Supporting information

Constructing Continuous Acceptor Fibrillar Networks and Achieving Uniform Phase Separation via Polymer-Assisted Morphology Control for 20.3% Efficient Additive-Free Organic Solar Cells

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Supplemental Experimental Procedures

Materials

Chloroform (Sigma-Aldrich, \geq 99%). D18, PM6 was purchased from HYPER Inc. L8-BO, N3, BTP-eC9, L8-BO-X, PY-DT, and PNDIT-F3N were obtained from Solarmer Material Inc. All the materials were used as received without further purification.

Methods

Gel Permeation Chromatography (GPC) measurement. The number average molecular weight (Mn) and polydispersity index (PDI) of D18 and PY-DT were measured using Agilent 1260 HT-GPC instrument with 1,2,4-trichlorobenzene as the eluent and polystyrene as a standard at 140 °C.

Cyclic voltammetry (CV) measurement. Cyclic voltammetry measurements were carried out on a CHI660A electrochemical workstation with a three-electrode configuration, using an Ag/AgNO₃ reference electrode, a platinum plate as the counter electrode, and glassy carbon as the working electrode. Tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile (0.1 mol L⁻¹) was used as the supporting electrolyte. The ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as internal standard and was assigned an absolute energy of – 4.8 eV versus vacuum. The Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energy levels of the materials were determined according to the equation $E_{HOMO/LUMO} = -(E_{ox onset}/E_{red onset} - E_{1/2}^{(Fc/Fc+)} + 4.80)$.

UV-vis absorption spectra. The UV–vis absorption spectra of the solutions and films were recorded using a Hitachi U-4100 spectrophotometer.

In-situ UV-vis absorption measurement. The in-situ UV-vis absorption measurement system is self-assembled consisting of the halogen lamp, a spectrometer and blade-coaters. The spectra were recorded by a spectrometer (NOVA-2S, Fuxiang Inc.) and the data was obtained by using a software (OPTOSKY Inc.), which can record the light intensity per 10 ms.

GIWAXS Characterization. GIWAXS characterization was conducted by 2D-GIWAXS experiments using a GANESHA 300XL+ system from JJ X-ray. The instrument is equipped with a Pilatus 300K detector with a pixel size of $172 \times 172 \,\mu\text{m}$. The X-ray source is a Genix 3D M icrofocus sealed tube X-Ray Cu-source with an integrated monochromator (30 W). The wavelength used was $\lambda = 1.5418$ Å. The detector moved in a vacuum chamber with a sample-to-detector distance varied between 0.115 m and 1.47 m, depending on the configuration, as calibrated by silver behenate (d001 = 58.380 Å). The minimized background scattering plus highperformance detector allowed for a detectable q-range varying from 3×10^{-3} to 3 Å⁻¹ (0.2 to 210 nm). The sample was placed vertically on the goniometer and tilted to a glancing angle of 0.2° with respect to the incoming beam. A small beam was then used to obtain better resolution. The accumulation time was 30 min for each measurement. In-plane and out-of-plane line-cuts were obtained using the SAXSGUI program.

Atomic force microscopy based infrared spectroscopy (AFM-IR). The atomic force microscopy-infrared spectroscopy measurements were performed on NanoIR2fs. AFM-IR is a photothermal technique that combines AFM and IR spectroscopy to unambiguously identify the chemical composition of a sample with tens-ofnanometers spatial resolution. When the sample absorbs photons from a pulsed tunable monochromatic IR laser light source, it heats up and rapidly expands, inducing an impulse to the AFM probe in contact with the sample. This causes an oscillation of the AFM cantilever at its contact resonant frequencies. The tip is then scanned across the sample surface, and the topography of the sample is recorded.

Transient Absorption Spectroscopy (**TAS**). For femtosecond transient absorption spectroscopy, the fundamental output from Yb:KGW laser (800 nm, 220 fs Gaussian fit, 100 kHz, Coherent Inc.) was separated into two light beams. One was introduced to NOPA (ORPHEUS-N, Coherent Inc. Ltd) to produce a certain wavelength for pump beam (here we use 750 nm, 30 fs pulse duration), the other was focused onto a YAG plate to generate white light continuum as the probe beam. The

pump and probe overlapped on the sample at a small angle of less than 10°. The transmitted probe light from the sample was collected by a linear CCD array.

