

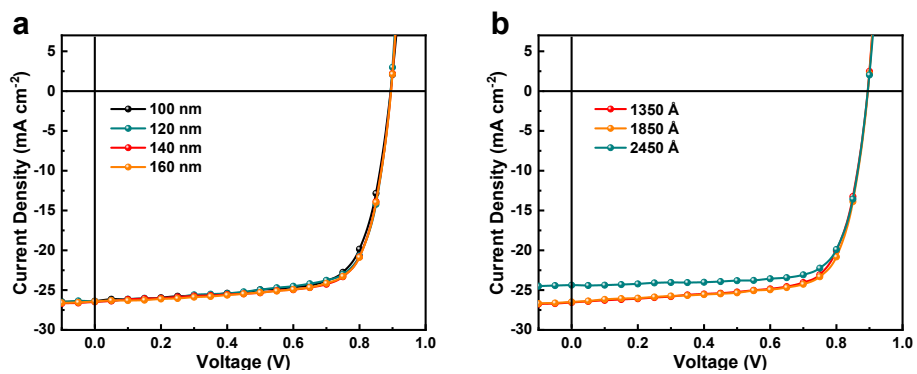
Supplementary Materials for

Revealing the Critical Role of In-Plane Charge Transport in Large-Scale

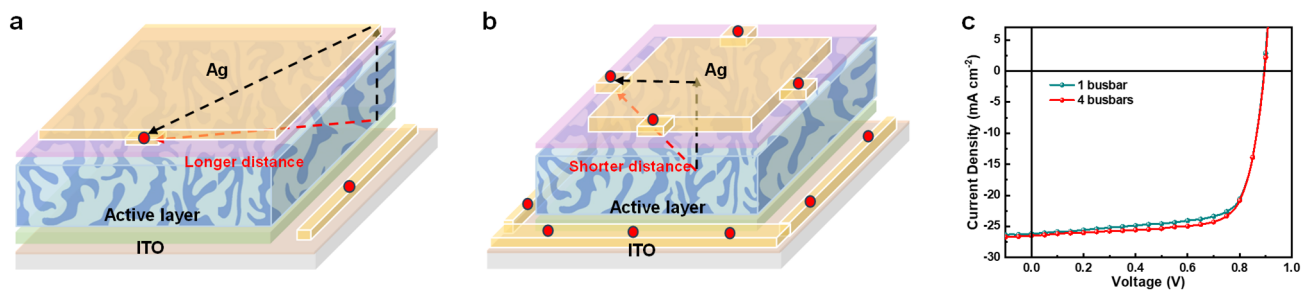
Organic Photovoltaics

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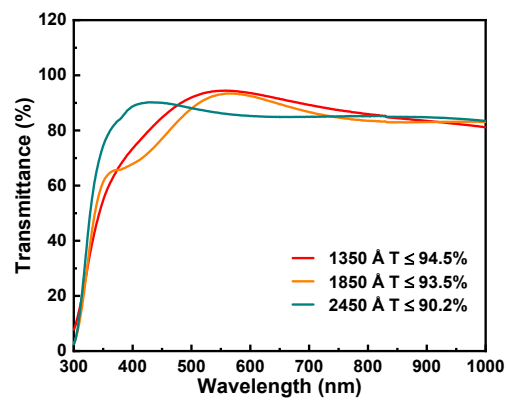
Corresponding author: Xiaopeng Duan, duanxp@buaa.edu.cn; Siwei Luo, sluoak@connect.ust.hk; Yanming Sun, sunym@buaa.edu.cn.



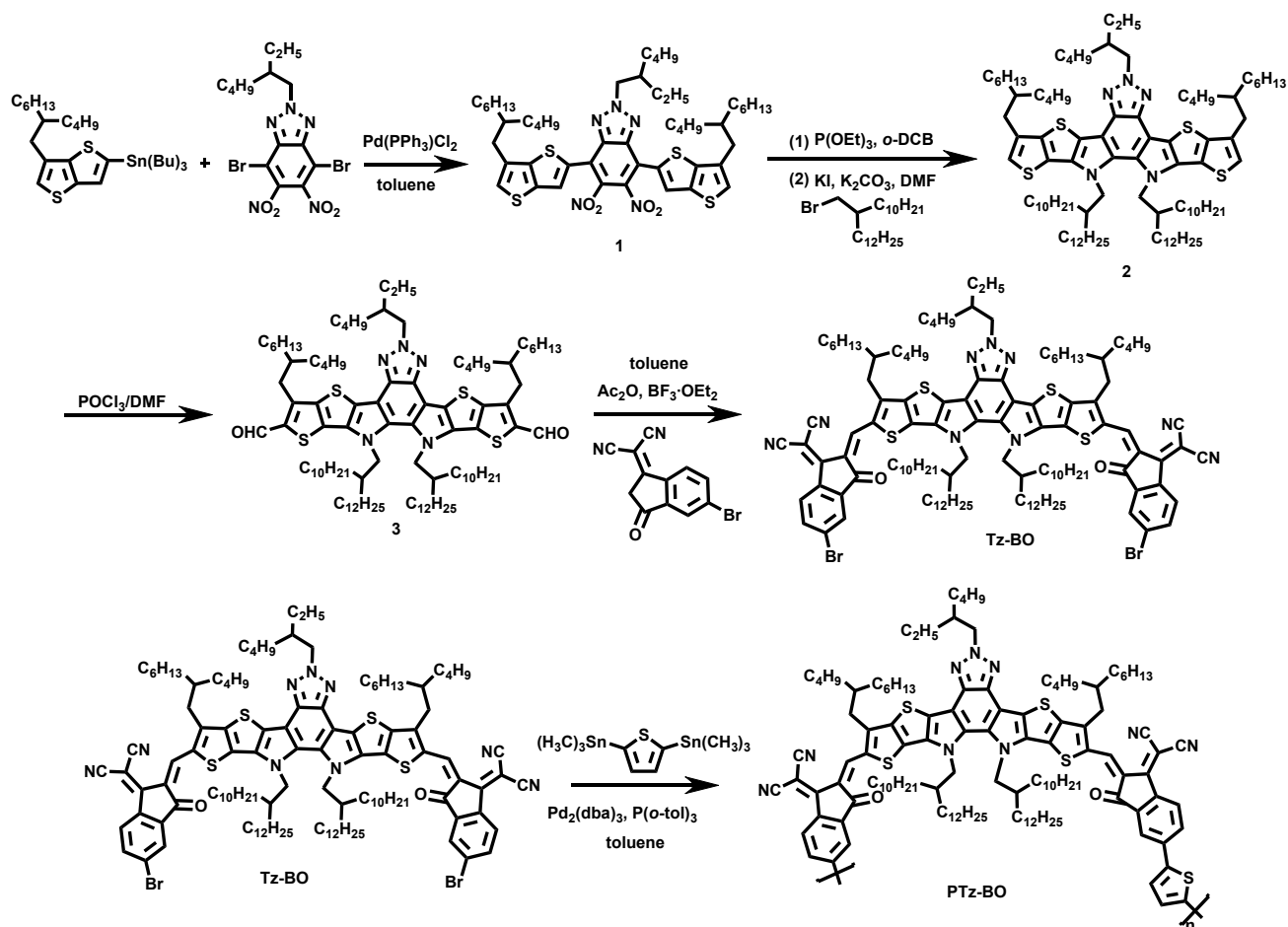
Supplementary Figure 1. J - V curves of 1.0 cm^2 PM6:L8-BO-X-based devices with different Ag (a) and ITO (b) thicknesses.



Supplementary Figure 2. Schematic illustration of charge transport under 1 busbar (a) and 4 buabars (b). The red dotted lines show the maximum transport distances of the photogenerated charges. c, J - V curves of 1.0 cm² PM6:L8-BO-X-based devices with different numbers of busbars.



Supplementary Figure 3. Transmission spectra of ITO glass with different ITO thicknesses.



1
2 **Supplementary Figure 4.** Synthetic routes of the polymer acceptors of PTz-BO.

3 **Synthesis of Compound 1:** 4,7-dibromo-2-(2-ethylhexyl)-5,6-dinitro-2H-benzo[d]-[1,2,3]-triazole (1.0 g, 2.1 mmol) and
4 tributyl(6-(2-butyloctyl)thieno[3,2-b]thiophen-2-yl)stannane (3.2 g, 5.4 mmol) were added in dry toluene, after which
5 Pd(PPh₃)₂Cl₂ (70.2 mg, 0.10 mmol) was added, the solution was degassed using a nitrogen. After the mixture was refluxed
6 under nitrogen for 12 hours, it was allowed to cool to room temperature and then concentrated under reduced pressure. The
7 crude product was chromatographically purified on silica gel column to afford compound 1 as an orange-red solid (1.5 g,
8 78%).

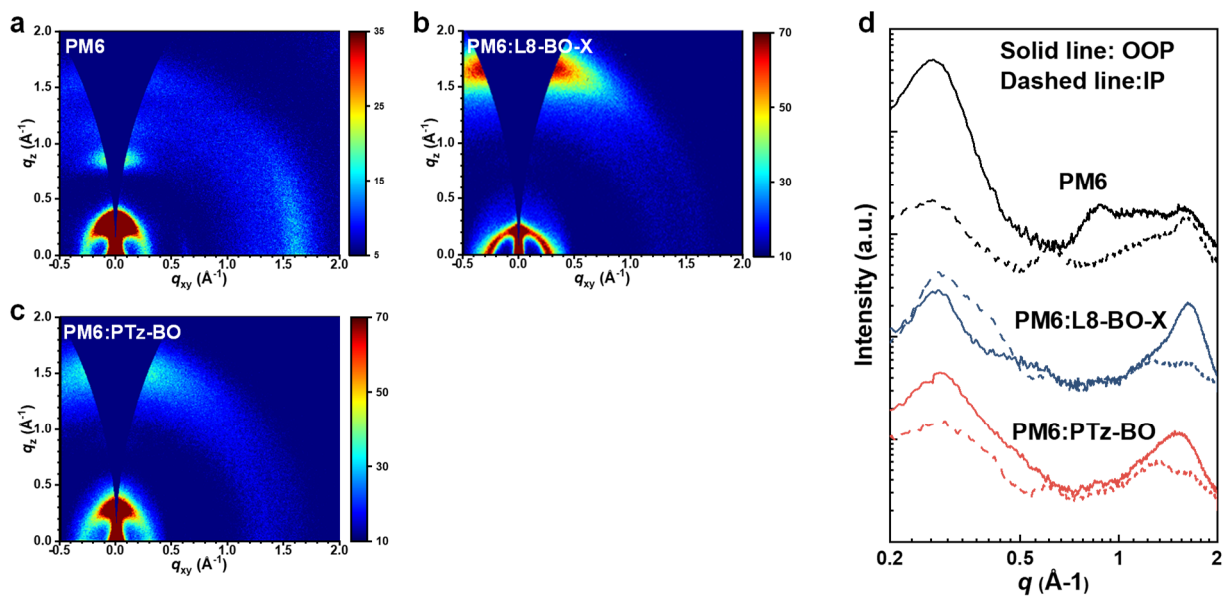
9 **Synthesis of Compound 2:** Compound 1 (1.50 g, 1.6 mmol) and triethyl phosphite (2.66 g, 16 mmol) were dissolved in *o*-
10 dichlorobenzene (*o*-DCB, 15 mL). After refluxing 8 hours, the reaction was cooled to room temperature. The solvent was
11 evaporated, leaving the precipitate, which was used without further purification. The precipitate, potassium iodide (266
12 mg, 1.6 mmol), potassium carbonate (2.65 g, 19.2 mmol), and 11-(bromomethyl)tricosane (8.02 g, 19.2 mmol) were
13 dissolved in 30 mL N,N-dimethylmethanamide (DMF), the solution was degassed using a nitrogen. After the mixture was
14 heated to 90 °C overnight under nitrogen atmosphere. The reaction solvent was extracted with dichloromethane and water,
15 and then concentrated under reduced pressure. The residue was purified roughly with column chromatography on silica
16 gel, which was used directly to the next reaction (0.99 g, 40%).

17 **Synthesis of Compound 3:** To a solution dry DMF (10 mL) at 0 °C, phosphorus oxychloride (1.96 g, 12.8 mmol) was
18 slowly added dropwise under N₂ atmosphere. After stirring at the room temperature for additional 0.5 h, the dichloroethane
19 solution of compound 2 (0.99 g, 0.64 mmol) was added, the solution was heated to 80 °C and stirred overnight. The reaction
20 mixture was allowed to cool to room temperature and the mixture was poured into ice water, neutralized with Na₂CO₃ (aq),

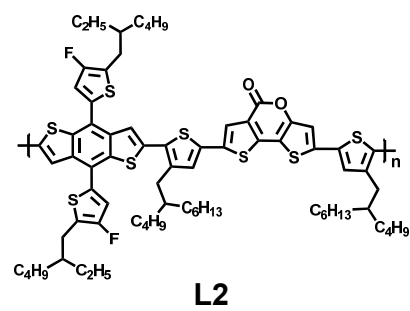
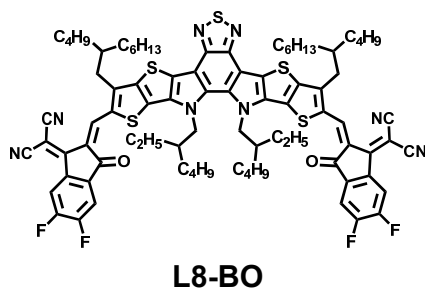
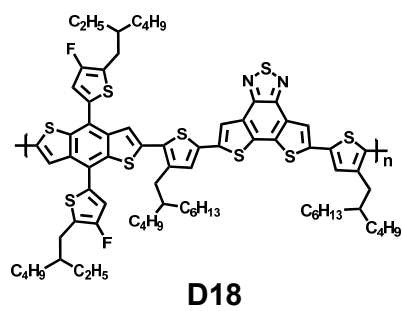
1 and then extracted with dichloromethane. After removal of solvent, the crude product was purified using silica gel using
2 petroleum ether:dichloromethane = 2:1 (v:v) as eluent, yielding an orange solid of compound 3 (0.82 g, 80%).

3 **Synthesis of Tz-BO:** Under the protection of nitrogen, compound 3 (0.32 g, 0.2 mmol) and 2-(5-bromo-3-oxo-2,3 dihydro-
4 1H-inden-1-ylidene)malononitrile (0.22 g, 0.5 mmol) were dissolved in dry chloroform (25 ml), to which 1 mL pyridine
5 was added after. After stirring at 62 °C overnight, the reaction mixture was allowed to cool to room temperature and the
6 mixture was poured into methanol. The precipitate was collected by filtration to get crude product, which was further
7 purified by column chromatography on silica gel with petroleum ether:dichloromethane (1.5:1) as an eluent to afford Tz-
8 BO (295.4 mg, 70%).

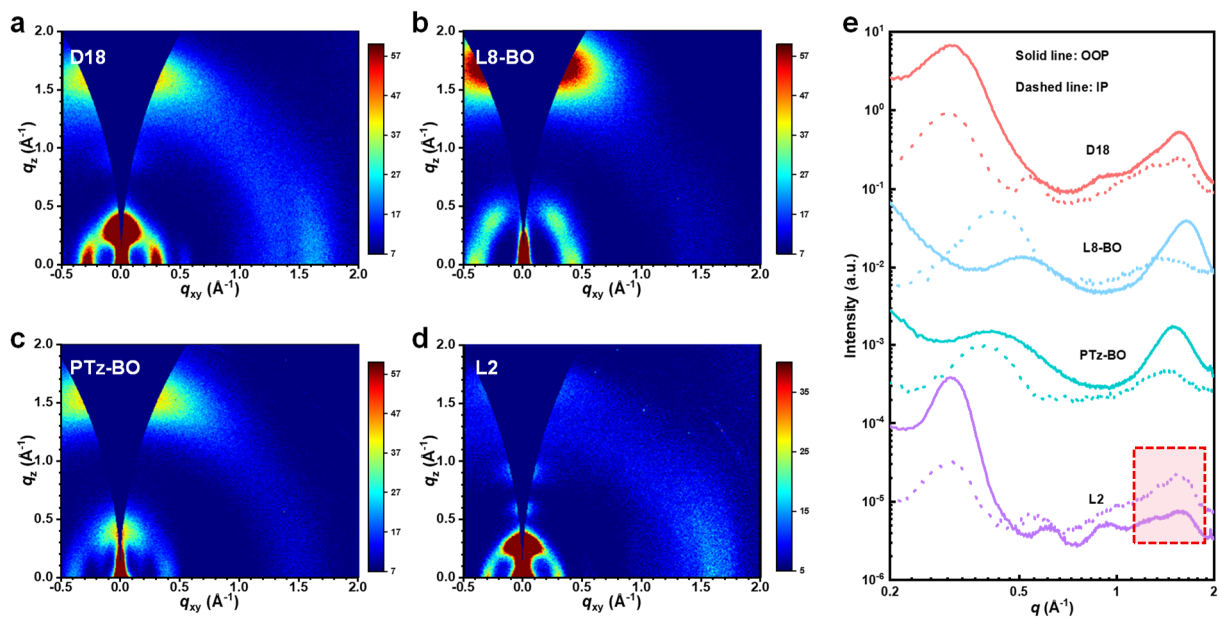
9 **Synthesis of polymer PTz-BO:** Under nitrogen protection, Tz-BO (211 mg, 0.1 mmol), 2,5-bis(trimethylstannyl)thiophene
10 (41.0 mg, 0.1 mmol), Pd₂(dba)₃ (2 mg) and P(o-tol)₃ (4 mg) and degassed toluene were added to 10 mL round bottom flask.
11 After the reaction, the mixture was stirred at 110 °C for 4 hours. Then the mixture was poured into methanol (50 mL) and
12 precipitation occurred. Then the resulting mixture was filtered. The obtained crude polymer was dissolved in warm
13 chloroform and then the solution was quickly filtered through a pre-prepared wet silica gel column with hot chloroform.
14 The collected chloroform solution was concentrated and precipitated in methanol to get PTz-BO as a dark solid (184 mg,
15 90%) (GPC: M_n = 16.7 kDa, M_w = 50.5 kDa; PDI = 3.0).



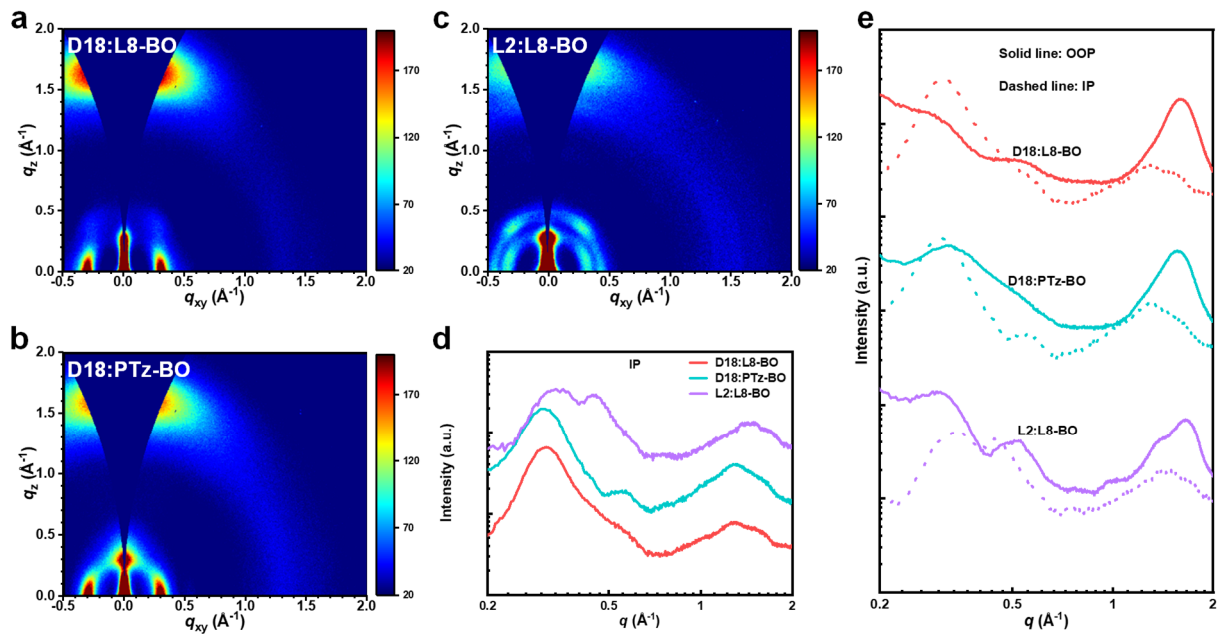
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2 **Supplementary Figure 5.** 2D GIWAXS patterns (a-c) and the corresponding OOP and IP line cuts (d) of PM6, PM6:L8-
3 BO-X and PM6:PTz-BO films.



