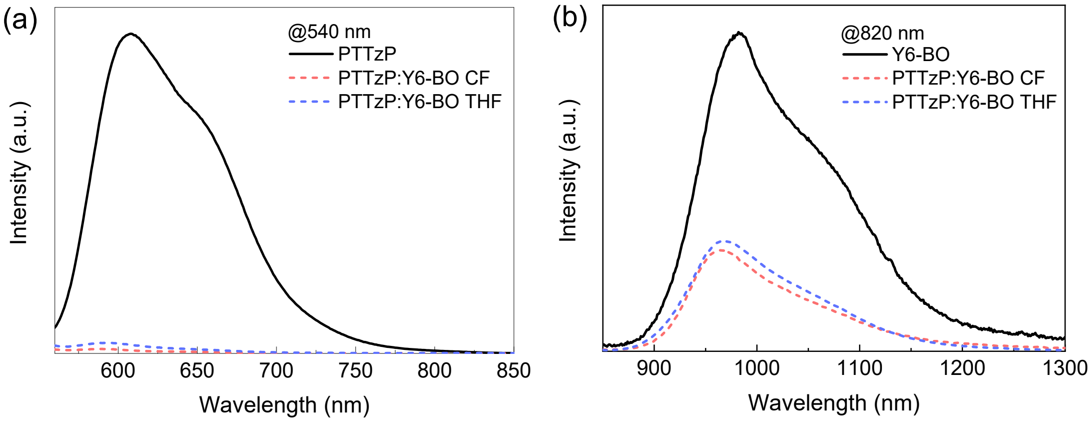


Figure S6. (a) PL spectra of PTTzP neat film and blend films with photoexcitation at 540 nm. (b) PL spectra of the Y6-BO neat film and blend films with photoexcitation at 820 nm.

Table S4. The PL quenching efficiency of PTTzP:Y6-BO blend films processed with CF and THF, respectively.

Active layer	solvent	ΔPL_D	ΔPL_A
PTTzP:Y6-BO	CF	99%	68%
	THF	97%	65%

Table S5. Electrical performance parameters and charge carrier mobilities of the neat films and PTTzP:Y6-BO blend films processed with CF and THF, respectively.

Active layer	solvent	μ_h (10^{-3} cm^2 V^{-1} s^{-1})	μ_e (10^{-3} cm^2 V^{-1} s^{-1})	μ_h/μ_e	α	n (kT/q)	P(E,T)
PTTzP	CF	1.45±0.54	-	-		-	-
Y6-BO	CF	-	0.88±0.11	-		-	-
PTTzP:Y6-BO	CF	0.54±0.10	0.57±0.08	0.95	0.986	1.042	95%
	THF	0.64±0.12	0.55±0.09	1.16	0.979	1.045	90%

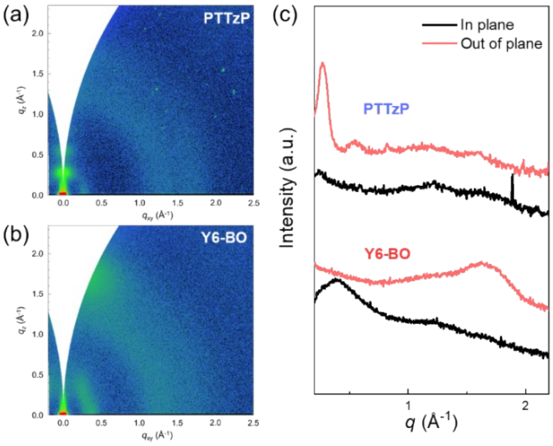


Figure S7. (a) Two-dimensional GIWAXS patterns and (b) one-dimensional line-cut profiles of PTTzP and Y6-BO neat films.

Table S6 Lattice parameters of the Y6-BO neat film and PTTzP:Y6-BO blend films processed with CF and THF, respectively.

Samples	In Plane (IP)		Out of Plane (OOP)	
	(100) distance (Å)	CCL^a (Å)	(010) distance (Å)	CCL^a (Å)
Y6-BO	16.36	23.8	3.78	17.2
PTTzP:Y6-BO (CF)	24.16	93.9	3.73	22.3
PTTzP:Y6-BO (THF)	24.25	92.2	3.83	18.9

[a] CCL represents crystal coherence length.

References

[1] M. Wakioka, S. Ishiki and F. Ozawa, *Macromolecules*, 2015, **48**, 8382.