Device characterisation

Device Fabrication. Devices with ITO/PEDOT:PSS /active layer/PNDIT-F3N/Ag structure were fabricated according to the following procedure. Patterned ITO glass substrates were sequential cleaned by ultrasonication in detergent, deionized water, acetone, and isopropyl alcohol for 15 min each and then dried at 80 °C for 5 min. The precleaned substrates were treated in an ultraviolet-ozone chamber for 20 min, then PEDOT:PSS was spin-cast onto the ITO surface at 4000 rpm for 30 s and annealed at 150 °C for 15min. The D18:L8-BO (1:1.2 w/w, 10 mg mL⁻¹ in total) and D18:L8-BO:PY-DT (1:1:0.2 w/w/w, 10 mg mL⁻¹ in total) solutions were stirred at 60 °C before spin-coating. Then, the solutions were spin-coated on top of the PEDOT: PSS film from chloroform (CF) solution followed by an annealing at 90 °C for 5 min. After the layers were fully cooled, the PNDIT-F3N (0.5 mg mL⁻¹ in methanol with 0.5 v% of acetic acid) was spin-coated on the BHJ layer at 3500 rpm. Finally, a 100 nm Ag layer was thermally deposited in vacuum (below 10⁻⁵ Torr). Photovoltaic cells were fabricated on the substrate with an effective area of 0.052 cm².

J-V and EQE. The *J-V* curves of all devices were measured under an illumination of AM 1.5G (100 mW/cm²) using a Keithley 2400 source meter generating from LSS-55 solar simulator (50*50mm spot size) of LightSky Technology CO. LTD. The light intensity was determined by a standardized mono silicon cell (KG5) calibrated. The *J-V* curves were measured by forward scanning in the range of -0.1-1.1*V*. The scan speed and dwell times were fixed at 0.02 *V*/step and 20 ms, respectively. The *J-V* testing was accomplished in a glove box in a nitrogen atmosphere with an ambient temperature of 25°C and 0% humidity. The EQE spectral were recorded utilizing spectral response measurement system LST-QE of LightSky Technology CO., LTD.

Space-charge-limited current (SCLC) mobility measurements. Hole-only and electron-only devices were fabricated to measure the hole and electron mobilities of

active layers by using the space charge limited current (SCLC) method with hole-only devices of ITO/PEDOT:PSS/active layer/MoO₃/Ag and electron-only devices of ITO/ZnO/active layer/PNDIT-F3N/Ag. The mobilities (μ_h or μ_e) were determined by fitting the dark current to the model of a single carrier SCLC, described by the equation:

$$J = \frac{9}{8}\varepsilon_0\varepsilon_r\mu\frac{V^2}{d^3}$$

where *J* is the current, ε_0 is the permittivity of free space, ε_r is the material relative permittivity, *d* is the thickness of the active layer, and *V* is the effective voltage. The effective voltage was obtained by subtracting the built-in voltage (*V*_{bi}, the built-in voltage due to the relative work function difference of the two electrodes) and the voltage drop (*V*_s, due to contact resistance and series resistance across the electrodes) from the applied voltage (*V*_{appl}), $V = V_{appl} - V_{bi} - V_s$ The mobility was calculated from the slope of the *J*_{1/2}-*V* curves. The thickness of the BHJ blend for SCLC measurement was about 90 nm.

TPV, TPC and recombination rate coefficient Measurements. TPV, TPC and recombination rate coefficient were performed with the all-in-one characterization platform, PAIOS instrumentation (Fluxim AG, Switzerland). Transient photovoltage (TPV) and Transient photocurrent (TPC) analyses measure the time-dependent extraction of photogenerated charge carriers. During the TPC measurement, the device is set under short-circuit condition; the light-pulse length was 20 μ s, the setting time and follow-up time were 100 μ s, the light intensities were 1%, 25.8%, 50.5%, 75.2% and 100%, respectively, rising from 0.01 sun to 1 sun. The photocurrent decay kinetics of all devices follow a mono-exponential decay:

$$y = A \exp(-x/t) + y_0$$

where A is a constant that fits the peak height, t is the charge extraction time, and T is the charge extraction time.

The exponential fitting was used to process the V-t curves measuring from the TPV signal to obtain the lifetime of carriers. The total charge generated by LED was obtained from the integrated TPC signal. Empirically, the differential capacitance

values are found to follow the exponential dependence on the open-circuit voltage given by

$$C = \frac{\Delta Q}{\Delta V_0} = C_0 \exp(\gamma V_{oc}) + D$$

where *C* is the differential capacitance (F), ΔQ is the total charge generated by a pulse (C), ΔV_0 is the TPV magnitude (V), C_0 is the exponential capacitance prefactor (F), γ is the capacitance exponential constant (V⁻¹), *D* is the effectively fixed capacitance (F).