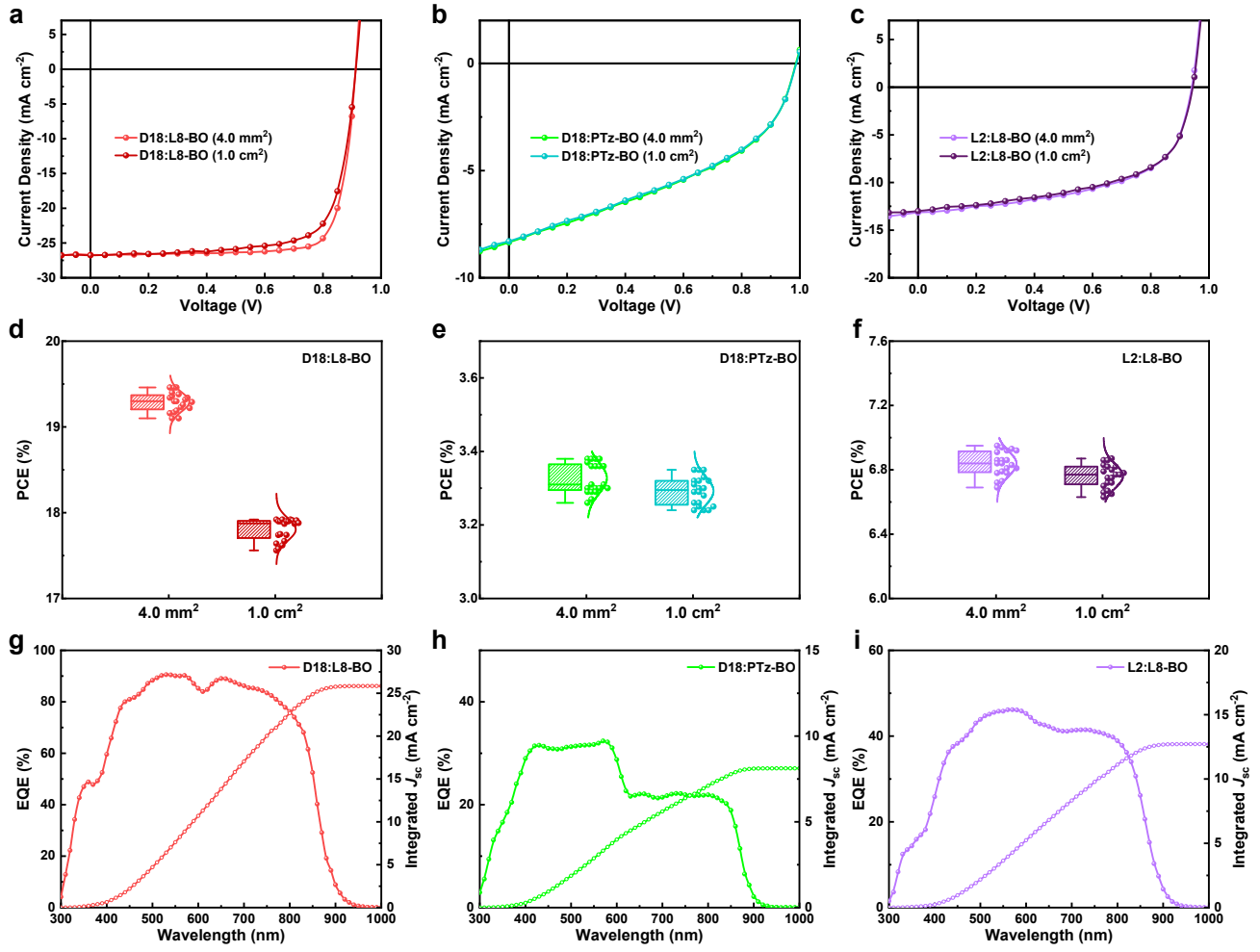
Supplementary Figure 6. Chemical structures of the photovoltaic materials, including D18, L8-BO and L2.



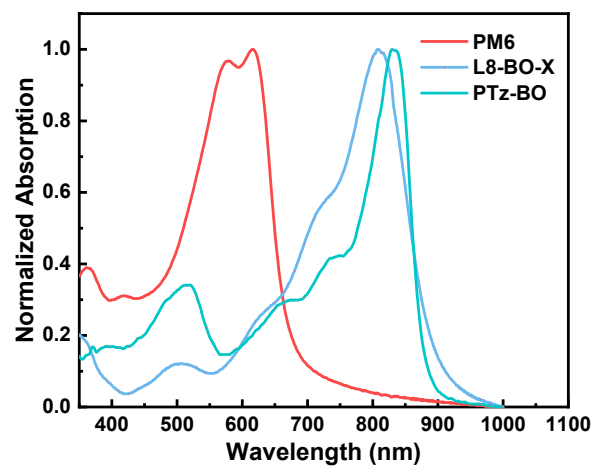
Supplementary Figure 7. 2D GIWAXS patterns (a-d) and the corresponding OOP and IP line cuts (e) of neat D18, L8-BO, PTz-BO and L2 films processed with CF.



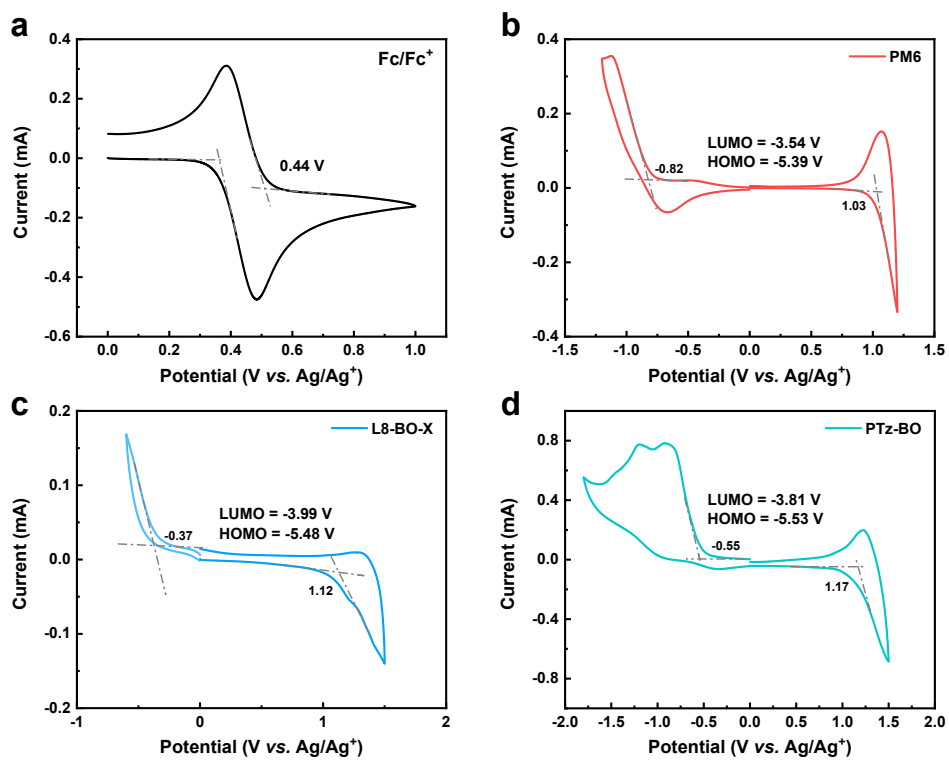
Supplementary Figure 8. 2D GIWAXS patterns (a-c) and the corresponding OOP and IP line cuts (d,e) of D18:L8-BO, D18:PTz-BO and L2:L8-BO blend films processed with CF.



Supplementary Figure 9. Representative J - V characteristics (a-c) and efficiency-distributed histograms (d-f) of OSCs based on different areas under simulated AM 1.5 G illumination at 100 mW cm⁻². g-i, The corresponding EQE spectra and the integrated J_{sc} s of OSCs with an aperture area of 4.0 mm².

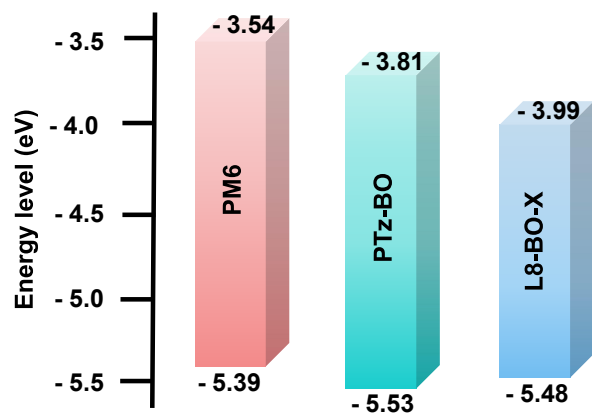


Supplementary Figure 10. Normalized absorption spectra of neat PM6, L8-BO-X and PTz-BO films.



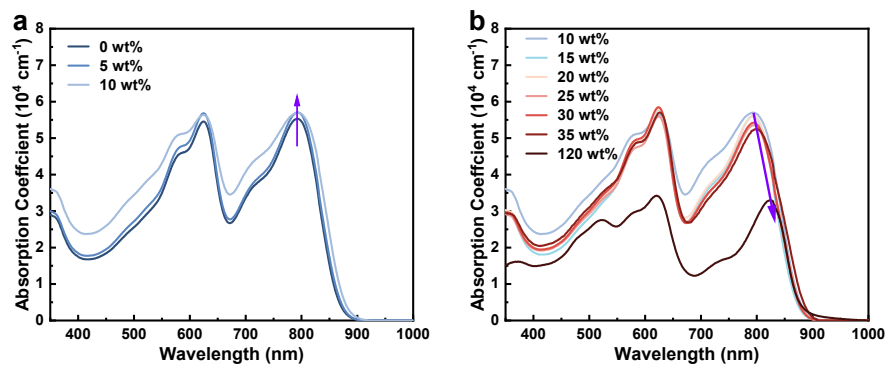
Supplementary Figure 11. Current-voltage curves of cyclic voltammetry (CV) measurements based on various organic photovoltaic materials.

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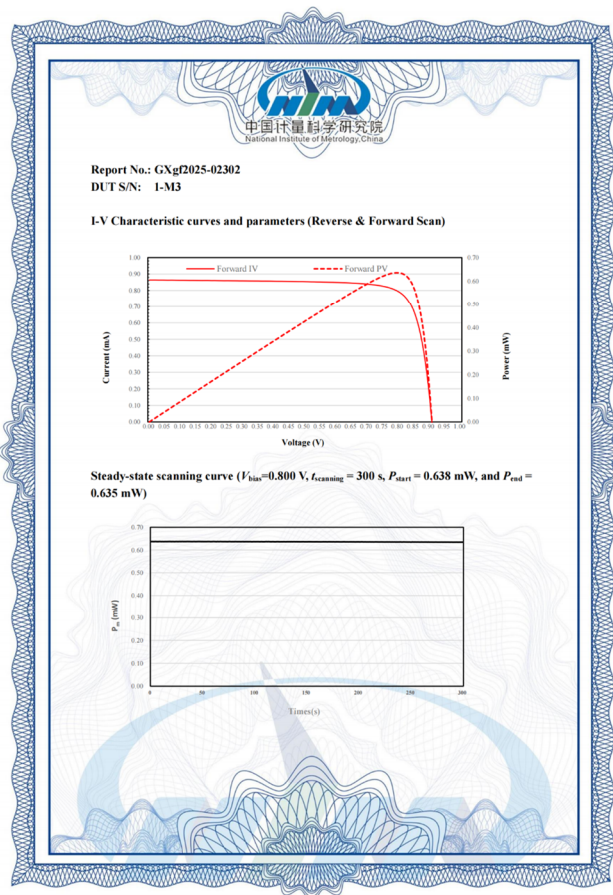
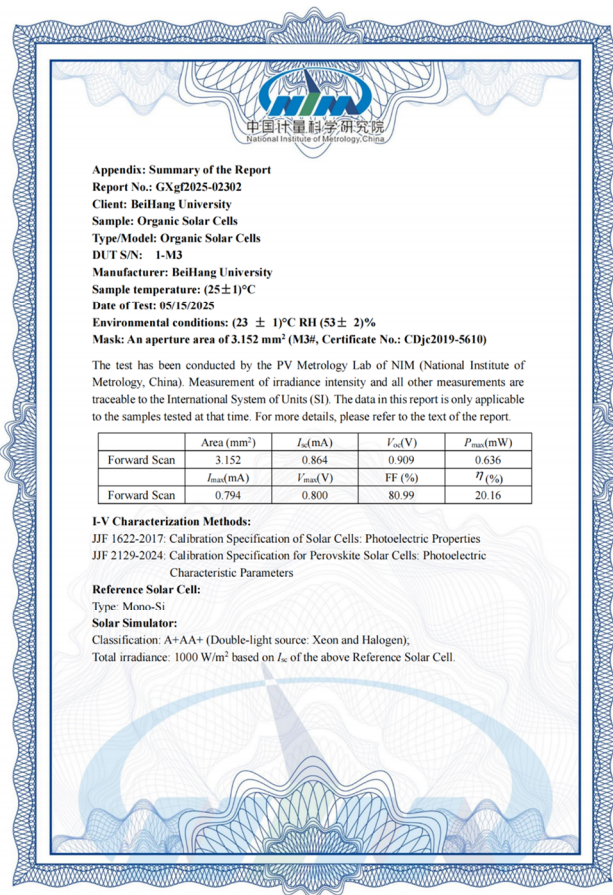
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3 **Supplementary Figure 12.** Energy level diagram of PM6, L8-BO-X, and PTz-BO.



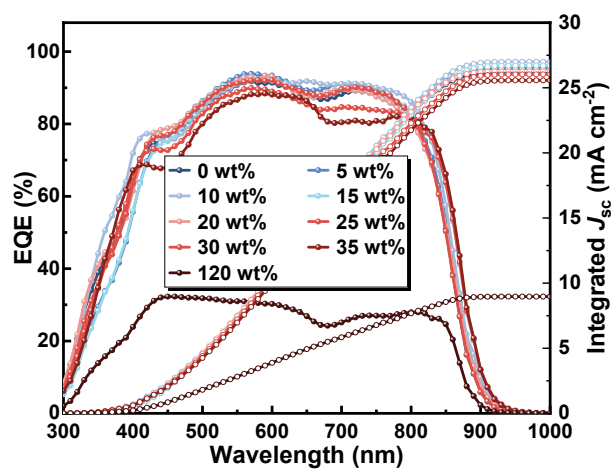
Supplementary Figure 13. Thin-film absorption coefficients of the binary and ternary films with varied PTz-BO contents.

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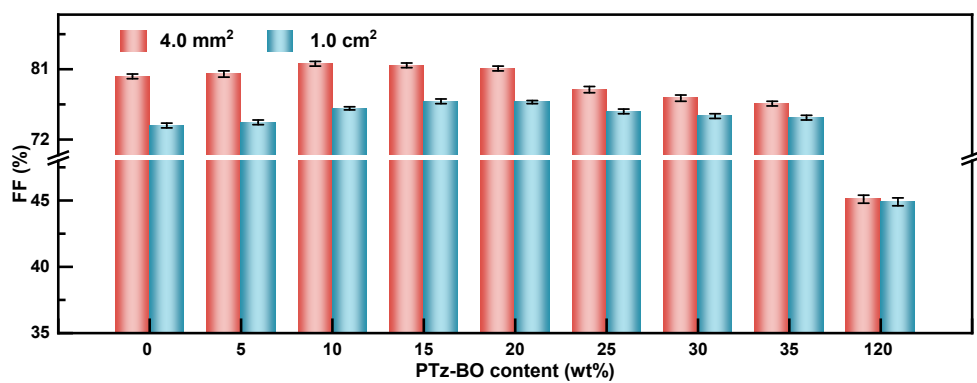


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3 **Supplementary Figure 14.** Certificated result of PM6:L8-BO-X:PTz-BO-based device processed with *o*-XY from
 4 National Institute of Metrology (NIM), China.

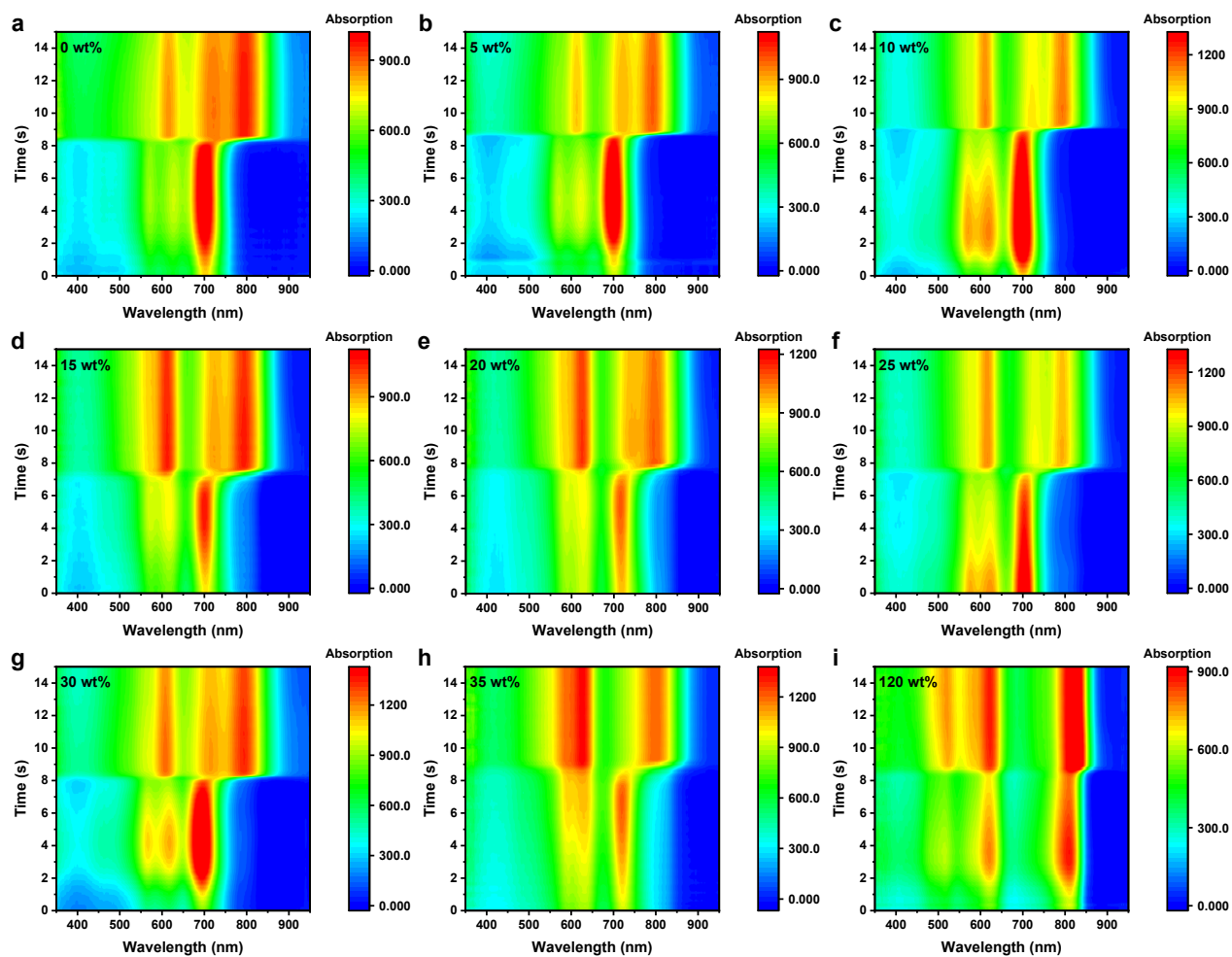


Supplementary Figure 15. External quantum efficiency (EQE) spectra of 4.0 mm² spin-coated devices with varied PTz-BO contents.