So, the charge carrier density as a function of *V*oc is given by treating the device as a parallel-plate capacitor and integrating with respect to voltage, as

$$n = \frac{1}{Aed} \int_{-\infty}^{V_{oc}} C_0 \exp(\gamma V) \, dV$$

n is the bulk charge-carrier density (m^{-3}) , *A* is the area of the device (m^2) , *d* is the thickness of the active layer (m).

Then, the recombination rate coefficient can be determined, which is defined by

$$k(n) = \frac{1}{T(n) \times n}$$

Calculation of trap state DoS. The defects density can be calculated form capacitance spectroscopy measurement in dark environment. The frequency axis can be scaled to energy axis through the follows

$$E_w = kTln(\frac{2f_0}{w})$$

where w is the angular frequency calculated by $w = 2\pi f$, f_0 is the attempt-to-excape frequency of 10⁹ Hz. The trap density at energy E_w can be acquired as

$$N_t(E_w) = -\frac{V_{bi}}{qd}\frac{dC}{dw}\frac{w}{kT}$$

d is the thickness of active layer and V_{bi} is the built-in voltage measured through Mott-Schottky characterization from CV data

$$\frac{1}{C^2} = \frac{2}{S^2 q \varepsilon_{\rm r} \varepsilon_0} \frac{V_{bi} - V}{N_A}$$

then the energy distribution can be described with Gaussion shape distribution

$$N_t(E) = \frac{N_t}{\sqrt{2\pi\sigma}} \exp\left[-\frac{(E_t - E)^2}{2\sigma^2}\right]$$

where N_t is the total density, E_t is the center of the Dos, σ is the disorder parameter.

Supplemental Figures



Figure S1. GPC traces of polymers (a) D18 and (b) PY-DT. High temperature GPC with 1,2,4-trichlorobenzene as the eluent and polystyrene as a standard at 140 °C.



Figure S2. (a) energy level diagram and (b) Cyclic voltammogram curves of the D18, L8-BO and PY-DT.



Figure S3. (a) The normalized absorption spectra of D18, L8-BO and PY-DT neat films. The absorption coefficients of (b) L8-BO, PY-DT and L8-BO:PY-DT films and (c) D18:L8-BO and D18:L8-BO:PY-DT blended films.



Figure S4. (a) Time-dependent contour maps of in situ UV-vis absorption spectra of L8-BO film during spin coating. (b) Time evolution of peak location and intensity of acceptor. (c) Time-dependent contour maps of in situ UV-vis absorption spectra of L8-BO:PY-DT blended film during spin coating. (d) Time evolution of peak location and intensity of acceptor.



Figure S5. The 2D GIWAXS patterns of (a) L8-BO, (b) PY-DT and (c) L8-BO:PY-DT films. (d) The 1D line cut profiles of the corresponding L8-BO, PY-DT and L8-BO:PY-DT films. (e) Pole figure of the (010) peaks, where ω denotes the polar angle.



Figure S6. The 2D GISAXS patterns of (a) L8-BO, (b) PY-DT and (c) L8-BO:PY-DT films.



Figure S7. Time-dependent contour maps of in situ UV-vis absorption spectra of (a) D18:L8-BO and (b) D18:L8-BO:PY-DT blended films during spin coating. Time evolution of peak location of acceptor and intensity of donor and acceptor.



Figure S8. Pole figure of the (010) peaks, where ω denotes the polar angle.



Figure S9. The 2D GISAXS patterns of (a) D18:L8-BO and (b) D18:L8-BO:PY-DT blended films.



Figure S10. (a) The Line A and (b) the Line B profiles to obtain the full width at half maximum (FWHM) of cross-sections though AFM-IR signals of D18:L8-BO and D18:L8-BO:PY-DT blended films. The fibril width is obtained from the FWHM.



Figure S11. The TEM images of (a) D18:L8-BO and (b) D18:L8-BO:PY-DT blended films.