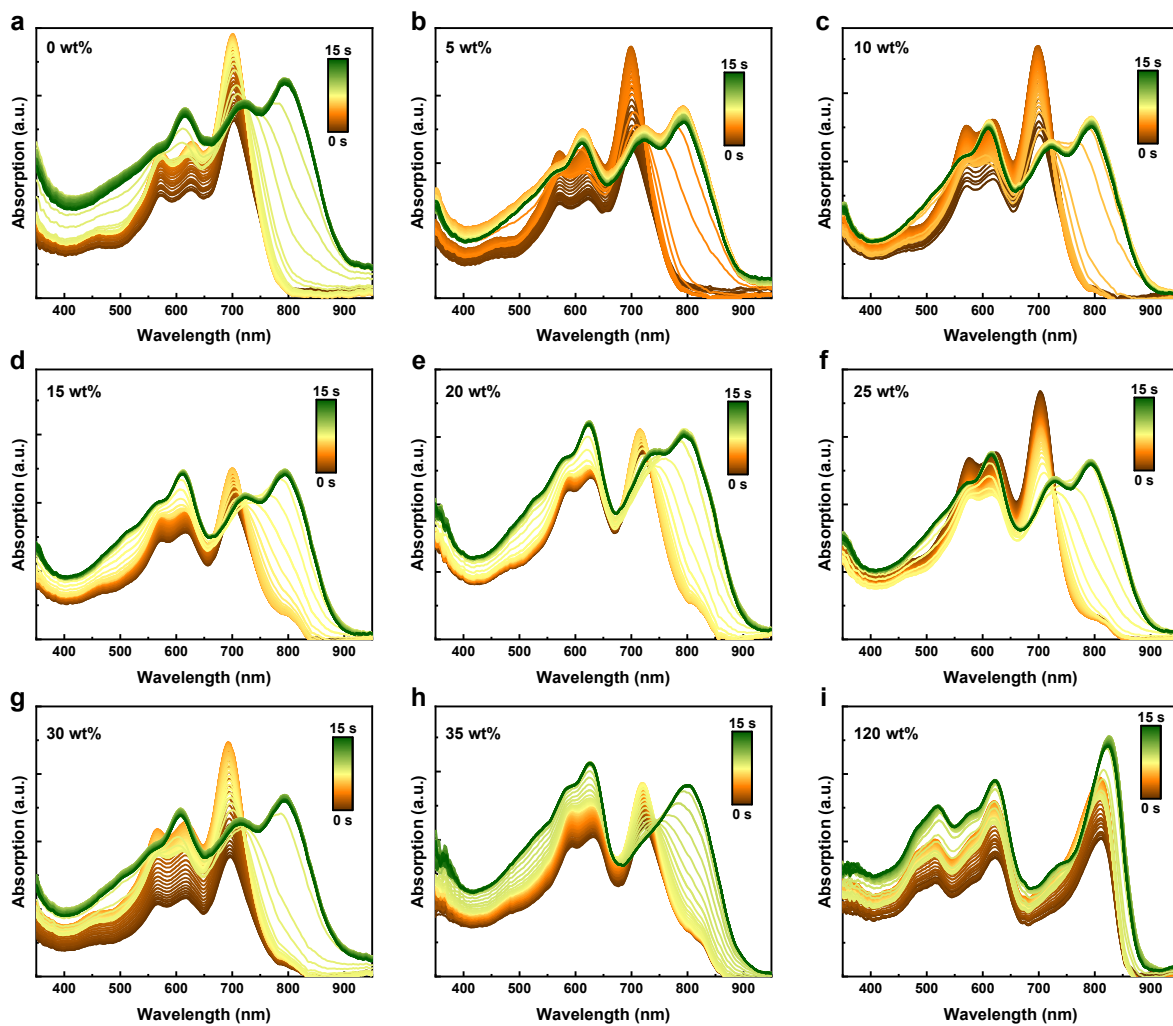


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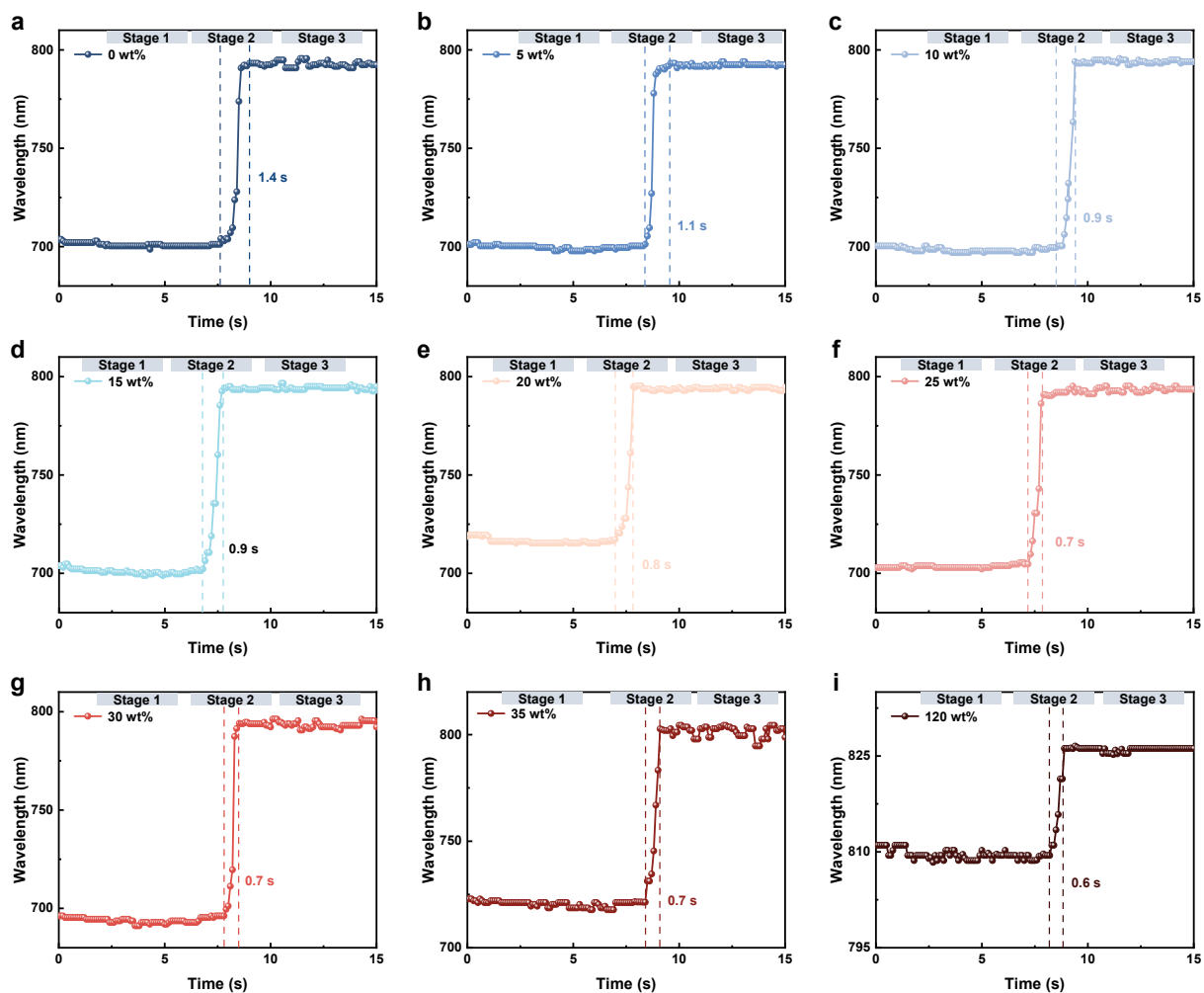
2 **Supplementary Figure 16.** FF statistics of binary and ternary devices with aperture areas of 4.0 mm² and 1.0 cm².



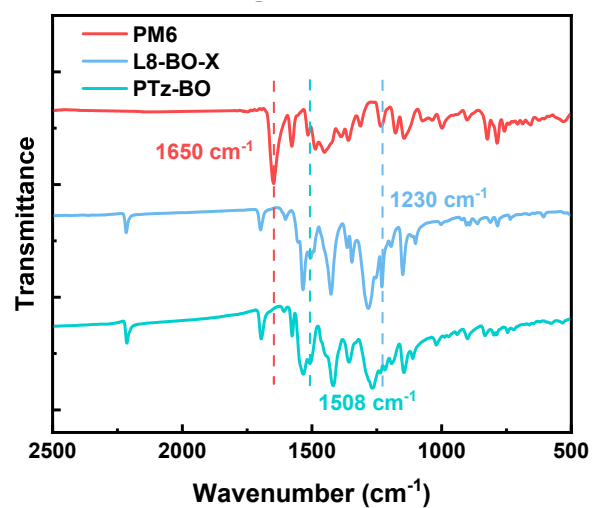
Supplementary Figure 17. *In-situ* 2D absorption spectra of the binary and ternary blends with varied PTz-BO contents during the solvent evaporation process.



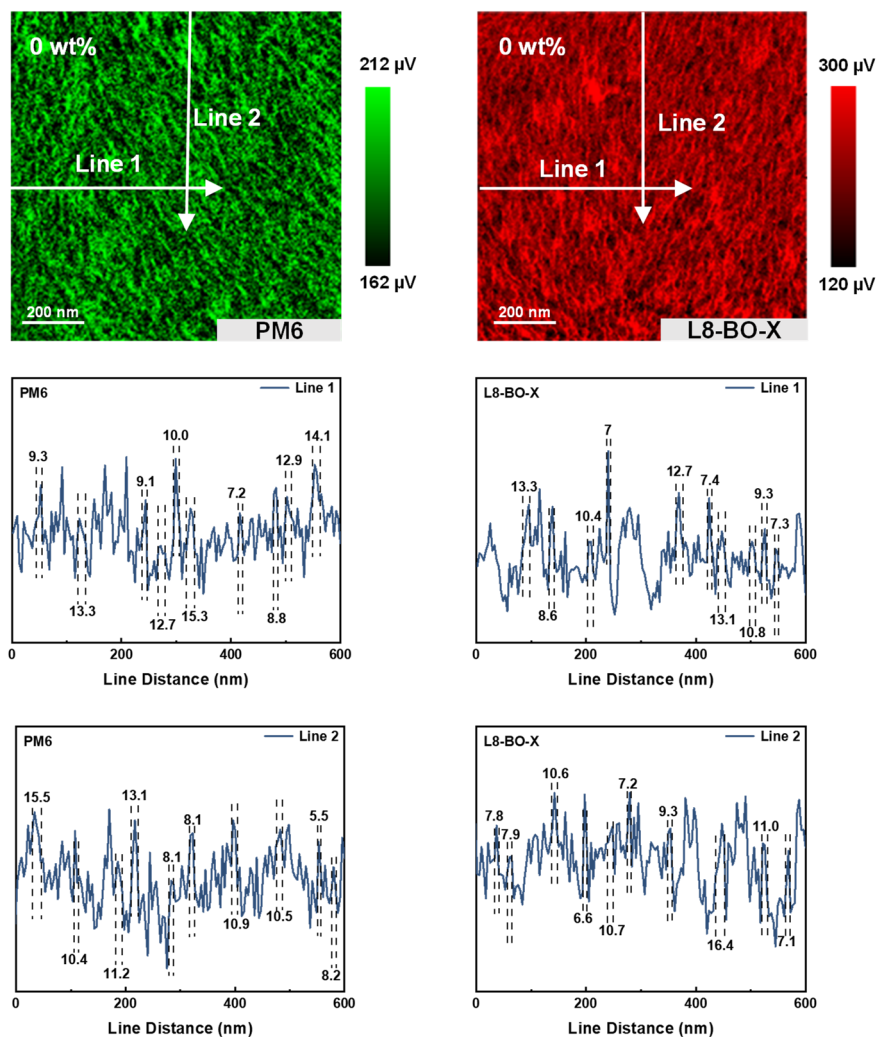
Supplementary Figure 18. *In-situ* UV-vis absorption spectra of the binary and ternary blends with varied PTz-BO contents during the solvent evaporation process.



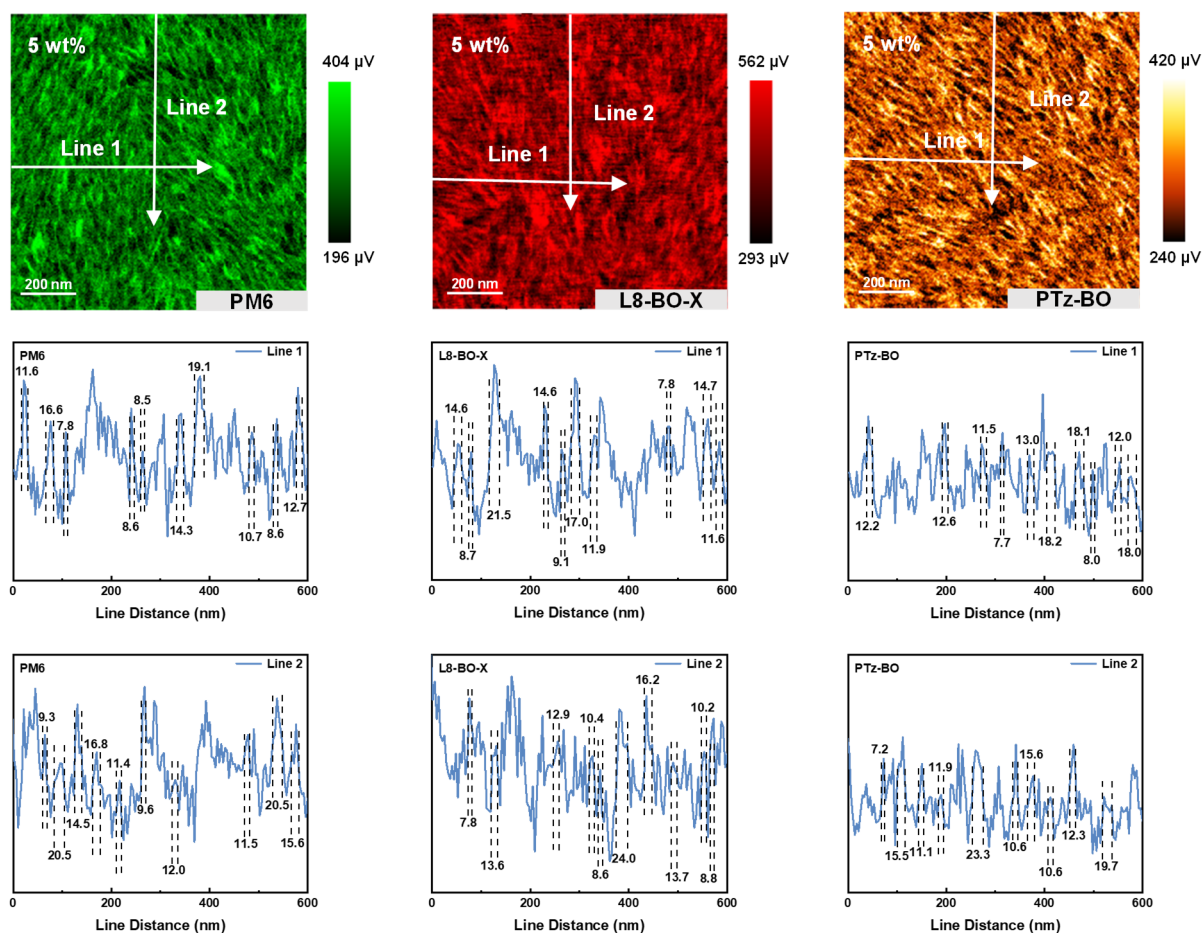
Supplementary Figure 19. The extracted time evolution of acceptors peak location of the binary and ternary blends with varied PTz-BO contents during the solvent evaporation process.



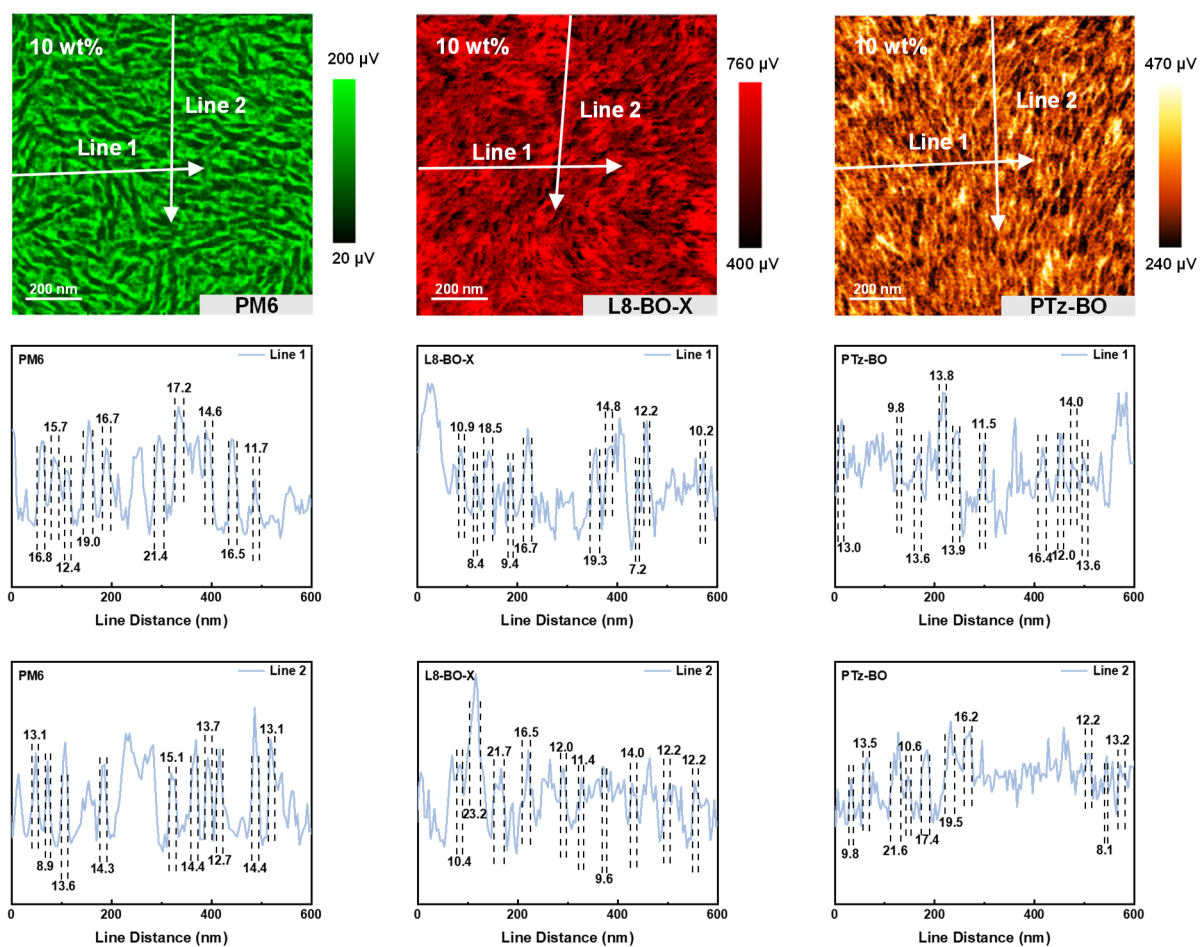
Supplementary Figure 20. FT-IR spectra of PM6 (red line), L8-BO-X (blue line) and PTz-BO (green line).



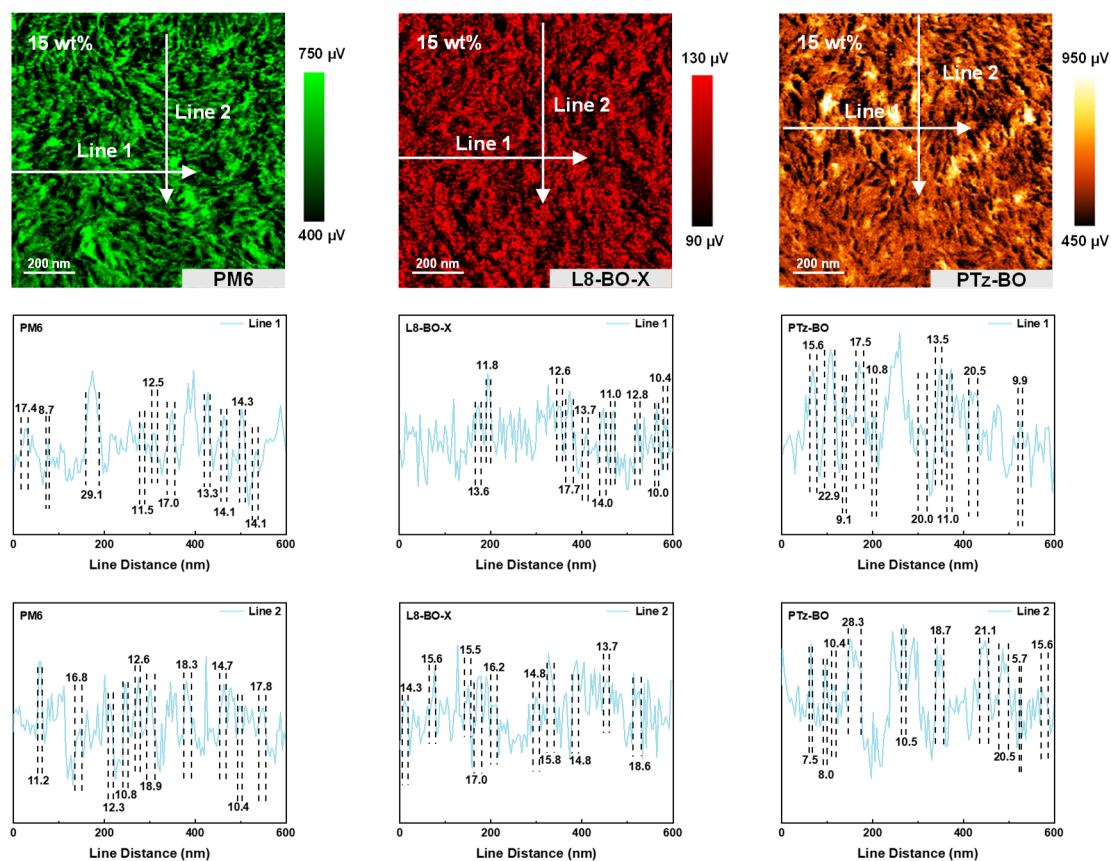
Supplementary Figure 21. PiFM images and the corresponding line profiles along the white arrows to obtain the fibril width for the PM6:L8-BO-X film.



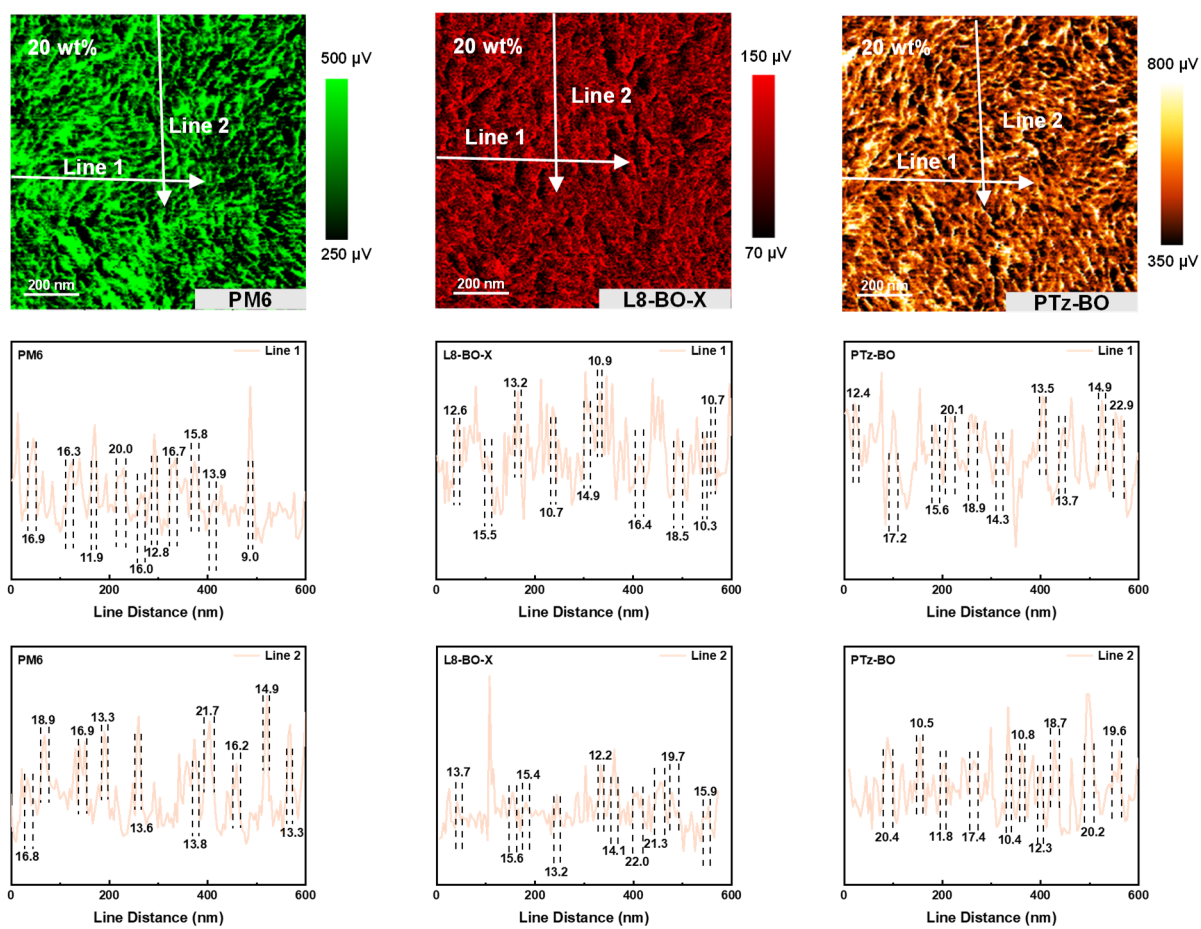
Supplementary Figure 22. PiFM images and the corresponding line profiles along the white arrows to obtain the fibril width for the PM6:L8-BO-X:PTz-BO film with 5 wt% PTz-BO.