Figure S12. The 2D GIWAXS patterns of (a, b, c) D18:L8-BO and (d, e, f) D18:L8-BO:PY-DT blended films measured at incident angles of 0.08°, 0.16° and 0.2°. The 1D line cut profiles of the corresponding (g) D18:L8-BO and (h) D18:L8-BO:PY-DT blended films.



Figure S13. The 2D GISAXS patterns of (a, b, c) D18:L8-BO and (d, e, f) D18:L8-BO:PY-DT blended films measured at incident angles of 0.08°, 0.16° and 0.2°. The 1D profiles of the corresponding (g) D18:L8-BO and (h) D18:L8-BO:PY-DT blended films.



Figure S14. *J-V* curves of optimal devices with the different content of PY-DT.



Figure S15. (a) *J-V* curve of the device based on D18:PY-DT blend. (b) AFM height image of the D18:PY-DT blend film. (c) 2D GIWAXS pattern and (d) corresponding line cut profiles of D18:PY-DT blend film.



Figure S16. The s-EQE and EL curves of the (a) D18:L8-BO and (b) D18:L8-BO:PY-DT-based OSCs. (c) EQE_{EL} curves of the optimal devices. (d) Comparison of ΔE_1 , ΔE_2 , and ΔE_3 values and E_{loss} of the D18:L8-BO and D18:L8-BO:PY-DT-based OSCs.



Figure S17. Dark *J-V* characteristics of hole-only and electron-only D18:L8-BO and D18:L8-BO:PY-DT-based OSCs.



Figure S18. Dark *J-V* characteristics of electron-only (a) L8-BO, (b) PY-DT and (c) L8-BO:PY-DT-based OSCs. (d) Carrier mobilities of the devices. Error bars represent the standard error of the mean.



Figure S19. (a) Mott-Shockley plots. (b) Lifetime and (c) charge-carriers density under different V_{oc} conditions. The solid lines represent the best fit to power-law dependence. (d) Charge lifetime in the devices as a function of charge density.



Figure S20. *J*–*V* curves of various high-performance active layer systems, including five representative additive-free binary systems ((a) PM6:L8-BO-X, (b) PM6:L8-BO, (c) D18:BTP-eC9, (d) D18:N3, and (e)D18:L8-BO-X) and their corresponding PY-DT-based ternary blends.



Figure S21. *J-V* curves of the D18:L8-BO:PY-DT-based devices with active layer thicknesses of 200 and 300 nm.



Figure S22. Normalized (a) J_{sc} , (b) V_{oc} and (c) FF of the devices under continuous illumination. The device was in a nitrogen atmosphere at 25°C and the light source was standard sunlight simulated by LEDs.

Supplemental Tables

inspersity index (1D1) information for D10 and 11-D1.				
	M _n [kDa]	PDI		
D18	61.1	2.04		
PY-DT	7.0	1.99		

Table S1. Summarized number-average molecular weight (Mn) and polymericdispersity index (PDI) information for D18 and PY-DT.

 Table S2. Spin-coating time of chloroform solution of acceptor material to form a film.

	<i>t</i> ₁ (<i>ms</i>)	<i>t</i> ₂ (<i>ms</i>)	<i>t</i> ₃ (<i>ms</i>)	$t_{\rm tal}$ (ms)
L8-BO	31	156	63	250
PY-DT	0	0	313	313
L8-BO:PY-DT	31	94	156	281

Table S3. Structural parameters of the 010 peak of the material in the out-of-plane (OOP). Position, and the full width at half maximum (FWHM) are available through multi-peak fitting and d-spacing, CCL can be calculated by Scherrer Equation: CCL = $2\pi K/\Delta q$, where K is the shape factor (K = 0.9) and Δq is the FWHM of diffraction peak.

	q (Å ⁻¹)	Distance (Å)	FWHM (Å ⁻¹)	CCL (Å)
L8-BO	1.70	3.69	0.37	15.27
PY-DT	1.61	3.90	0.39	14.62
L8-BO:PY-DT	1.74	3.61	0.33	17.13

	2Rg (nm)	ξ (nm)
L8-BO	36.7	/
PY-DT	32.4	/
L8-BO:PY-DT	49.1	/

Table S4. Fitting domain size parameters of the 1D GISAXS profiles for L8-BO, PY-DT and L8-BO:PY-DT films.

Table S5. Spin-coating time of chloroform solution of Donor/Acceptor material to form a film.

	$t_1 (ms)$	<i>t</i> ₂ (<i>ms</i>)	<i>t</i> ₃ (<i>ms</i>)	$t_{\rm tal} (ms)$
D18:L8-BO	34	559	125	718
D18:L8-BO:PY-DT	94	438	218	750

Table S6. Structural parameters of the 010 peak of the material in the out-of-plane (OOP). Position, and the full width at half maximum (FWHM) are available through multi-peak fitting and d-spacing, CCL can be calculated by Scherrer Equation: CCL = $2\pi K/\Delta q$, where K is the shape factor (K = 0.9) and Δq is the FWHM of diffraction peak.

	q (Å ⁻¹)	Distance (Å)	FWHM (Å ⁻¹)	CCL (Å)
D18:L8-BO	1.69	3.72	0.27	20.9
D18:L8-BO:PY-DT	1.71	3.66	0.25	22.7
D18:PY-DT	1.63	3.85	0.29	19.5

Table S7. Fitting domain size parameters of the 1D GISAXS profiles for D18:L8-BOand D18:L8-BO:PY-DT blended films.

	2Rg (nm)	ξ (nm)
D18:L8-BO	29.7	57.89
D18:L8-BO:PY-DT	35.5	45.65

Table S8. Structural parameters of the 010 peak of the material in the out-of-plane (OOP). Position, and the full width at half maximum (FWHM) are available through multi-peak fitting and d-spacing, CCL can be calculated by Scherrer Equation: CCL = $2\pi K/\Delta q$, where K is the shape factor (K = 0.9) and Δq is the FWHM of diffraction peak.

Angles		q (Å ⁻¹)	Distance (Å)	FWHM (Å ⁻¹)	CCL (Å)
0.08°	D18:L8-BO	1.69	3.71	0.57	9.93
0.08	D18:L8-BO:PY-DT	1.71	3.67	0.27	20.78
0.160	D18:L8-BO	1.70	3.70	0.30	19.16
0.16°	D18:L8-BO:PY-DT	1.71	3.67	0.27	21.09
0.2°	D18:L8-BO	1.70	3.69	0.28	19.97
	D18:L8-BO:PY-DT	1.71	3.66	0.27	21.09

Table S9. Fitting domain size parameters of the 1D GISAXS profiles for D18:L8-BO and D18:L8-BO:PY-DT blended films at different angles.

Angles		2Rg (nm)	ξ (nm)
0.08°	D18:L8-BO	13.9	22.4
0.00	D18:L8-BO:PY-DT	26.5	47.6
0.16°	D18:L8-BO	32.1	51.6
	D18:L8-BO:PY-DT	25.4	50.1
0.2°	D18:L8-BO	29.4	33.3
	D18:L8-BO:PY-DT	31.8	45.6

D18:L8- BO:PY-DT	$V_{\rm oc}$	$J_{\rm sc}$ [mA/cm ²]	FF [%]	PCE ^[a]
1.1 2.0	0.905	26.2	79.2	18.8
1.1.2.0	(0.903 ± 0.003)	(26.1 ± 0.2)	(78.8 ± 0.4)	(18.6 ± 0.2)
	0.912	27.0	79.4	19.6
1:1.1:0.1	(0.911 ± 0.001)	(26.7 ± 0.3)	(78.0 ± 0.5)	(10.2 ± 0.4)
	(0.911 ± 0.001)	(20.7 ± 0.3)	(70.9 ± 0.3)	(19.2 ± 0.4)
1 1 0 0	0.917	27.2	81.4	20.3
1:1:0.2	(0.917 ± 0.002)	(269 ± 01)	(80.9 ± 0.3)	(20.0 ± 0.2)
	(0.917 ± 0.002)	(20.9 ± 0.1)	(00.9 ± 0.9)	(20.0 ± 0.2)
1.0.0.0.2	0.929	26.5	79.1	19.5
1:0.9:0.3	(0.929 ± 0.001)	(26.3 ± 0.2)	(78.8 ± 0.3)	(19.3 ± 0.2)
		(,	(,	(,
1.0 7.0 5	0.942	26.0	76.6	18.7
1.0.7.0.5	(0.940 ± 0.002)	(25.7 ± 0.3)	(76.1 ± 0.5)	(18.4 ± 0.3)
	0.070	00.4	FF 1	10.1
1:0:1.2	0.979	22.4	55.1	12.1
1.0.1.2	(0978 ± 0.002)	(22.1 ± 0.2)	(54.6 ± 0.4)	(11.8 ± 0.2)

Table S10. Photovoltaic parameters of OSCs with different PY-DT content under the illumination of AM 1.5 G, 100 mW/cm^2 .