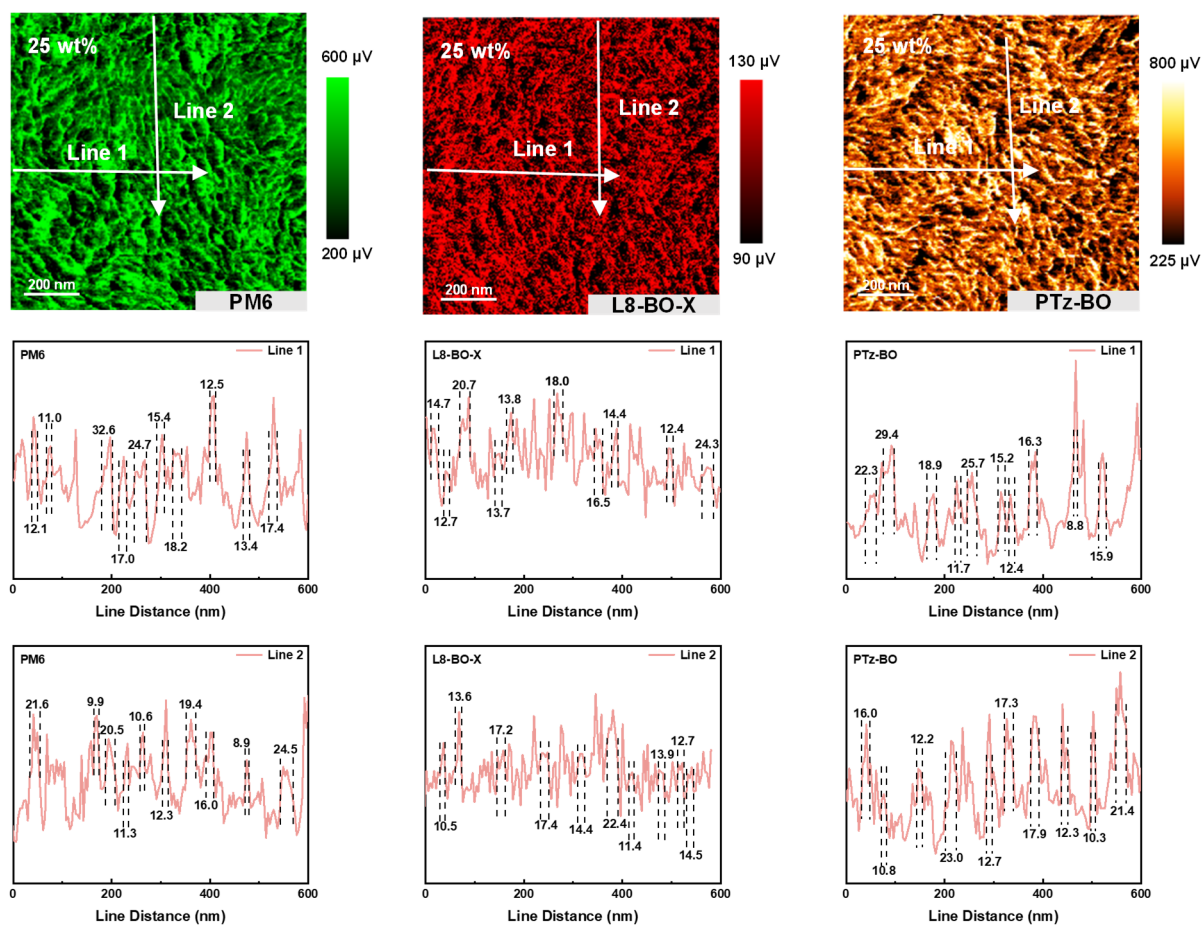
Supplementary Figure 23. PiFM images and the corresponding line profiles along the white arrows to obtain the fibril width for the PM6:L8-BO-X:PTz-BO film with 10 wt% PTz-BO.



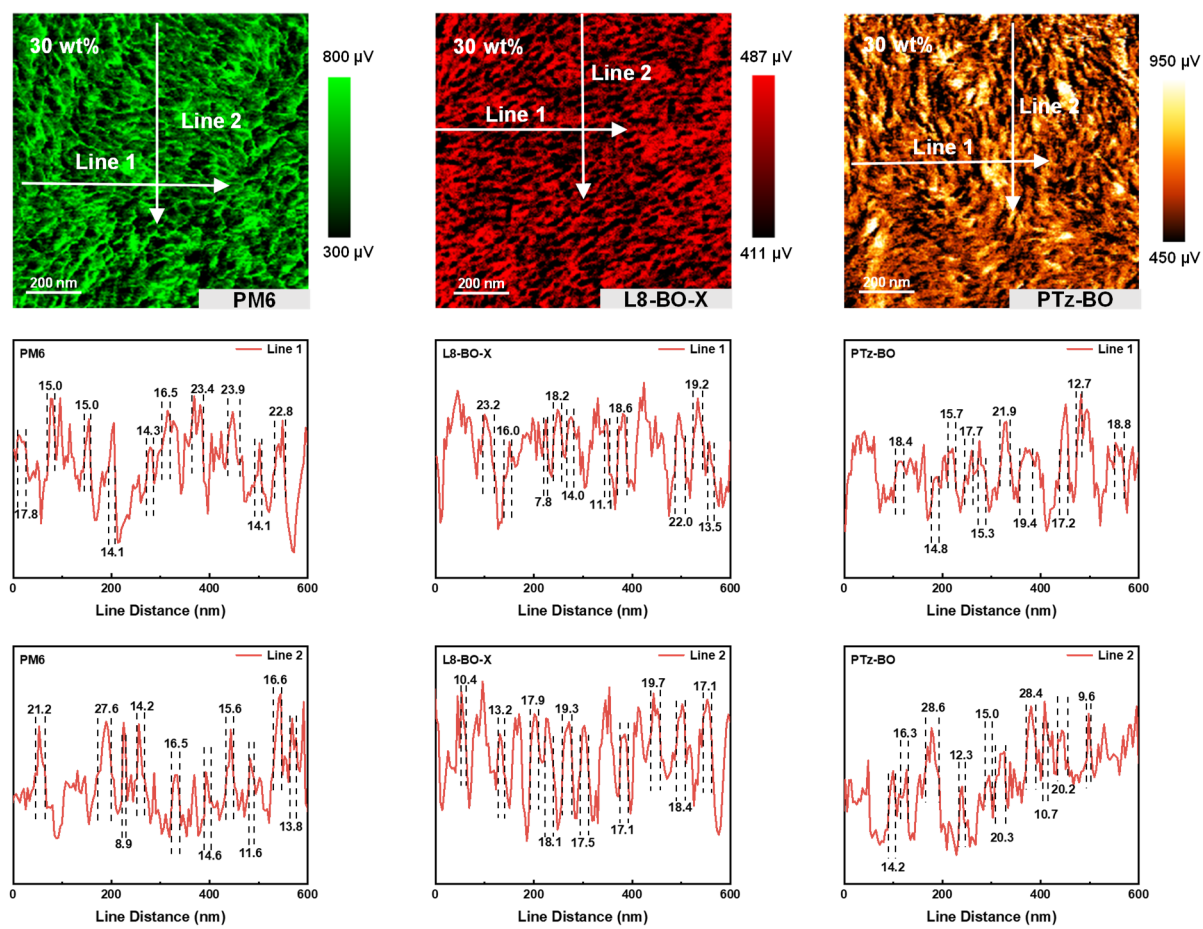
Supplementary Figure 24. PiFM images and the corresponding line profiles along the white arrows to obtain the fibril width for the PM6:L8-BO-X:PTz-BO film with 15 wt% PTz-BO.



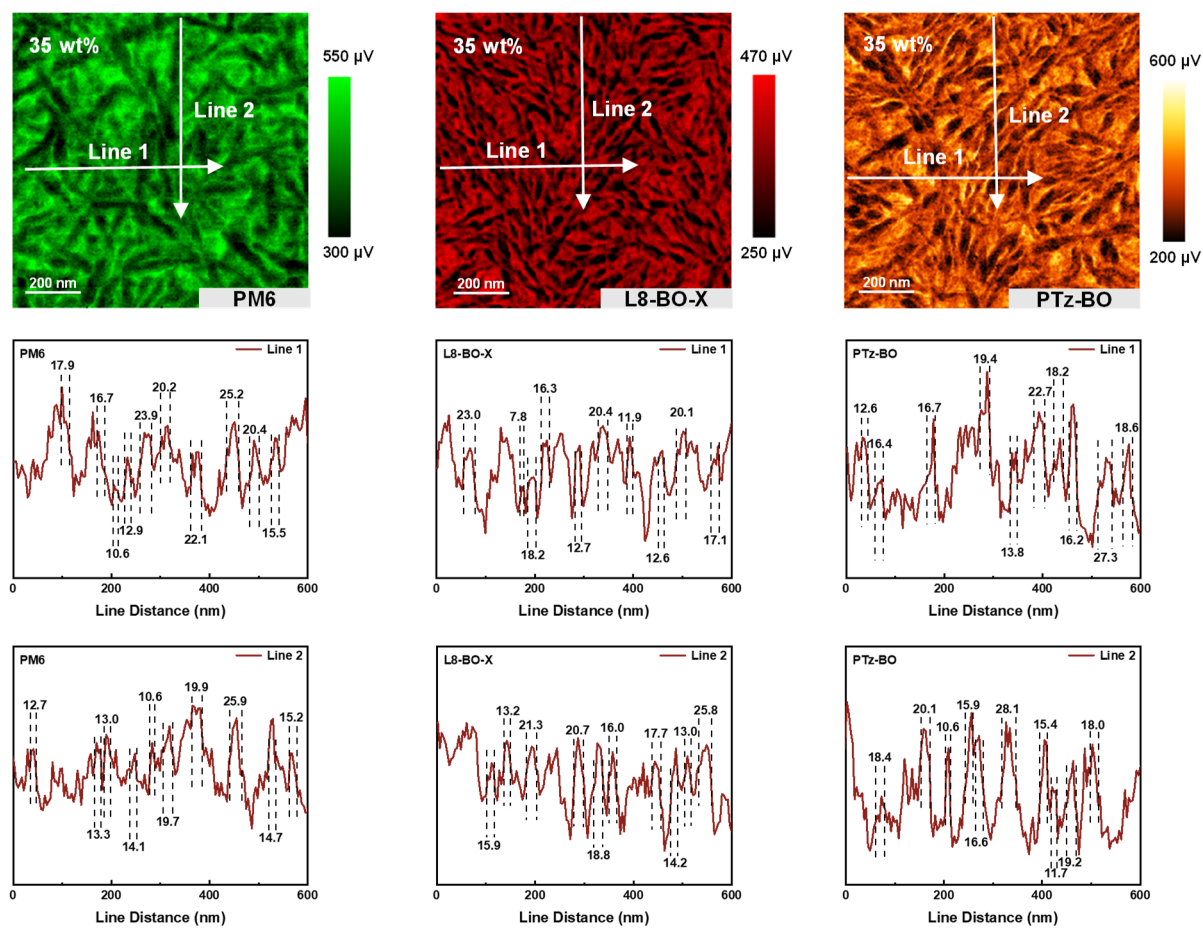
Supplementary Figure 25. PiFM images and the corresponding line profiles along the white arrows to obtain the fibril width for the PM6:L8-BO-X:PTz-BO film with 20 wt% PTz-BO.



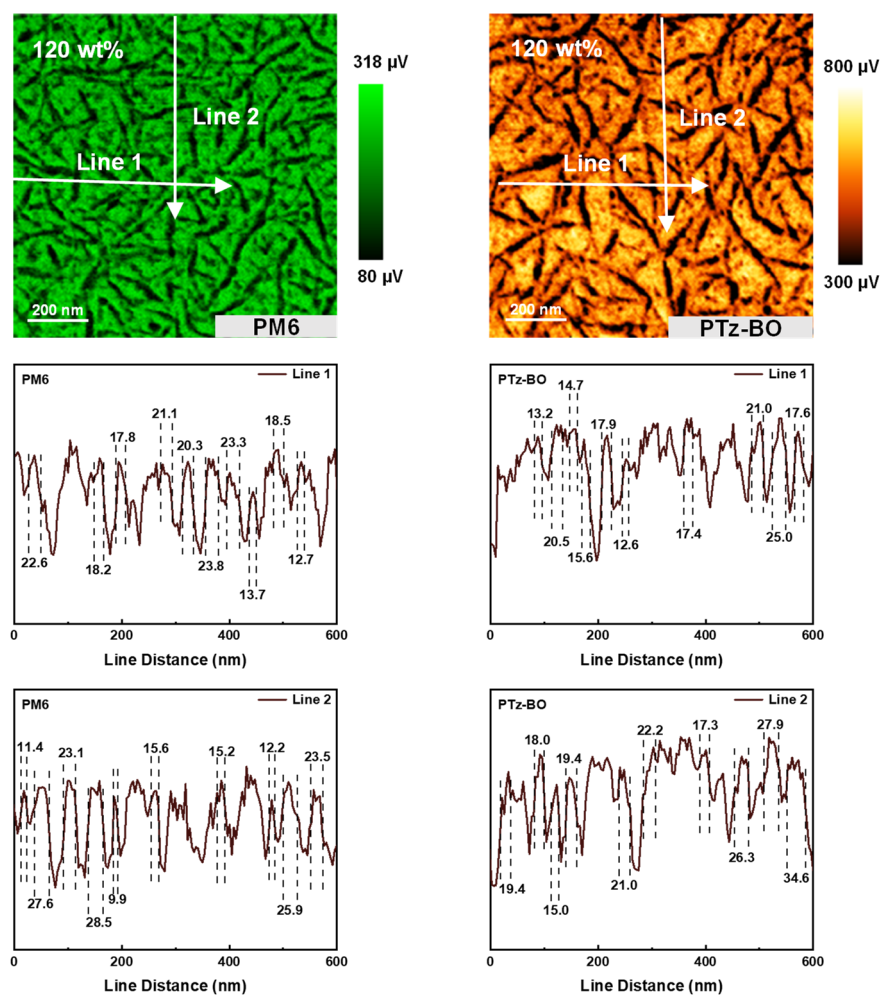
Supplementary Figure 26. PiFM images and the corresponding line profiles along the white arrows to obtain the fibril width for the PM6:L8-BO-X:PTz-BO film with 25 wt% PTz-BO.



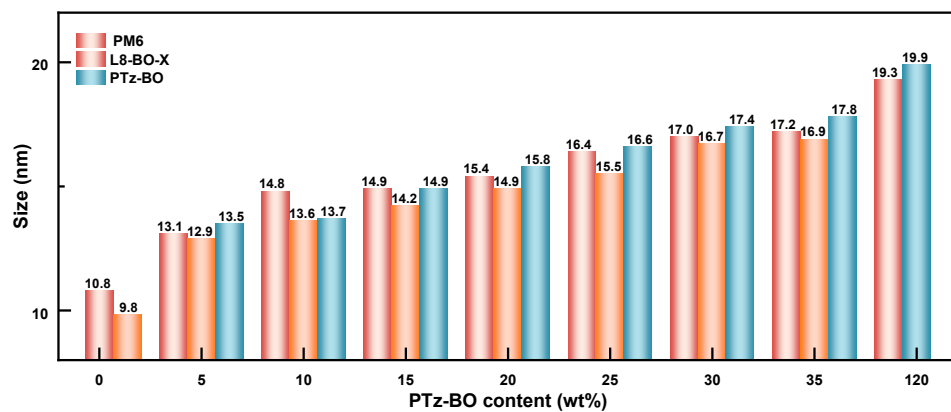
Supplementary Figure 27. PiFM images and the corresponding line profiles along the white arrows to obtain the fibril width for the PM6:L8-BO-X:PTz-BO film with 30 wt% PTz-BO.



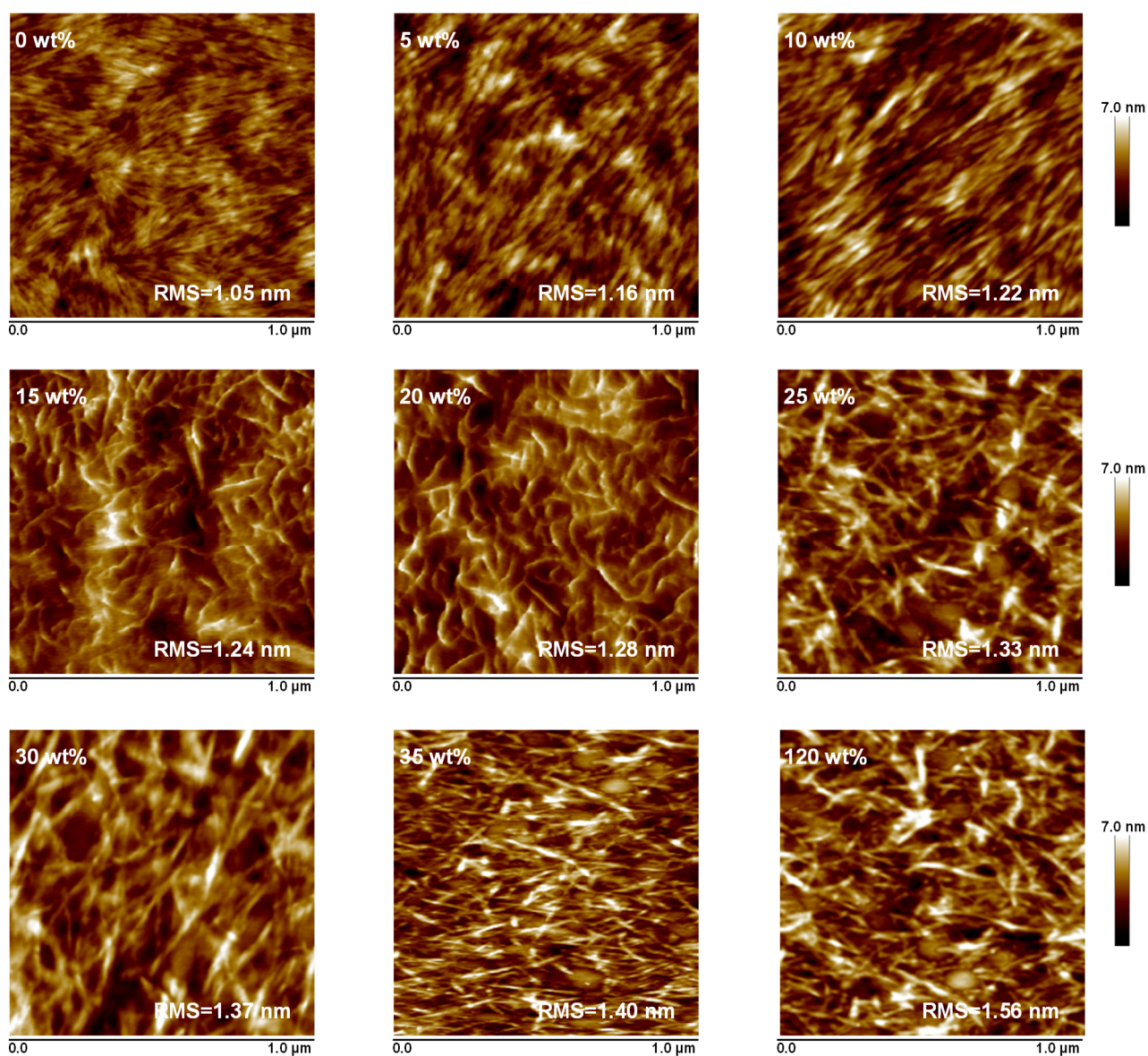
Supplementary Figure 28. PiFM images and the corresponding line profiles along the white arrows to obtain the fibril width for the PM6:L8-BO-X:PTz-BO film with 35 wt% PTz-BO.