^[a]The values in parentheses are average PCEs calculated from 20 independent cells.

Table S11. Detailed device parameters of the reported representative additive-free

 OSCs and this work.

Time [Year]	Active layer	$V_{ m oc}$ [V]	J _{sc} [mA/cm ²]	FF [%]	PCE [%]	Ref.
2020	PBDB-T:ITIC	0.861	16.80	70.8	10.22	1
2020	PBDB-TAZ20:ITIC	0.865	19.03	73.5	12.02	1
2020	PBDB-TAZ40:ITIC	0.841	18.46	71.5	11.10	1
2020	PM7:IT-4F	0.931	17.14	73.42	11.72	2
2020	PM7:IT-4Cl	0.891	19.05	74.81	12.52	2
2020	PTB7-Th:T-FPDI	0.780	13.4	53.0	5.50	3
2020	PTB7-Th:TT-FPDI	0.791	14.4	62.9	7.17	3
2020	PTB7-Th:FT-FPDI	0.805	14.4	58.2	6.75	3
2020	PTB7-Th:FTT-FPDI	0.822	16.5	56.4	7.66	3
2020	PTB7-Th:IEICS-4F	0.75	22.0	58.8	9.7	4
2020	PM6:Y6	0.82	25.3	62.8	13.1	4
2021	PBDB-T-H:Y6	0.79	20.99	55	9.05	5
2021	PBDB-T-I:Y6	0.76	25.11	66	12.63	5
2021	PBDB-T-OAc:Y6	0.79	26.04	62	12.59	5
2021	PTQ10:m-DTC-2Cl	0.992	16.67	73.42	12.14	6
2021	PTB7-Th:BTPV-4F-Ec9	0.661	28.20	68.48	12.77	6
2021	PTB7-Th:T2-Cy6PRH	1.03	11.04	40	4.60	7

	PTB7-Th:T2-	1.00	10.10		< 0.1	_
2021	Cy6PRH:PCBM	1.00	12.12	58	6.91	7
2021	PTQ10:Y6	0.842	26.08	74.93	16.45	8
2021	PBDB-T:SNC2C4-F	0.85	10.63	47.0	4.25	9
2021	PBDB-T: SNC4C6-F	0.86	19.10	65.2	10.71	9
2021	PBDB-T: SNC6C8-F	0.89	16.74	62.1	9.25	9
2021	TPD-3F:IT-4F	0.911	20.25	76	13.84	10
2022	D18-Cl:BTF	0.860	27.19	72.05	16.83	11
2022	D18-Cl:BTFM	0.875	26.72	73.12	17.10	11
2022	PTB7:PC70BM	0.74	11.3	55	4.64	12
2022	J52:Y6	0.736	19.34	42.25	6.02	13
2022	PCN1:Y6	0.871	22.65	61.23	12.07	13
2022	PCN2:Y6	0.862	25.35	69.48	15.20	13
2023	PM6:Y7	0.84	25.88	70.73	15.62	14
2023	PM6:BTA-ERh	0.82	21.41	65.03	10.65	14
2023	PM6:Y7:PC71BM	0.84	27.55	73.46	16.98	14
2023	PM6:Y7:BTA-ERh	0.85	26.96	73.85	17.15	14
2023	PM6:Y7:PC71BM:BTA-ERh	0.87	28.60	76.32	18.90	14
2023	PM6:Y7	0.80	25.88	69.27	14.98	15
2023	TP-0.8-EG:Y7	0.77	16.24	61.72	7.72	15
2023	PM6:TP-0.8-EG:Y7	0.84	26.94	73.18	16.52	15
2023	PM6:BTP-eC9	0.840	26.21	75.91	16.72	16
2023	PM6:L8-BO	0.865	24.03	76.47	15.89	16
2023	PM6:BTP-eC9:L8-BO	0.862	26.78	79.34	18.30	16
2023	PM7-D3:PTI04	0.90	23.88	69	14.91	17
2023	PM7-D3:Y12	0.86	23.76	54	11.06	17
2023	PM7-D3:DTY6	0.86	20.29	65	11.28	17
2023	PM7-D5:PTI04	0.87	17.17	64	9.61	17
2024	PM6:IPC1F-BBO-IC2F	0.915	18.0	59.80	9.83	18
2024	PM6:IPC1F-BBO-IC2Cl	0.886	21.3	64.92	12.2	18
2024	PM6:IPC1Cl-BBO-IC2F	0.888	21.2	65.74	12.4	18
2024	PM6:IPC1Cl-BBO-IC2Cl	0.890	22.1	66.36	13.1	18
2024	PM6:IPC2F-BBO-IC2F	0.908	22.7	66.62	13.7	18
2024	PM6:IPC2F-BBO-IC2Cl	0.902	23.0	68.47	14.2	18
2024	PM6:IPC2Cl-BBO-IC2F	0.905	24.8	66.56	15.0	18
2024	PM6:IPC2C1-BBO-IC2C1	0.889	24.8	70.63	15.5	18
2024	PBQx-TF:DTB21	0.802	25.32	74.6	15.13	19
2024	PBQx-TF:DTB22	0.808	27.00	77.9	17.00	19

2024	PBQx-TF:DTB23	0.819	25.94	73.5	15.63	19
2024	D18:BTP-H17	0.887	25.64	76.82	17.46	20
2024	D18:BTP-H15	0.877	26.81	78.49	18.46	20
2024	D18:BTP-H13	0.862	24.92	71.44	15.35	20
2024	D18:BTP-H17:BTP-H15	0.881	27.35	80.36	19.36	20
2025	D18:L8-BO	0.905	26.2	79.2	18.8	This
2025	D18:L8-BO:PY-DT	0.917	27.2	81.4	20.3	Work

Table S12. Detailed information on energy losses of the D18:L8-BO and D18:L8-BO:PY-DT-based devices.

Active layer	E_g [eV]	<i>qV_{oc}</i> [eV]	E _{loss} [eV]	ΔE_1 [eV]	ΔE_2 [eV]	ΔE_3 [eV]	EQE _{EL} [%]
D18:L8-BO	1.451	0.905	0.546	0.268	0.069	0.209	3.103×10 ⁻²
D18:L8-BO:PY-DT	1.459	0.917	0.542	0.268	0.069	0.205	3.579×10 ⁻²

Table S13. Electron and hole mobility values for the D18:L8-BO and D18:L8-BO:PY-DT-based devices.

Active layer	$\mu_{\rm e} ({\rm cm}^2 {\rm V}^{-1} {\rm s}^{-1})^{ a}$	$\mu_{\rm h}({\rm cm}^2~{\rm V}^{-1}~{\rm s}^{-1})^{\rm a}$	$\mu_{ m e}$ / $\mu_{ m h}$
D18:L8-BO	$(4.34\pm0.51){\times}10^{-4}$	$(5.62\pm 0.21)\!\!\times\!\!10^{-4}$	0.77
D18:L8-BO:PY-DT	$(5.79 \pm 0.25) \times 10^{-4}$	$(5.59\pm 0.11)\!\!\times\!\!10^{-4}$	1.04

^aThe average values are obtained from 12 devices.

Table S14. Ele	ctron mobility v	values for the	L8-BO, PY-	DT and L8-B	D:PY-DT-based
devices.					

Active layer	$\mu_{ m e}~({ m cm}^2~{ m V}^{-1}~{ m s}^{-1})^{ m a}$
L8-BO	$(7.78 \pm 0.71) \times 10^{-4}$
PY-DT	$(6.17 \pm 0.55) \times 10^{-4}$
L8-BO:PY-DT	$(9.50\pm0.15){ imes}10^{-4}$

^aThe average values are obtained from 12 devices

Active layer	P _{diss} (%) ^a	$P_{\rm coll}$ (%) ^b	α^{c}	n^{d}
D18:L8-BO	96.8	88.9	0.97	1.11
D18:L8-BO:PY-DT	98.6	91.5	0.99	1.03

Table S15. The exciton dissociation and collection, charge recombination parametersfor the D18:L8-BO and D18:L8-BO:PY-DT-based devices.