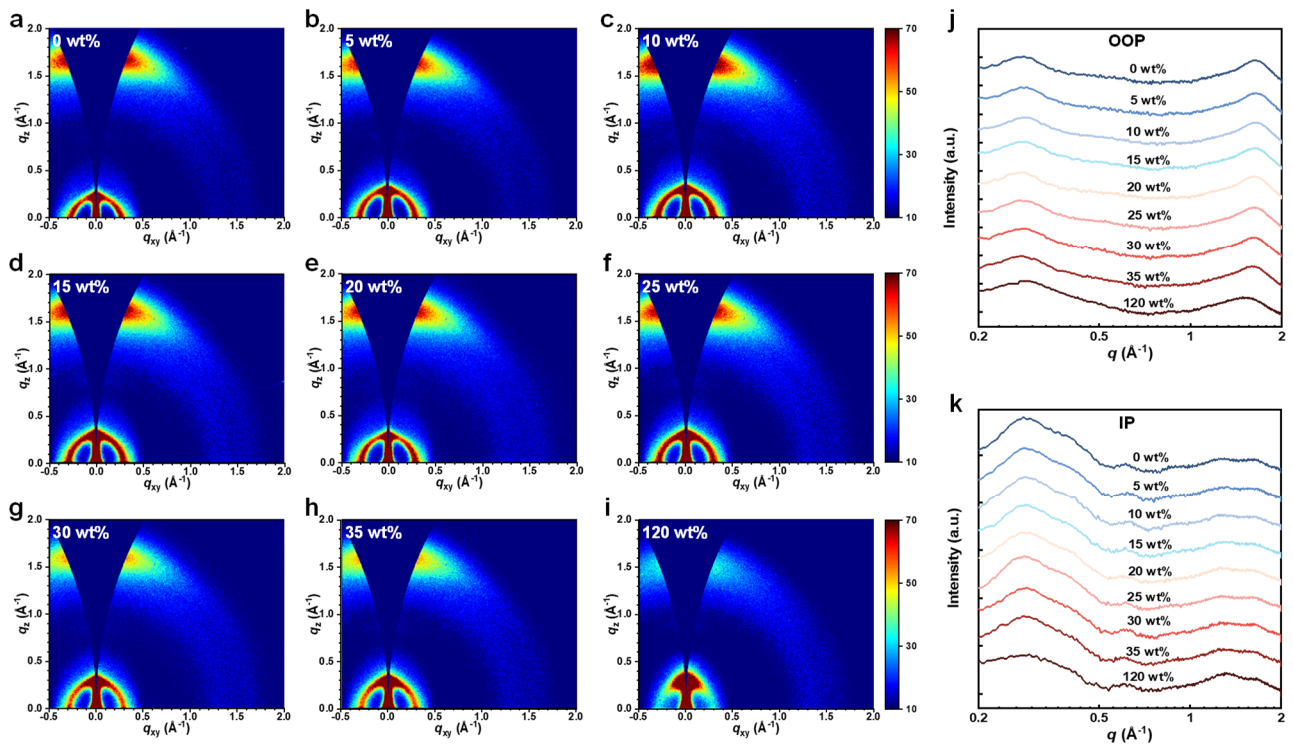
Supplementary Figure 29. PiFM images and the corresponding line profiles along the white arrows to obtain the fibril width for the PM6:PTz-BO film.



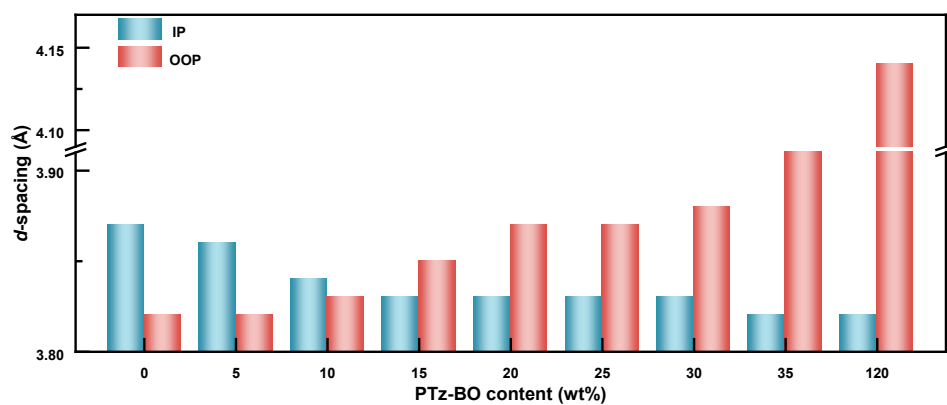
Supplementary Figure 30. Average PM6, L8-BO-X and PTz-BO fibril widths of binary and ternary blends with varied PTz-BO contents.



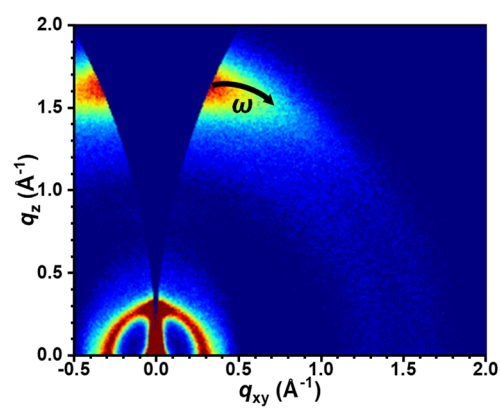
Supplementary Figure 31. AFM height images of the binary and ternary blends with varied PTz-BO contents.



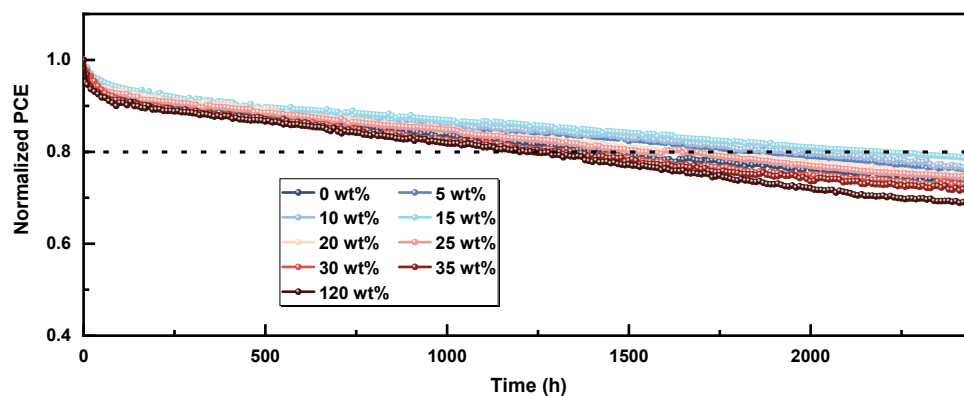
Supplementary Figure 32. 2D GIWAXS patterns (a-i) and corresponding OOP and IP line cuts (j,k) of the bianry and ternary blends with varied PTz-BO contents.



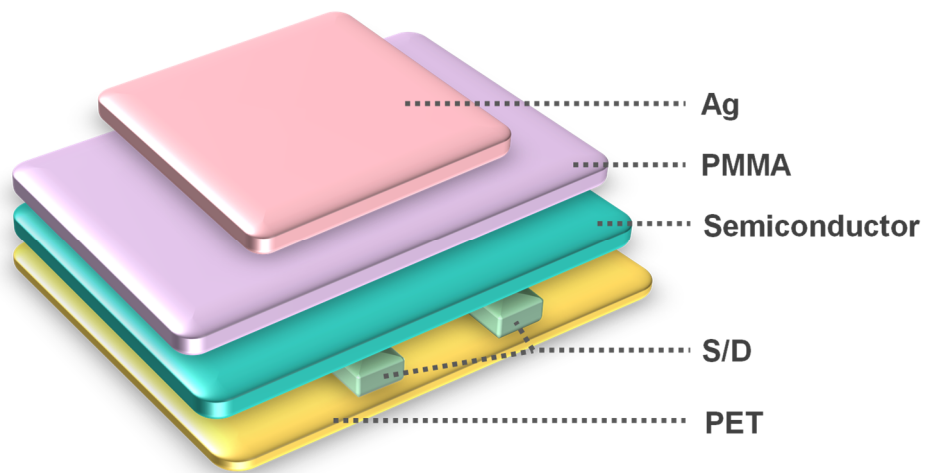
Supplementary Figure 33. Statistics of d -spacing of the (010) peaks in the IP and OOP direction of the binary and ternary blends with varied PTz-BO contents.



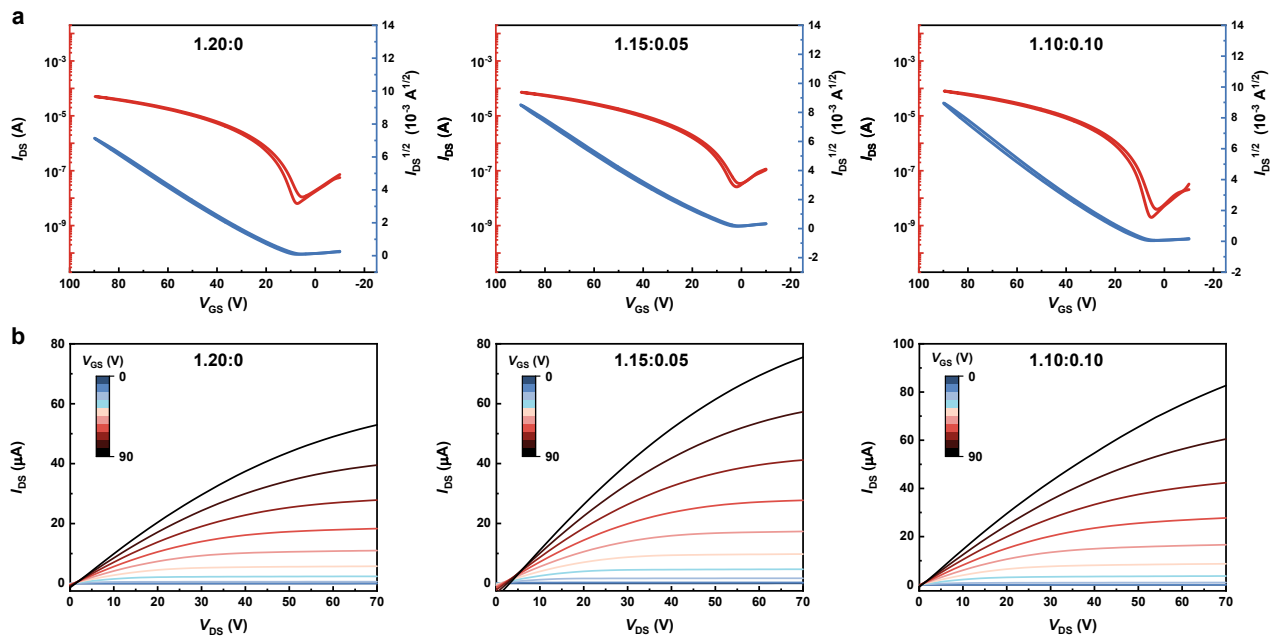
1
2 **Supplementary Figure 34.** Schematic illustration of polar angle (ω) in polar figure.
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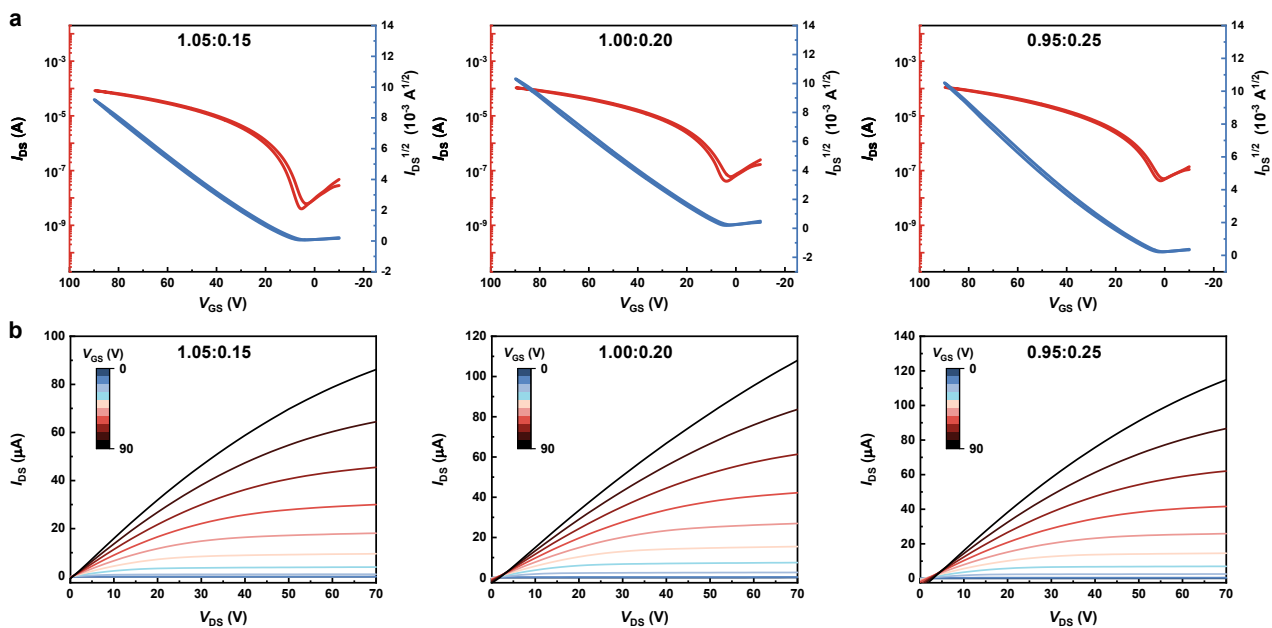
Supplementary Figure 35. Normalized PCE degradation curves of the binary and ternary OSC devices with varied PTz-BO contents under continuous LED illumination by using MPP tracking mode in the ambient air conditions (the average humidity was 30%, the average tested temperature was 45 °C).



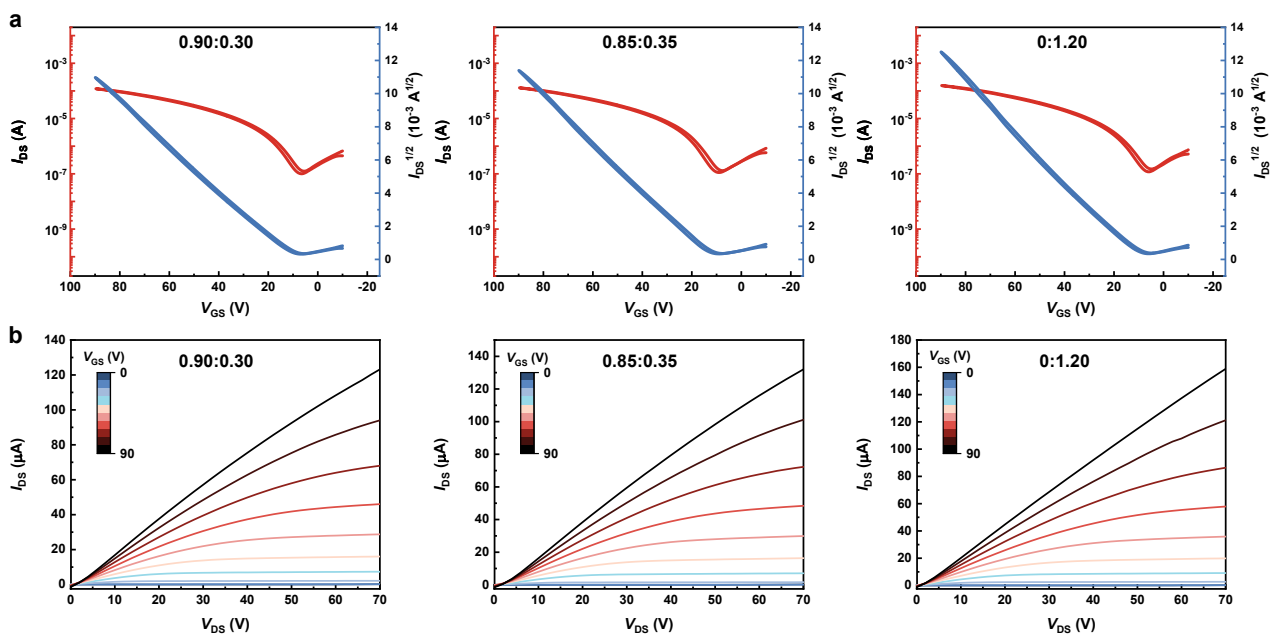
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2 **Supplementary Figure 36.** Diagram of top gate/bottom contact device configuration.
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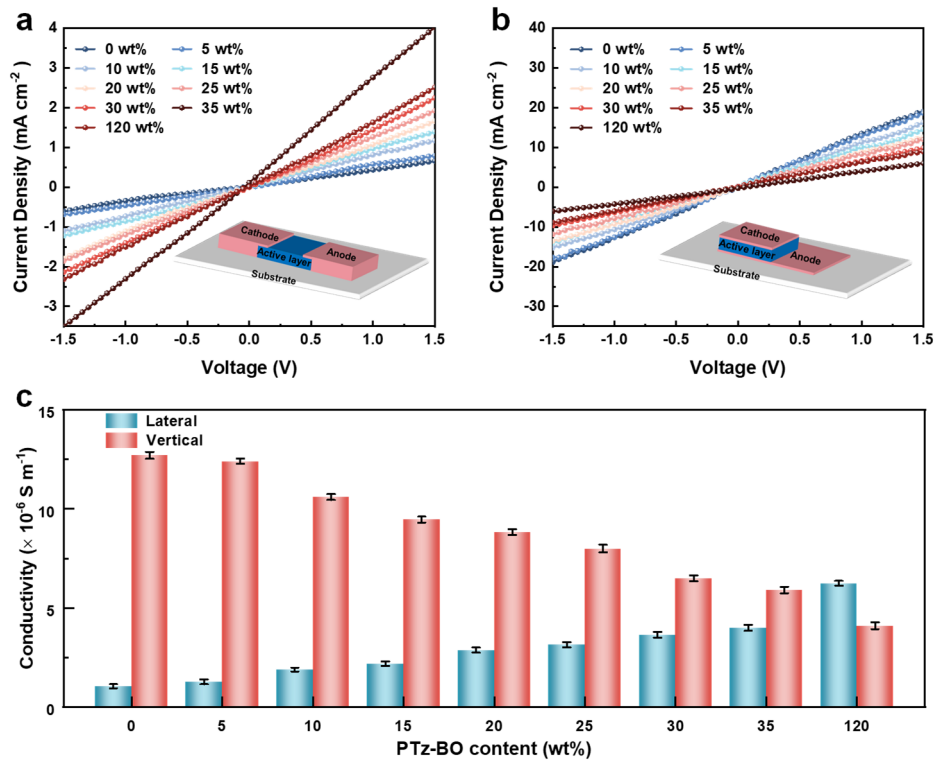
Supplementary Figure 37. Typical transfer (a) and output (b) characteristics of OFET devices with different L8-BO-X:PTz-BO blending ratios.

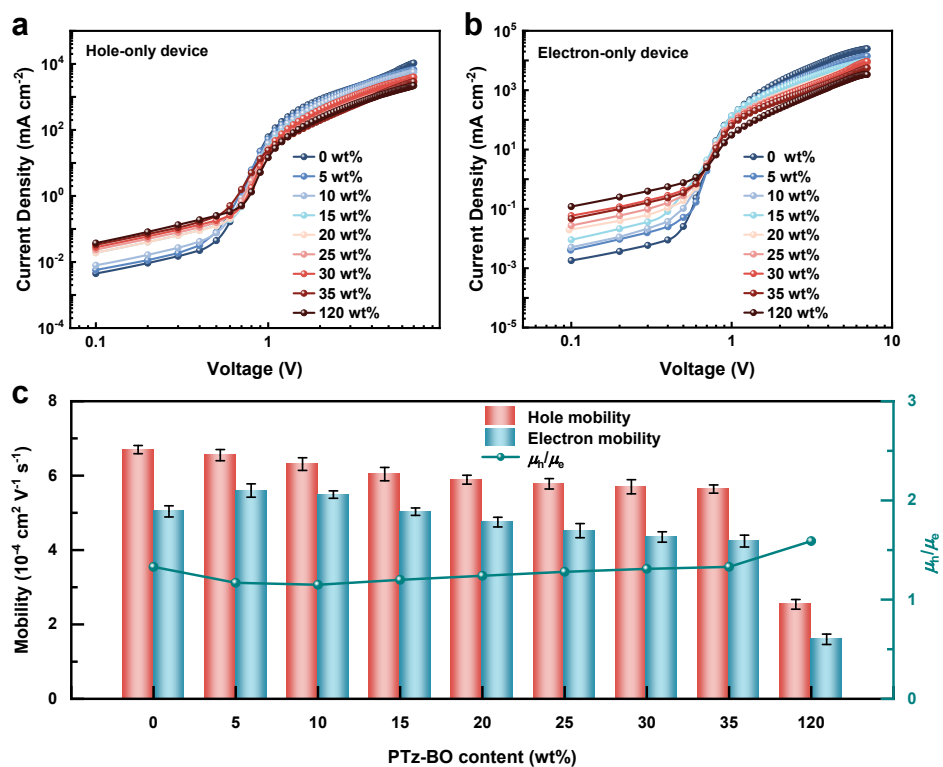


Supplementary Figure 38. Typical transfer (a) and output (b) characteristics of OFET devices with different L8-BO-X:PTz-BO blending ratios.

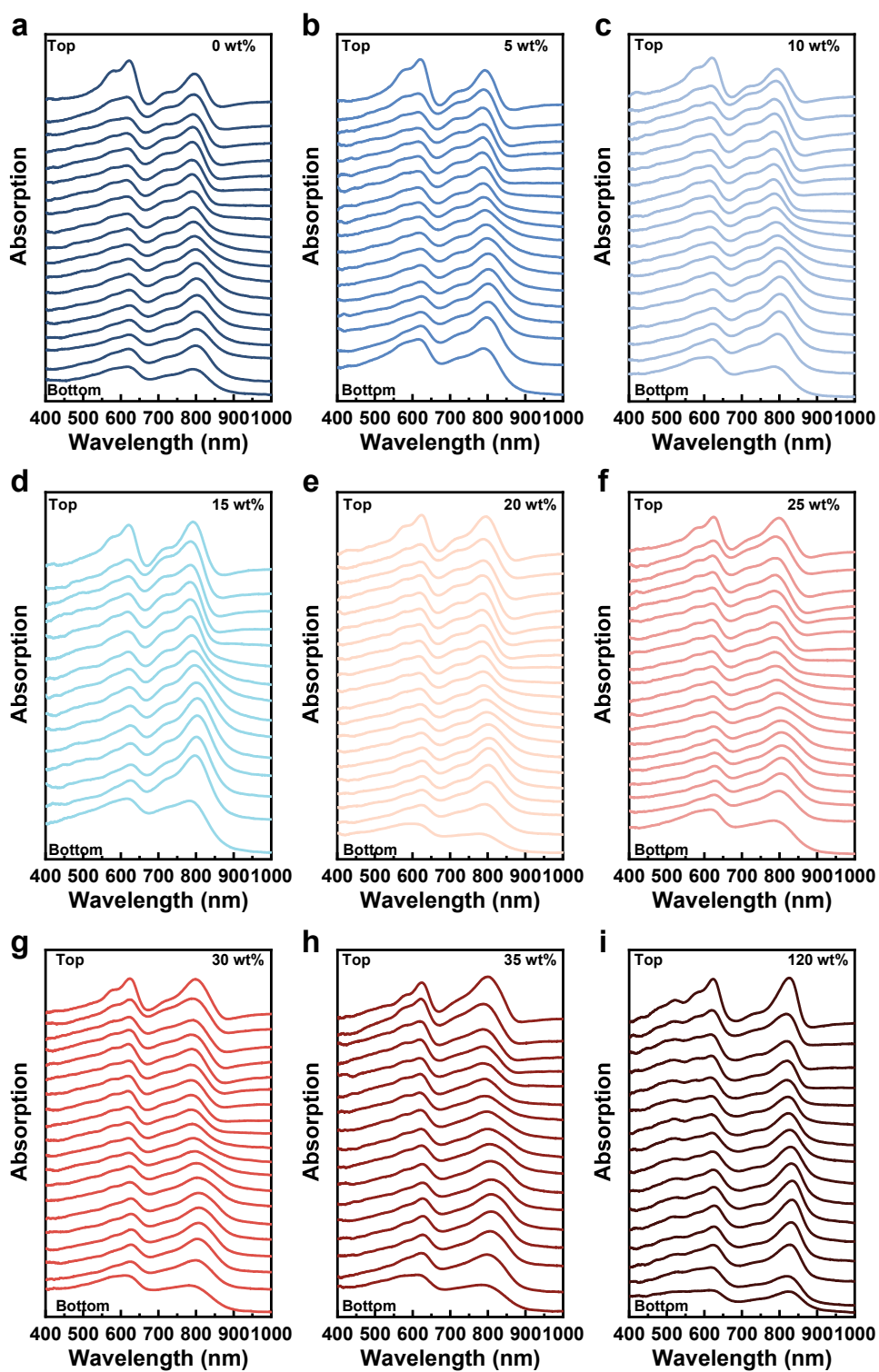


Supplementary Figure 39. Typical transfer (a) and output (b) characteristics of OFET devices with different L8-BO-X:PTz-BO blending ratios.