^aCalculated by the formula: $P_{\text{diss}} = J_{\text{sc}}/J_{\text{sat}}$. ^bCalculated by the formula: $P_{\text{coll}} = J_{\text{MPP}}/J_{\text{sat}}$. ^cCalculated by the formula: $J_{\text{sc}} \propto P_{\text{light}}^{\alpha}$. ^dCalculated by the formula: $V_{\text{oc}} \propto n \text{kT/q ln } P_{\text{light}}$

Table S16. The lifetime of the hole transfer process in blended films. The data was achieved through the biexponential fitting.

t_1 (ps)	<i>t</i> ₂ (ps)
0.325 ± 0.044	3.23 ± 0.401
0.207 ± 0.041	2.15 ± 0.190
	$t_1 (ps)$ 0.325 ± 0.044 0.207 ± 0.041

Table S17. Photovoltaic parameters of the additive-free OSCs (PM6:L8-BO-X, PM6:L8-BO, D18:BTP-eC9, D18:N3, and D18:L8-BO-X) and their corresponding PY-DT-based ternary OSCs under the illumination of AM 1.5 G, 100 mW/cm².

A ativa lavar	$V_{ m oc}$	$J_{ m sc}$	FF	PCE ^[a]
Active layer	[V]	[mA/cm ²]	[%]	[%]
DM6.DTD CO	0.869	25.3	71.2	15.7
PINIO.DIP-eC9	(0.868 ± 0.002)	(25.1 ± 0.2)	(70.9 ± 0.4)	(15.4 ± 0.4)
PM6:BTP-	0.883	25.5	74.3	16.7
eC9:PY-DT	(0.882 ± 0.001)	(25.3 ± 0.2)	(74.1 ± 0.2)	(16.5 ± 0.2)
DM6-L 8 DO	0.904	24.5	75.0	16.6
PIVIO.Lo-DU	(0.903 ± 0.001)	(24.3 ± 0.1)	(74.8 ± 0.2)	(16.4 ± 0.2)
PM6:L8-BO:PY-	0.917	24.9	77.3	17.7
DT	(0.915 ± 0.003)	(24.8 ± 0.1)	(76.9 ± 0.3)	(17.5 ± 0.2)
DMGI 9 DO V	0.891	25.0	74.5	16.6
PM0.Lo-DO-A	(0.889 ± 0.002)	(24.8 ± 0.3)	(74.2 ± 0.3)	(16.4 ± 0.2)
PM6:L8-BO-	0.908	25.4	77.0	17.8
X:PY-DT	(0.908 ± 0.001)	(25.2 ± 0.2)	(76.5 ± 0.4)	(17.5 ± 0.3)
D19.N2	0.838	27.5	77.1	17.8
D16.N5	(0.837 ± 0.001)	(27.2 ± 0.3)	(76.8 ± 0.3)	(17.5 ± 0.3)
D19.N2.DV DT	0.850	27.8	78.1	18.5
D18.N3.P1-D1	(0.848 ± 0.002)	(27.5 ± 0.2)	(77.9 ± 0.2)	(18.2 ± 0.2)
D18.1 8 PO V	0.901	26.7	77.7	18.7
D10.L0-DU-A	(0.899 ± 0.002)	(26.4 ± 0.3)	(77.4 ± 0.3)	(18.4 ± 0.3)
D18:L8-BO-	0.913	27.1	79.4	19.6
X :PY-DT	(0.913 ± 0.001)	(26.9 ± 0.2)	(79.2 ± 0.2)	(19.5 ± 0.1)

^[a]The values in parentheses are average PCEs calculated from 20 independent cells.

Table S18. Photovoltaic parameters of OSCs with active layer thicknesses of 200 and300 nm under illumination of AM 1.5 G, 100 mW/cm².

Active layer	Thickness (nm)	$V_{ m oc}$ [V]	J _{sc} [mA/cm ²]	FF [%]	PCE ^[a] [%]
D18:L8-	200nm	$\begin{array}{c} 0.919 \\ (0.918 \pm 0.001) \end{array}$	27.3 (27.1 ± 0.2)	77.3 (76.8 ± 0.4)	19.4 (19.1 ± 0.3)
BO:PY-DT	300nm	$\begin{array}{c} 0.919 \\ (0.917 \pm 0.003) \end{array}$	27.2 (26.9 ± 0.3)	74.7 (74.2 ± 0.3)	18.7 (18.3 ± 0.3)

^[a]The values in parentheses are average PCEs calculated from 20 independent cells.

Table S19. Photovoltaic parameters of the OSCs for the stability evaluation under the illumination of AM 1.5 G, 100 mW/cm^2 .

Active layer	$V_{ m oc}$ [V]	J _{sc} [mA/cm ²]	FF [%]	PCE [%]
D18:L8-BO	0.905	26.1	79.0	18.7
D18:L8-BO:PY-DT	0.917	27.0	81.2	20.1

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