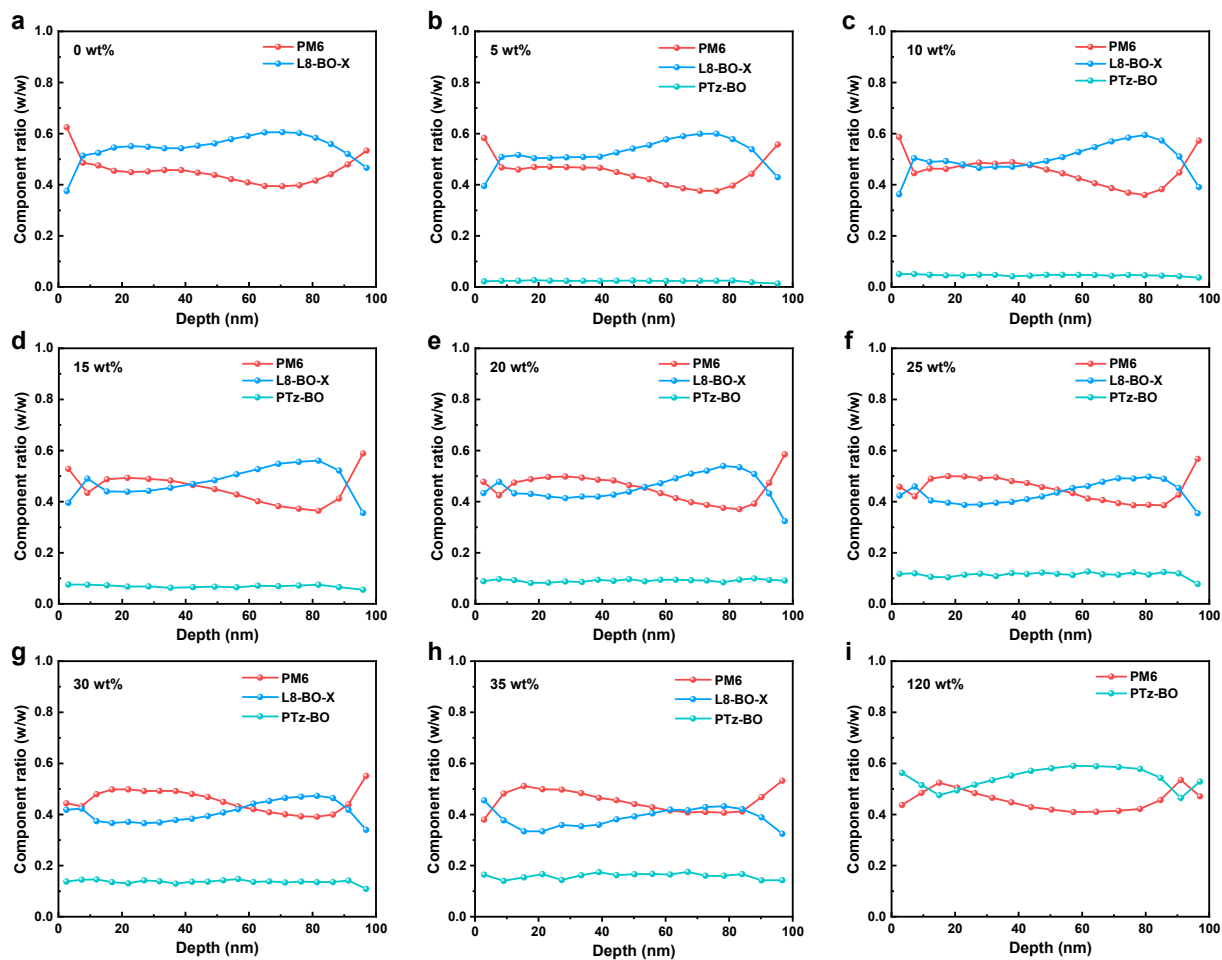




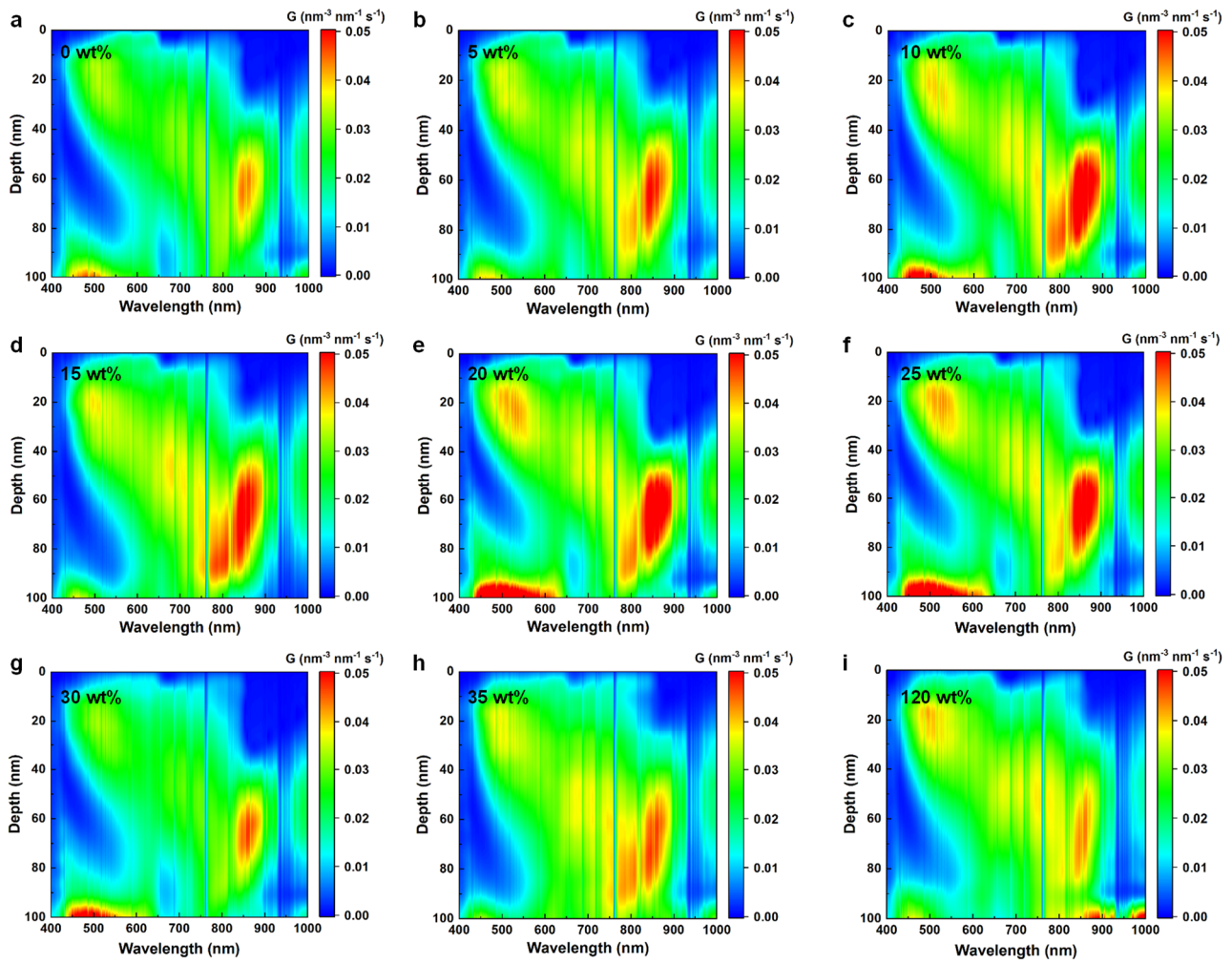
Supplementary Figure 41. *J-V* characteristics of hole-only (a) and electron-only (b) devices based on PM6:L8-BO-X:PTz-BO blends with varied PTz-BO contents. c, Vertical mobility statistics of the PM6:L8-BO-X:PTz-BO blends based on varied PTz-BO contents. The error bars represent the standard deviations ($n = 5$).



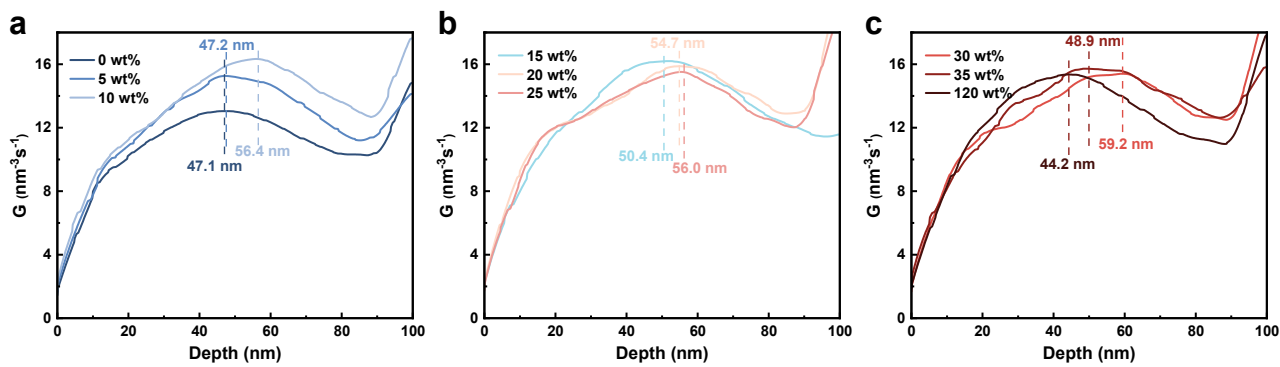
Supplementary Figure 42. The film-depth-dependent light absorption spectra of the binary and ternary blends with varied PTz-BO contents. The spectra were vertically-shifted for clarity.



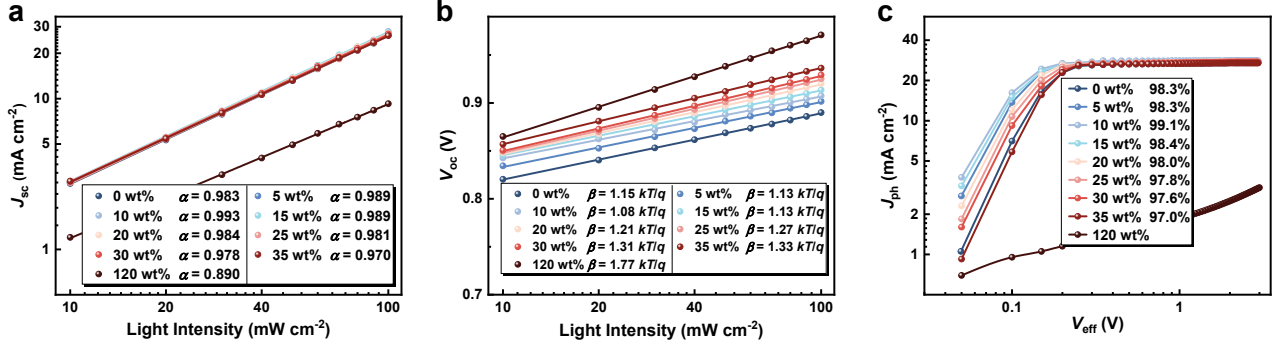
Supplementary Figure 43. Composition distribution profiles at different film-depths of the binary and ternary films with varied PTz-BO contents.



Supplementary Figure 44. Numerical simulations for the exciton generation contours of the binary and ternary films with varied PTz-BO contents.



Supplementary Figure 45. Film depth dependence of simulated exciton generation rate (G) of the binary and ternary films with varied PTz-BO contents.

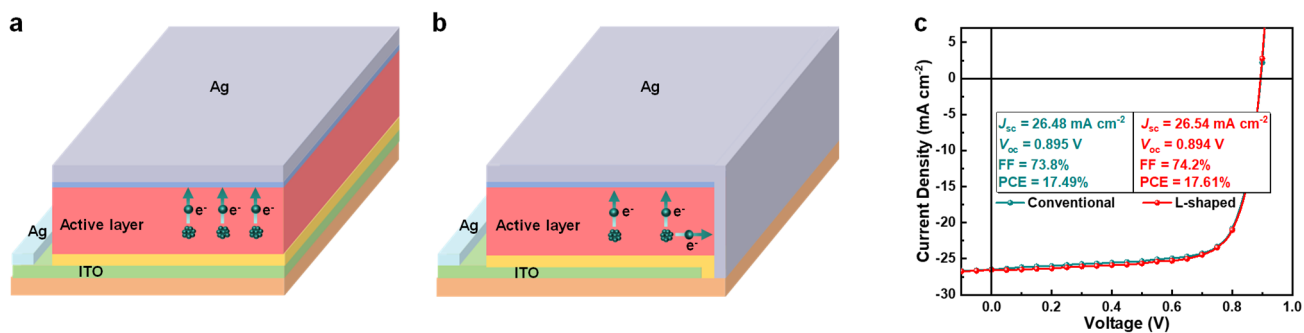


Supplementary Figure 46. a,b, J_{sc} (a) and V_{oc} (b) versus light intensity characteristics based on the binary and ternary devices with varied PTz-BO contents. Here, $J_{sc} \propto (P_{light})^\alpha$ and $V_{oc} \propto \beta \ln P_{light}$, where α and β are exponential factors that indicate the probability of recombination. c, J_{ph} versus V_{eff} characteristics based on the binary and ternary devices with varied PTz-BO contents.

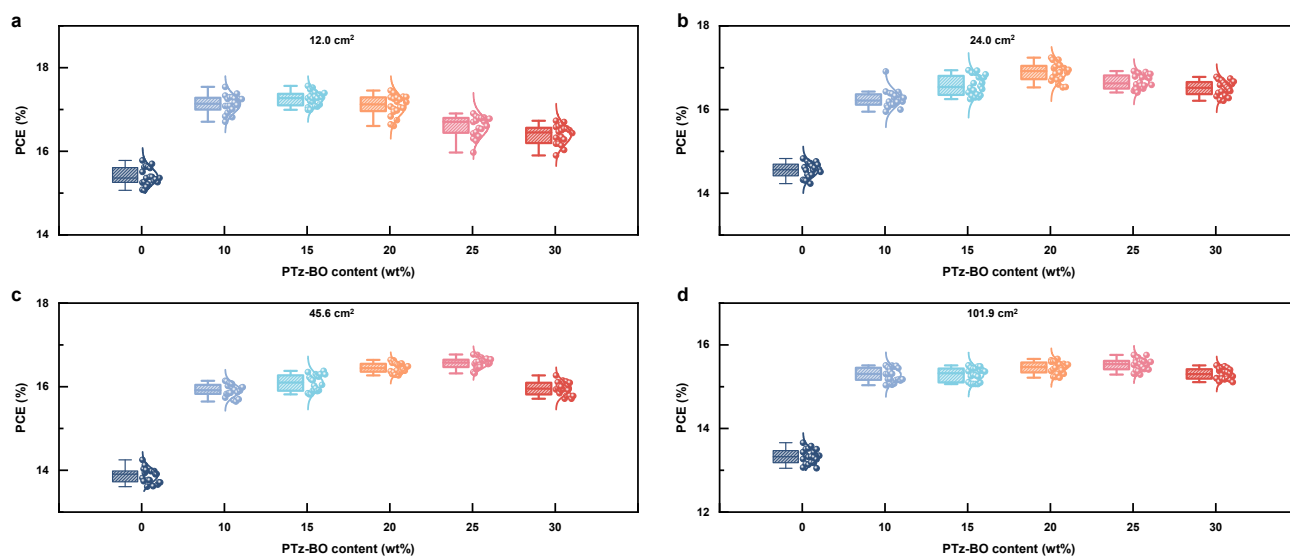


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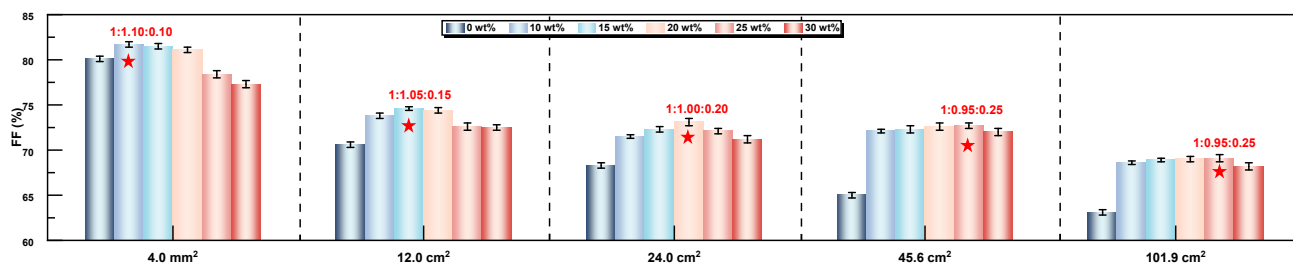
2 **Supplementary Figure 47.** Optical photograph of the PM6:L8-BO-X:PTz-BO-based rigid modules (101.9 cm^2) processed
3 with *o*-XY. For modules with aperture areas of 101.9 cm^2 , the sub-cell width is 6.5 mm and the sub-cell count is 28.



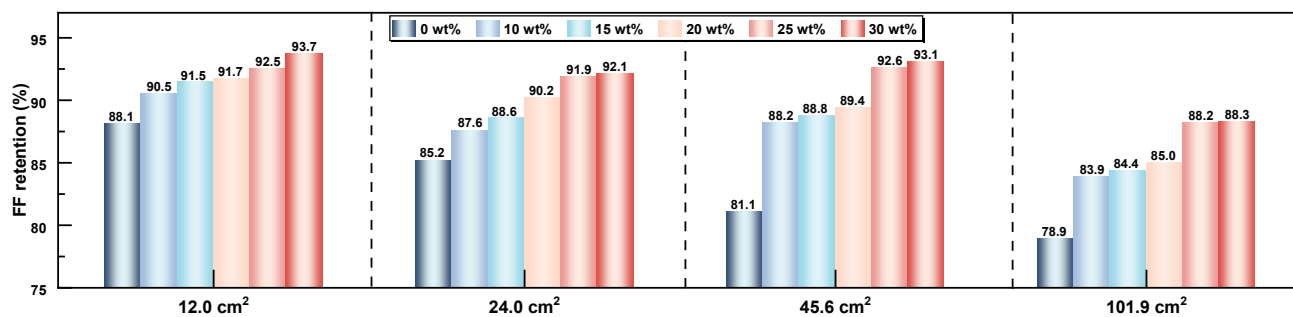
Supplementary Figure 48. a,b, Schematic diagram of large-area devices (1.0 cm²) based on conventional silver electrode structure (a) and the “L-shaped” silver electrode structure commonly employed in OSC modules (b). Compared to conventional Ag electrodes, the “L-shaped” structure enables photogenerated charges to be collected efficiently by the electrode not only through longitudinal transport, but also directly extracted from the lateral interface where the Ag electrode contacts the active layer. c, Representative J - V characteristics for PM6:L8-BO-X-based OSCs (1.0 cm²) with different silver electrode structures.



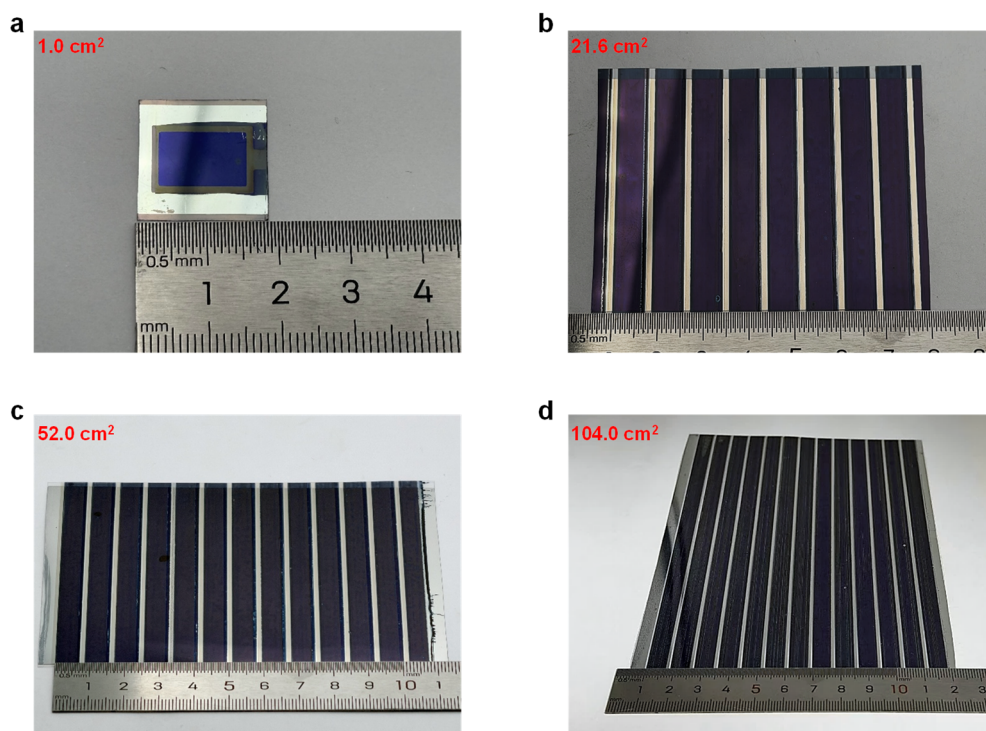
Supplementary Figure 49. Efficiency-distributed histograms of the PM6:L8-BO-X:PTz-BO-based rigid modules processed with *o*-XY under simulated AM 1.5 G illumination at 100 mW cm⁻².



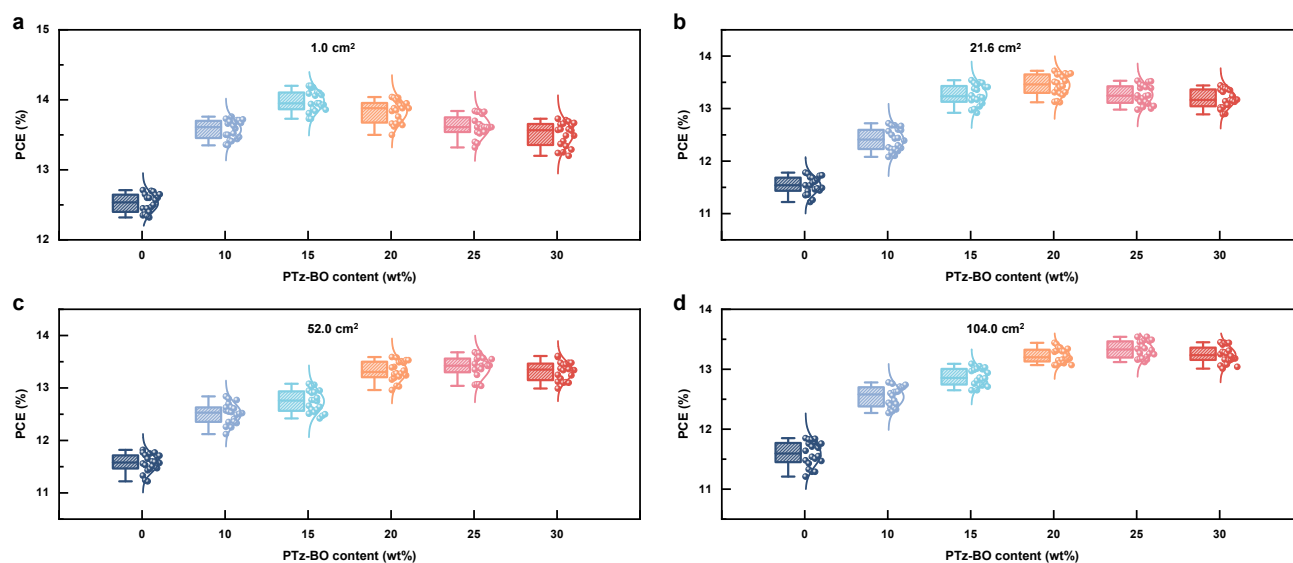
Supplementary Figure 50. The FF statistics of PM6:L8-BO-X:PTz-BO-based rigid organic photovoltaic modules with varying PTz-BO contents across different areas.



Supplementary Figure 51. The FF retention statistics of PM6:L8-BO-X:PTz-BO-based rigid organic photovoltaic modules with varying PTz-BO contents across different aperture areas. FF retention is defined as the FF ratio between a large-area OSC and a 4.0 mm² small-area counterpart.



Supplementary Figure 52. Optical photograph of the R2R printed PM6:L8-BO-X:PTz-BO-based devices and modules processed with *o*-XY. For modules with active areas of 21.6 cm², 52 cm² and 104 cm², the widths of each individual sub-cell are 5.0 mm, 6.0 mm and 7.5 mm respectively.



Supplementary Figure 53. Efficiency-distributed histograms of the PM6:L8-BO-X:PTz-BO-based flexible modules processed with *o*-XY under simulated AM 1.5 G illumination at 100 mW cm⁻².

1 **Supplementary Table 1.** Photovoltaic parameters of 1.0 cm² PM6:L8-BO-X-based OSCs with different Ag electrode
2 thicknesses.

Thickness (nm)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE ^a (%)
100	0.893 (0.890 ± 0.003)	26.39 (26.17 ± 0.13)	72.5 (72.2 ± 0.2)	17.08 (16.86 ± 0.15)
120	0.892 (0.889 ± 0.003)	26.41 (26.29 ± 0.11)	73.3 (73.1 ± 0.2)	17.27 (17.07 ± 0.13)
140	0.895 (0.893 ± 0.003)	26.48 (26.32 ± 0.14)	73.8 (73.5 ± 0.3)	17.49 (17.25 ± 0.12)
160	0.895 (0.892 ± 0.003)	26.43 (26.29 ± 0.12)	73.8 (73.4 ± 0.3)	17.46 (17.20 ± 0.10)

3 ^a Average values with standard deviation were obtained from 20 independent devices.

4

1 **Supplementary Table 2.** Photovoltaic parameters of 1.0 cm² PM6:L8-BO-X-based OSCs with different ITO electrode
2 thicknesses.

Thickness (Å)	Transmittance (%)	Sheet Resistance (Ω/sq)	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE ^a (%)
1350	≤ 94.5	10-15	0.895 (0.893 ± 0.003)	26.55 (26.39 ± 0.14)	72.8 (72.6 ± 0.3)	17.30 (17.13 ± 0.12)
1850	≤ 93.5	6-8	0.895 (0.893 ± 0.003)	26.48 (26.32 ± 0.14)	73.8 (73.5 ± 0.3)	17.49 (17.25 ± 0.12)
2450	≤ 90.2	4-5	0.894 (0.891 ± 0.003)	24.38 (24.24 ± 0.13)	76.5 (76.2 ± 0.2)	16.67 (16.45 ± 0.12)

3 ^a Average values with standard deviation were obtained from 20 independent devices.

4

1 **Supplementary Table 3.** Photovoltaic parameters of 1.0 cm² PM6:L8-BO-X-based OSCs with different busbar numbers.

Busbar number	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE ^a (%)
4	0.895 (0.893 ± 0.003)	26.48 (26.32 ± 0.14)	73.8 (73.5 ± 0.3)	17.49 (17.25 ± 0.12)
1	0.892 (0.889 ± 0.003)	26.17 (26.07 ± 0.12)	72.6 (72.3 ± 0.3)	16.95 (16.69 ± 0.15)

2 ^a Average values with standard deviation were obtained from 20 independent devices.

3

Supplementary Table 4. Crystal coherence lengths and the d -spacings of the (010) peaks in the IP direction of the neat films.

Neat film	Amorphous ^c		(010) peak ^c			
	q ($\text{\AA}^{-1}$)	d -spacing ^a ($\text{\AA}$)	q ($\text{\AA}^{-1}$)	d -spacing ^a ($\text{\AA}$)	FWHM ($\text{\AA}^{-1}$)	CCL ^b ($\text{\AA}$)
L8-BO-X	1.214	5.17	1.502	4.18	0.433	12.91
PTz-BO	1.328	4.73	1.667	3.77	0.269	20.78
PM6	1.277	4.92	1.620	3.88	0.282	19.82

^a Obtained by the equation of $d = 2\pi/q$, in which q is the corresponding x -coordinate of diffraction peak.

^b Calculated using the equation: $\text{CCL} = 2\pi K/\text{FWHM}$, in which FWHM is the full width at half maxima and K is a form factor (0.89 here).

^c The peak at around $1.5\text{--}1.7 \text{\AA}^{-1}$ is the π - π stacking signal, while the signal approximately $1.2\text{--}1.5 \text{\AA}^{-1}$ represents the average molecular spacing within the amorphous phase. Due to the overlap between these two signals, we employed two Gaussian peaks to fit the curve within the $1.0\text{--}2.0 \text{\AA}^{-1}$ range and obtained the corresponding parameters.

Supplementary Table 5. Crystal coherence lengths and the d -spacings of the (010) peaks in the OOP direction of the neat films.

Neat film	Amorphous ^c		(010) peak ^c			
	q ($\text{\AA}^{-1}$)	d -spacing ^a ($\text{\AA}$)	q ($\text{\AA}^{-1}$)	d -spacing ^a ($\text{\AA}$)	FWHM ($\text{\AA}^{-1}$)	CCL ^b ($\text{\AA}$)
L8-BO-X	1.308	4.80	1.637	3.84	0.359	15.57
PTz-BO	1.288	4.88	1.623	3.87	0.419	13.34
PM6	1.158	5.42	1.605	3.91	0.354	15.79

^a Obtained by the equation of $d = 2\pi/q$, in which q is the corresponding x -coordinate of diffraction peak.

^b Calculated using the equation: $\text{CCL} = 2\pi K/\text{FWHM}$, in which FWHM is the full width at half maxima and K is a form factor (0.89 here).

^c The peak at around $1.5\text{--}1.7 \text{\AA}^{-1}$ is the π - π stacking signal, while the signal approximately $1.2\text{--}1.5 \text{\AA}^{-1}$ represents the average molecular spacing within the amorphous phase. Due to the overlap between these two signals, we employed two Gaussian peaks to fit the curve within the $1.0\text{--}2.0 \text{\AA}^{-1}$ range and obtained the corresponding parameters.

Supplementary Table 6. Crystal coherence lengths and the d -spacings of (100) peaks in the IP direction of the neat films.

Neat film	Peak 1 ^c				Peak 2 ^c			
	q ($\text{\AA}^{-1}$)	d -spacing ^a ($\text{\AA}$)	FWHM ($\text{\AA}^{-1}$)	CCL ^b ($\text{\AA}$)	q ($\text{\AA}^{-1}$)	d -spacing ^a ($\text{\AA}$)	FWHM ($\text{\AA}^{-1}$)	CCL ^b ($\text{\AA}$)
L8-BO-X	0.295	21.29	0.095	59.14	0.382	16.44	0.106	52.73
PTz-BO	0.281	22.35	0.104	53.74	0.321	19.56	0.067	83.67
PM6	0.256	24.53	0.110	50.81	0.299	21.00	0.063	88.44

^a Obtained by the equation of $d=2\pi/q$, in which q is the corresponding x -coordinate of diffraction peak.

^b Calculated using the equation: $\text{CCL}=2\pi K/\text{FWHM}$, in which FWHM is the full width at half maxima and K is a form factor (0.89 here).

^c The peaks located around 0.2-0.4 $\text{\AA}^{-1}$ correspond to the multiple-order diffraction peaks of lamellar stacking. Due to the overlap between these two signals, we employed two Gaussian peaks to fit the curve within the 0.2-0.4 $\text{\AA}^{-1}$ range and obtained the corresponding parameters.

Supplementary Table 7. Crystal coherence lengths and the d -spacings of (010) peaks in the IP direction of the PM6:L8-BO-X:PTz-BO blends based on varied PTz-BO contents.

Blend film	Amorphous ^c		(010) peak ^c			
	q ($\text{\AA}^{-1}$)	d -spacing ^a ($\text{\AA}$)	q ($\text{\AA}^{-1}$)	d -spacing ^a ($\text{\AA}$)	FWHM ($\text{\AA}^{-1}$)	CCL ^b ($\text{\AA}$)
0 wt%	1.281	4.90	1.623	3.87	0.277	20.18
5 wt%	1.292	4.86	1.629	3.86	0.270	20.70
10 wt%	1.398	4.49	1.637	3.84	0.261	21.41
15 wt%	1.303	4.82	1.638	3.83	0.255	21.92
20 wt%	1.305	4.81	1.638	3.83	0.240	23.29
25 wt%	1.305	4.81	1.640	3.83	0.234	23.89
30 wt%	1.311	4.79	1.641	3.83	0.226	24.73
35 wt%	1.314	4.78	1.642	3.82	0.217	25.76
120 wt%	1.323	4.75	1.644	3.82	0.206	27.13

^a Obtained by the equation of $d=2\pi/q$, in which q is the corresponding x -coordinate of diffraction peak.

^b Calculated using the equation: $\text{CCL}=2\pi K/\text{FWHM}$, in which FWHM is the full width at half maxima and K is a form factor (0.89 here).

^c The peak at around 1.5-1.7 $\text{\AA}^{-1}$ is the π - π stacking signal, while the signal approximately 1.2-1.5 $\text{\AA}^{-1}$ represents the average molecular spacing within the amorphous phase. Due to the overlap between these two signals, we employed two Gaussian peaks to fit the curve within the 1.0-2.0 $\text{\AA}^{-1}$ range and obtained the corresponding parameters.

Supplementary Table 8. Crystal coherence lengths and the d -spacings of (010) peaks in the OOP direction of the PM6:L8-BO-X:PTz-BO blends based on varied PTz-BO contents.

Neat film	Amorphous ^c		(010) peak ^c			
	q ($\text{\AA}^{-1}$)	d -spacing ^a ($\text{\AA}$)	q ($\text{\AA}^{-1}$)	d -spacing ^a ($\text{\AA}$)	FWHM ($\text{\AA}^{-1}$)	CCL ^b ($\text{\AA}$)
0 wt%	1.311	4.79	1.645	3.82	0.312	17.91
5 wt%	1.310	4.79	1.644	3.82	0.314	17.80
10 wt%	1.310	4.79	1.639	3.83	0.319	17.52
15 wt%	1.310	4.79	1.630	3.85	0.319	17.52
20 wt%	1.286	4.88	1.624	3.87	0.319	17.52
25 wt%	1.286	4.88	1.622	3.87	0.329	16.99
30 wt%	1.286	4.88	1.618	3.88	0.329	16.99
35 wt%	1.286	4.88	1.606	3.91	0.331	16.89
120 wt%	1.178	5.33	1.518	4.14	0.416	13.44

^a Obtained by the equation of $d=2\pi/q$, in which q is the corresponding x -coordinate of diffraction peak.

^b Calculated using the equation: $\text{CCL}=2\pi K/\text{FWHM}$, in which FWHM is the full width at half maxima and K is a form factor (0.89 here).

^c The peak at around 1.5-1.7 $\text{\AA}^{-1}$ is the π - π stacking signal, while the signal approximately 1.2-1.5 $\text{\AA}^{-1}$ represents the average molecular spacing within the amorphous phase. Due to the overlap between these two signals, we employed two Gaussian peaks to fit the curve within the 1.0-2.0 $\text{\AA}^{-1}$ range and obtained the corresponding parameters.

Supplementary Table 9. Crystal coherence lengths and the d -spacings of (100) peaks in the IP direction of the PM6:L8-BO-X:PTz-BO blends based on varied PTz-BO contents.

Neat film	Peak 1 ^c				Peak 2 ^c			
	q (Å ⁻¹)	d -spacing ^a (Å)	FWHM (Å ⁻¹)	CCL ^b (Å)	q (Å ⁻¹)	d -spacing ^a (Å)	FWHM (Å ⁻¹)	CCL ^b (Å)
0 wt%	0.282	22.27	0.083	67.02	0.373	16.84	0.119	46.97
5 wt%	0.283	22.19	0.087	64.24	0.370	16.97	0.134	41.71
10 wt%	0.283	22.19	0.089	62.73	0.370	16.97	0.136	41.10
15 wt%	0.283	22.19	0.091	61.42	0.365	17.21	0.136	41.10
20 wt%	0.279	22.51	0.095	58.71	0.365	17.21	0.138	40.50
25 wt%	0.279	22.51	0.096	58.16	0.354	17.74	0.164	34.08
30 wt%	0.277	22.67	0.096	58.22	0.353	17.79	0.164	34.08
35 wt%	0.276	22.75	0.105	53.23	0.350	17.94	0.165	33.87
120 wt%	0.260	24.15	0.160	34.93	0.351	17.89	0.166	33.67

^a Obtained by the equation of $d = 2\pi/q$, in which q is the corresponding x -coordinate of diffraction peak.

^b Calculated using the equation: $CCL = 2\pi K / FWHM$, in which FWHM is the full width at half maxima and K is a form factor (0.89 here).

^c The peaks located around 0.2-0.4 Å⁻¹ correspond to the multiple-order diffraction peaks of lamellar stacking. Due to the overlap between these two signals, we employed two Gaussian peaks to fit the curve within the 0.2-0.4 Å⁻¹ range and obtained the corresponding parameters.

Supplementary Table 10. Photovoltaic parameters of 1.0 cm² spin-coated binary and ternary OSCs with different PTz-BO contents.

PTz-BO content	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	FF Retention ^a (%)	PCE ^b (%)	PCE Retention ^c (%)
0 wt%	0.894 (0.891 ± 0.003)	26.54 (26.44 ± 0.10)	74.2 (73.8 ± 0.3)	92.2	17.61 (17.36 ± 0.11)	92.1
5 wt%	0.903 (0.900 ± 0.003)	27.06 (26.96 ± 0.10)	74.5 (74.2 ± 0.3)	92.4	18.20 (17.99 ± 0.10)	92.4
10 wt%	0.906 (0.903 ± 0.002)	27.70 (27.48 ± 0.14)	76.3 (76.0 ± 0.2)	93.0	19.15 (18.90 ± 0.13)	93.0
15 wt%	0.916 (0.913 ± 0.002)	27.24 (27.05 ± 0.10)	77.2 (76.9 ± 0.3)	94.3	19.26 (19.03 ± 0.10)	94.0
20 wt%	0.920 (0.918 ± 0.003)	27.05 (26.93 ± 0.11)	77.0 (76.8 ± 0.2)	94.5	19.16 (18.99 ± 0.11)	94.5
25 wt%	0.922 (0.920 ± 0.003)	26.66 (26.53 ± 0.11)	75.9 (75.6 ± 0.3)	96.3	18.66 (18.53 ± 0.10)	95.8
30 wt%	0.928 (0.925 ± 0.003)	26.15 (26.02 ± 0.10)	75.3 (75.0 ± 0.3)	96.9	18.27 (18.02 ± 0.15)	96.7
35 wt%	0.937 (0.934 ± 0.003)	25.88 (25.76 ± 0.10)	75.1 (74.8 ± 0.3)	97.7	18.21 (18.00 ± 0.12)	97.1
120 wt%	0.973 (0.969 ± 0.003)	9.12 (9.08 ± 0.06)	45.2 (44.9 ± 0.3)	99.8	4.02 (3.94 ± 0.04)	99.0

^a FF retention is defined as the FF ratio between a large-area OSC and a 4.0 mm² small-area counterpart.

^b Average values with standard deviation were obtained from 20 independent devices.

^c PCE retention is defined as the PCE ratio between a large-area OSC and a 4.0 mm² small-area counterpart.

Supplementary Table 11. Crystal coherence lengths and the d -spacings of (010) peaks in the IP direction of the neat and blend films processed with CF.

Materials	Amorphous ^c		(010) peak ^c			
	q ($\text{\AA}^{-1}$)	d -spacing ^a ($\text{\AA}$)	q ($\text{\AA}^{-1}$)	d -spacing ^a ($\text{\AA}$)	FWHM ($\text{\AA}^{-1}$)	CCL ^b ($\text{\AA}$)
D18	1.286	4.88	1.587	3.96	0.266	21.01
L8-BO	1.310	4.79	1.508	4.16	0.368	15.19
PTz-BO	1.314	4.78	1.508	4.16	0.293	19.08
L2	1.468	4.28	1.588	3.95	0.208	26.87
D18:L8-BO	1.298	4.84	1.588	3.96	0.221	28.45
D18:PTz-BO	1.308	4.80	1.639	3.83	0.203	30.94
L2:L8-BO	1.458	4.31	1.643	3.82	0.211	29.76

^a Obtained by the equation of $d=2\pi/q$, in which q is the corresponding x -coordinate of diffraction peak.

^b Calculated using the equation: $CCL=2\pi K/FWHM$, in which FWHM is the full width at half maxima and K is a form factor (0.89 here).

^c The peak at around 1.5-1.7 $\text{\AA}^{-1}$ is the π - π stacking signal, while the signal approximately 1.2-1.5 $\text{\AA}^{-1}$ represents the average molecular spacing within the amorphous phase. Due to the overlap between these two signals, we employed two Gaussian peaks to fit the curve within the 1.0-2.0 $\text{\AA}^{-1}$ range and obtained the corresponding parameters.

Supplementary Table 12. Crystal coherence lengths and the d -spacings of (010) peaks in the OOP direction of the neat and blend films processed with CF.

Materials	Amorphous ^c		(010) peak ^c			
	q ($\text{\AA}^{-1}$)	d -spacing ^a ($\text{\AA}$)	q ($\text{\AA}^{-1}$)	d -spacing ^a ($\text{\AA}$)	FWHM ($\text{\AA}^{-1}$)	CCL ^b ($\text{\AA}$)
D18	1.449	4.33	1.588	3.95	0.271	20.62
L8-BO	1.333	4.71	1.638	3.83	0.359	15.57
PTz-BO	1.469	4.28	1.571	4.00	0.428	13.06
L2	1.278	4.91	1.584	3.96	0.280	19.96
D18:L8-BO	1.260	4.98	1.601	3.92	0.344	16.31
D18:PTz-BO	1.260	4.99	1.565	4.01	0.344	16.29
L2:L8-BO	1.334	4.71	1.641	3.83	0.356	15.77

^a Obtained by the equation of $d = 2\pi/q$, in which q is the corresponding x -coordinate of diffraction peak.

^b Calculated using the equation: $\text{CCL} = 2\pi K/\text{FWHM}$, in which FWHM is the full width at half maxima and K is a form factor (0.89 here).

^c The peak at around 1.5-1.7 $\text{\AA}^{-1}$ is the π - π stacking signal, while the signal approximately 1.2-1.5 $\text{\AA}^{-1}$ represents the average molecular spacing within the amorphous phase. Due to the overlap between these two signals, we employed two Gaussian peaks to fit the curve within the 1.0-2.0 $\text{\AA}^{-1}$ range and obtained the corresponding parameters.

Supplementary Table 13. Crystal coherence lengths and the d -spacings of (100) peaks in the IP direction of the neat and blend films processed with CF.

Materials	Peak 1 ^c				Peak 2 ^c			
	q (Å ⁻¹)	d -spacing ^a (Å)	FWHM (Å ⁻¹)	CCL ^b (Å)	q (Å ⁻¹)	d -spacing ^a (Å)	FWHM (Å ⁻¹)	CCL ^b (Å)
D18	0.283	22.19	0.077	82.09	0.325	19.32	0.075	74.52
L8-BO	0.373	16.84	0.096	65.42	0.457	13.74	0.121	46.19
PTz-BO	0.348	18.05	0.096	65.55	0.419	14.99	0.125	44.71
L2	0.280	22.43	0.10	61.57	0.314	20.00	0.075	74.23
D18:L8-BO	0.299	21.02	0.065	86.40	0.333	18.89	0.091	61.16
D18:PTz-BO	0.293	21.46	0.078	71.41	0.316	19.85	0.094	59.78
L2:L8-BO	0.331	18.97	0.090	62.12	0.449	13.98	0.119	47.13

^a Obtained by the equation of $d = 2\pi/q$, in which q is the corresponding x -coordinate of diffraction peak.

^b Calculated using the equation: $CCL = 2\pi K / FWHM$, in which FWHM is the full width at half maxima and K is a form factor (0.89 here).

^c The peaks located around 0.2-0.4 Å⁻¹ correspond to the multiple-order diffraction peaks of lamellar stacking. Due to the overlap between these two signals, we employed two Gaussian peaks to fit the curve within the 0.2-0.4 Å⁻¹ range and obtained the corresponding parameters.

1 **Supplementary Table 14.** Photovoltaic parameters of CF-processed OSCs with different aperture areas.

Active layer	V_{oc} (V)	J_{sc} (mA cm ⁻²)	J_{sc}^{cal} (mA cm ⁻²)	FF (%)	PCE ^a (%)	PCE Retention ^b (%)
D18:L8-BO (4.0 mm ²)	0.910 (0.907 ± 0.003)	26.70 (26.64 ± 0.10)	25.84	80.1 (79.8 ± 0.3)	19.46 (19.29 ± 0.11)	92.1
D18:L8-BO (1.0 cm ²)	0.912 (0.910 ± 0.004)	26.77 (26.73 ± 0.10)	--	73.4 (73.2 ± 0.3)	17.92 (17.81 ± 0.13)	
D18:PTz-BO (4.0 mm ²)	0.986 (0.984 ± 0.003)	8.35 (8.29 ± 0.06)	8.12	41.1 (40.8 ± 0.4)	3.38 (3.33 ± 0.04)	99.1
D18:PTz-BO (1.0 cm ²)	0.988 (0.985 ± 0.003)	8.30 (8.25 ± 0.06)	--	40.8 (40.5 ± 0.3)	3.35 (3.29 ± 0.04)	
L2:L8-BO (4 mm ²)	0.941 (0.935 ± 0.004)	13.15 (13.08 ± 0.08)	12.71	56.2 (55.9 ± 0.3)	6.95 (6.84 ± 0.07)	98.7
L2:L8-BO (1.0 cm ²)	0.944 (0.939 ± 0.004)	13.00 (12.94 ± 0.07)	--	55.9 (55.6 ± 0.3)	6.86 (6.76 ± 0.07)	

2 ^a Average values with standard deviation were obtained from 20 independent devices.

3 ^b PCE retention is defined as the PCE ratio between a large-area OSC and a 4.0 mm² small-area counterpart.

4

1 **Supplementary Table 15.** TG OFET performance parameters of acceptors at different blending ratios.

Materials	μ_e^a (10^{-2} cm ² V ⁻¹ s ⁻¹)	I_{on}/I_{off}
L8-BO-X:PTz-BO (1.20:0)	7.8 ± 0.11	10^4 to 10^5
L8-BO-X:PTz-BO (1.15:0.05)	10.2 ± 0.12	10^4 to 10^5
L8-BO-X:PTz-BO (1.10:0.10)	12.8 ± 0.14	10^4 to 10^5
L8-BO-X:PTz-BO (1.05:0.15)	13.5 ± 0.10	10^4 to 10^5
L8-BO-X:PTz-BO (1.00:0.20)	14.6 ± 0.16	10^4 to 10^5
L8-BO-X:PTz-BO (0.95:0.25)	16.4 ± 0.17	10^4 to 10^5
L8-BO-X:PTz-BO (0.90:0.30)	17.2 ± 0.14	10^4 to 10^5
L8-BO-X:PTz-BO (0.85:0.35)	19.1 ± 0.11	10^4 to 10^5
L8-BO-X:PTz-BO (0:1.20)	22.5 ± 0.13	10^4 to 10^5

2 ^a Average value with standard deviation were obtained from 5 devices.

3

1 **Supplementary Table 16.** Vertical electron mobility statistics of acceptors at different blending ratios.

Materials	μ_e^a (10^{-4} cm ² V ⁻¹ s ⁻¹)
L8-BO-X:PTz-BO (1.20:0)	6.46 ± 0.15
L8-BO-X:PTz-BO (1.15:0.05)	6.15 ± 0.16
L8-BO-X:PTz-BO (1.10:0.10)	5.98 ± 0.12
L8-BO-X:PTz-BO (1.05:0.15)	5.77 ± 0.17
L8-BO-X:PTz-BO (1.00:0.20)	5.63 ± 0.10
L8-BO-X:PTz-BO (0.95:0.25)	5.55 ± 0.11
L8-BO-X:PTz-BO (0.90:0.30)	5.31 ± 0.13
L8-BO-X:PTz-BO (0.85:0.35)	4.97 ± 0.15
L8-BO-X:PTz-BO (0:1.20)	1.57 ± 0.13

2 ^a Average value with standard deviation were obtained from 5 devices.

3

1 **Supplementary Table 17.** The lateral and vertical conductivity of the acceptor films at different blending ratios.

Active layer	Lateral conductivity ^a ($\times 10^{-6}$ S m ⁻¹)	Vertical conductivity ^a ($\times 10^{-6}$ S m ⁻¹)
L8-BO-X:PTz-BO (1.20:0)	0.93 $\pm$ 0.09	9.02 $\pm$ 0.14
L8-BO-X:PTz-BO (1.15:0.05)	1.02 $\pm$ 0.09	8.26 $\pm$ 0.16
L8-BO-X:PTz-BO (1.10:0.10)	1.16 $\pm$ 0.10	7.83 $\pm$ 0.15
L8-BO-X:PTz-BO (1.05:0.15)	1.25 $\pm$ 0.10	6.53 $\pm$ 0.14
L8-BO-X:PTz-BO (1.00:0.20)	1.44 $\pm$ 0.13	5.83 $\pm$ 0.16
L8-BO-X:PTz-BO (0.95:0.25)	1.50 $\pm$ 0.11	4.86 $\pm$ 0.14
L8-BO-X:PTz-BO (0.90:0.30)	1.60 $\pm$ 0.12	4.05 $\pm$ 0.15
L8-BO-X:PTz-BO (0.85:0.35)	1.75 $\pm$ 0.10	3.42 $\pm$ 0.13
L8-BO-X:PTz-BO (0:1.20)	3.32 $\pm$ 0.17	1.54 $\pm$ 0.10

2 ^a Average value with standard deviation were obtained from 5 devices.

3

1 **Supplementary Table 18.** The lateral and vertical conductivity statistics of the PM6:L8-BO-X:PTz-BO devices based on
2 varied PTz-BO contents.

PTz-BO content	Lateral conductivity ^a ($\times 10^{-6}$ S m ⁻¹)	vertical conductivity ^a ($\times 10^{-6}$ S m ⁻¹)
0 wt%	1.06 $\pm$ 0.10	12.7 $\pm$ 0.17
5 wt%	1.28 $\pm$ 0.12	12.4 $\pm$ 0.13
10 wt%	1.90 $\pm$ 0.10	10.6 $\pm$ 0.15
15 wt%	2.19 $\pm$ 0.11	9.46 $\pm$ 0.15
20 wt%	2.88 $\pm$ 0.13	8.83 $\pm$ 0.14
25 wt%	3.15 $\pm$ 0.13	8.00 $\pm$ 0.19
30 wt%	3.65 $\pm$ 0.14	6.50 $\pm$ 0.15
35 wt%	4.00 $\pm$ 0.15	5.91 $\pm$ 0.16
120 wt%	6.25 $\pm$ 0.12	4.11 $\pm$ 0.17

3 ^a Average value with standard deviation were obtained from 5 devices.

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1 **Supplementary Table 19.** Vertical electron mobility and hole mobility statistics of PM6:L8-BO-X:PTz-BO devices based
2 on varied PTz-BO contents.

PTz-BO content	$\mu_{\text{h}}^{\text{a}}$ ($10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	$\mu_{\text{e}}^{\text{a}}$ ($10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$)	$\mu_{\text{h}}/\mu_{\text{e}}$
0 wt%	6.70 ± 0.11	5.04 ± 0.15	1.33
5 wt%	6.55 ± 0.15	5.60 ± 0.18	1.17
10 wt%	6.31 ± 0.17	5.49 ± 0.10	1.15
15 wt%	6.04 ± 0.18	5.03 ± 0.10	1.20
20 wt%	5.89 ± 0.12	4.75 ± 0.13	1.24
25 wt%	5.78 ± 0.14	4.52 ± 0.19	1.28
30 wt%	5.70 ± 0.19	4.35 ± 0.14	1.31
35 wt%	5.64 ± 0.11	4.24 ± 0.16	1.33
120 wt%	2.54 ± 0.13	1.60 ± 0.14	1.59

3 ^a Average value with standard deviation were obtained from 5 devices.

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1 **Supplementary Table 20.** Photovoltaic parameters of 1.0 cm² PM6:L8-BO-X-based OSCs with conventional and “L-
2 shaped” silver electrode structure processed with *o*-XY.

Silver electrode structure	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE ^a (%)
Conventional structure	0.895 (0.893 ± 0.003)	26.48 (26.32 ± 0.14)	73.8 (73.5 ± 0.3)	17.49 (17.25 ± 0.12)
L-shaped structure	0.894 (0.891 ± 0.003)	26.54 (26.44 ± 0.10)	74.2 (73.8 ± 0.3)	17.61 (17.36 ± 0.11)

3 ^a Average values with standard deviation were obtained from 20 independent devices.

4

Supplementary Table 21. Photovoltaic parameters of 12.0 cm² PM6:L8-BO-X:PTz-BO-based rigid modules with different PTz-BO contents.

PTz-BO content	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	FF Retention ^a (%)	PCE ^b (%)	PCE Retention ^c (%)
0 wt%	10.698 (10.674 ± 0.020)	2.08 (2.00 ± 0.03)	70.9 (70.6 ± 0.3)	88.1	15.78 (15.39 ± 0.21)	82.5
10 wt%	10.842 (10.820 ± 0.019)	2.18 (2.12 ± 0.05)	74.2 (73.8 ± 0.3)	90.5	17.54 (17.13 ± 0.20)	85.2
15 wt%	10.862 (10.836 ± 0.022)	2.16 (2.10 ± 0.03)	74.9 (74.6 ± 0.2)	91.5	17.56 (17.26 ± 0.17)	85.7
20 wt%	10.867 (10.841 ± 0.023)	2.15 (2.07 ± 0.04)	74.7 (74.4 ± 0.3)	91.7	17.45 (17.09 ± 0.24)	86.1
25 wt%	10.879 (10.863 ± 0.017)	2.13 (2.06 ± 0.05)	72.9 (72.6 ± 0.4)	92.5	16.90 (16.61 ± 0.24)	86.8
30 wt%	10.889 (10.867 ± 0.016)	2.11 (2.05 ± 0.06)	72.8 (72.5 ± 0.3)	93.7	16.73 (16.39 ± 0.22)	88.5

^a FF retention is defined as the FF ratio between a large-area OSC and a 4.0 mm² small-area counterpart.

^b Average values with standard deviation were obtained from 20 independent devices.

^c PCE retention is defined as the PCE ratio between a large-area OSC and a 4.0 mm² small-area counterpart.

1 **Supplementary Table 22.** Photovoltaic parameters of 24.0 cm² PM6:L8-BO-X:PTz-BO-based rigid modules with
2 different PTz-BO contents.

PTz-BO content	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	FF Retention ^a (%)	PCE ^b (%)	PCE Retention ^c (%)
0 wt%	13.419 (13.390 ± 0.025)	1.61 (1.56 ± 0.03)	68.6 (68.3 ± 0.3)	85.2	14.83 (14.55 ± 0.17)	77.6
10 wt%	13.510 (13.487 ± 0.021)	1.69 (1.64 ± 0.04)	71.8 (71.5 ± 0.2)	87.6	16.43 (16.25 ± 0.20)	79.8
15 wt%	13.556 (13.529 ± 0.022)	1.72 (1.69 ± 0.03)	72.6 (72.3 ± 0.3)	88.6	16.94 (16.58 ± 0.23)	82.7
20 wt%	13.572 (13.553 ± 0.019)	1.73 (1.70 ± 0.04)	73.5 (73.1 ± 0.4)	90.2	17.24 (16.90 ± 0.21)	85.0
25 wt%	13.601 (13.577 ± 0.019)	1.72 (1.69 ± 0.02)	72.4 (72.1 ± 0.3)	91.9	16.92 (16.66 ± 0.16)	86.9
30 wt%	13.630 (13.608 ± 0.023)	1.72 (1.68 ± 0.04)	71.6 (71.2 ± 0.4)	92.1	16.78 (16.51 ± 0.17)	88.8

3 ^a FF retention is defined as the FF ratio between a large-area OSC and a 4.0 mm² small-area counterpart.

4 ^b Average values with standard deviation were obtained from 20 independent devices.

5 ^c PCE retention is defined as the PCE ratio between a large-area OSC and a 4.0 mm² small-area counterpart.

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1 **Supplementary Table 23.** Photovoltaic parameters of 45.6 cm² PM6:L8-BO-X:PTz-BO-based rigid modules with
2 different PTz-BO contents.

PTz-BO content	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	FF Retention ^a (%)	PCE ^b (%)	PCE Retention ^c (%)
0 wt%	14.044 (14.020 ± 0.021)	1.55 (1.51 ± 0.03)	65.3 (65.0 ± 0.3)	81.1	14.25 (13.87 ± 0.17)	74.5
10 wt%	14.092 (14.068 ± 0.023)	1.58 (1.54 ± 0.04)	72.3 (72.1 ± 0.2)	88.2	16.14 (15.91 ± 0.15)	78.4
15 wt%	14.113 (14.088 ± 0.025)	1.59 (1.55 ± 0.05)	72.7 (72.3 ± 0.4)	88.8	16.35 (16.09 ± 0.19)	79.8
20 wt%	14.176 (14.153 ± 0.020)	1.61 (1.58 ± 0.03)	72.9 (72.6 ± 0.4)	89.4	16.64 (16.45 ± 0.11)	82.0
25 wt%	14.205 (14.179 ± 0.024)	1.62 (1.59 ± 0.04)	73.0 (72.7 ± 0.3)	92.6	16.77 (16.56 ± 0.12)	86.1
30 wt%	14.232 (14.201 ± 0.026)	1.58 (1.53 ± 0.04)	72.3 (72.0 ± 0.4)	93.1	16.27 (15.96 ± 0.15)	86.1

3 ^a FF retention is defined as the FF ratio between a large-area OSC and a 4.0 mm² small-area counterpart.

4 ^b Average values with standard deviation were obtained from 20 independent devices.

5 ^c PCE retention is defined as the PCE ratio between a large-area OSC and a 4.0 mm² small-area counterpart.

1 **Supplementary Table 24.** Photovoltaic parameters of 101.9 cm² PM6:L8-BO-X:PTz-BO-based rigid modules with
2 different PTz-BO contents.

PTz-BO content	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	FF Retention ^a (%)	PCE ^b (%)	PCE Retention ^c (%)
0 wt%	24.537 (24.501 ± 0.033)	0.876 (0.869 ± 0.008)	63.5 (63.1 ± 0.3)	78.9	13.66 (13.33 ± 0.17)	71.4
10 wt%	24.936 (24.905 ± 0.029)	0.904 (0.897 ± 0.005)	68.8 (68.6 ± 0.2)	83.9	15.51 (15.29 ± 0.16)	75.3
15 wt%	24.953 (24.924 ± 0.026)	0.899 (0.891 ± 0.006)	69.1 (68.9 ± 0.2)	84.4	15.51 (15.29 ± 0.16)	75.7
20 wt%	24.996 (24.961 ± 0.030)	0.902 (0.893 ± 0.007)	69.3 (69.0 ± 0.3)	85.0	15.63 (15.46 ± 0.14)	77.1
25 wt%	25.016 (24.990 ± 0.025)	0.906 (0.900 ± 0.004)	69.5 (69.1 ± 0.4)	88.2	15.76 (15.53 ± 0.13)	80.9
30 wt%	25.038 (25.009 ± 0.028)	0.902 (0.894 ± 0.004)	68.6 (68.2 ± 0.4)	88.3	15.51 (15.30 ± 0.13)	82.0

3 ^a FF retention is defined as the FF ratio between a large-area OSC and a 4.0 mm² small-area counterpart.

4 ^b Average values with standard deviation were obtained from 20 independent devices.

5 ^c PCE retention is defined as the PCE ratio between a large-area OSC and a 4.0 mm² small-area counterpart.

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1 **Supplementary Table 25.** Photovoltaic parameters of 1.0 cm² R2R printed PM6:L8-BO-X:PTz-BO-based OSCs with
2 different PTz-BO contents.

PTz-BO content	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE ^a (%)
0 wt%	0.866 (0.864 ± 0.003)	22.01 (21.83 ± 0.14)	66.71 (66.43 ± 0.27)	12.71 (12.52 ± 0.13)
10 wt%	0.867 (0.865 ± 0.003)	23.30 (23.16 ± 0.11)	67.99 (67.75 ± 0.22)	13.73 (13.58 ± 0.13)
15 wt%	0.869 (0.867 ± 0.005)	24.02 (23.87 ± 0.14)	68.00 (67.75 ± 0.28)	14.20 (13.99 ± 0.15)
20 wt%	0.874 (0.870 ± 0.004)	23.72 (23.62 ± 0.11)	67.72 (67.51 ± 0.27)	14.04 (13.84 ± 0.16)
25 wt%	0.874 (0.870 ± 0.005)	23.70 (23.58 ± 0.13)	66.79 (66.52 ± 0.29)	13.84 (13.62 ± 0.15)
30 wt%	0.876 (0.871 ± 0.005)	23.49 (23.20 ± 0.22)	66.72 (66.47 ± 0.27)	13.73 (13.51 ± 0.17)

3 ^a Average values with standard deviation were obtained from 20 independent devices.

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Supplementary Table 26. Photovoltaic parameters of 21.6 cm² R2R printed PM6:L8-BO-X:PTz-BO-based OSCs with different PTz-BO contents.

PTz-BO content	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE ^a (%)
0 wt%	6.260 (6.261 ± 0.008)	2.91 (2.86 ± 0.04)	64.72 (64.54 ± 0.23)	11.78 (11.54 ± 0.16)
10 wt%	6.272 (6.265 ± 0.007)	3.07 (3.01 ± 0.04)	66.04 (65.78 ± 0.27)	12.72 (12.40 ± 0.21)
15 wt%	6.315 (6.307 ± 0.006)	3.19 (3.15 ± 0.04)	67.21 (67.02 ± 0.19)	13.54 (13.26 ± 0.19)
20 wt%	6.343 (6.336 ± 0.006)	3.22 (3.17 ± 0.05)	67.24 (67.03 ± 0.18)	13.72 (13.45 ± 0.19)
25 wt%	6.353 (6.348 ± 0.004)	3.21 (3.18 ± 0.04)	66.4 (66.20 ± 0.20)	13.53 (13.26 ± 0.18)
30 wt%	6.355 (6.350 ± 0.004)	3.21 (3.16 ± 0.04)	65.90 (65.66 ± 0.21)	13.44 (13.20 ± 0.17)

^a Average values with standard deviation were obtained from 20 independent devices.

1 **Supplementary Table 27.** Photovoltaic parameters of 52.0 cm² R2R printed PM6:L8-BO-X:PTz-BO-based with different
2 PTz-BO contents.

PTz-BO content	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE ^a (%)
0 wt%	10.173 (10.167 ± 0.007)	1.81 (1.75 ± 0.04)	64.13 (63.93 ± 0.20)	11.82 (11.57 ± 0.17)
10 wt%	10.278 (10.269 ± 0.007)	1.90 (1.86 ± 0.03)	65.61 (65.36 ± 0.18)	12.84 (12.51 ± 0.19)
15 wt%	10.376 (10.366 ± 0.008)	1.90 (1.87 ± 0.03)	66.21 (66.05 ± 0.14)	13.08 (12.75 ± 0.21)
20 wt%	10.446 (10.434 ± 0.007)	1.94 (1.90 ± 0.04)	67.01 (66.83 ± 0.32)	13.59 (13.32 ± 0.19)
25 wt%	10.458 (10.449 ± 0.007)	1.95 (1.92 ± 0.03)	67.07 (66.87 ± 0.18)	13.68 (13.40 ± 0.20)
30 wt%	10.486 (10.475 ± 0.007)	1.95 (1.91 ± 0.03)	66.46 (66.23 ± 0.20)	13.59 (13.32 ± 0.17)

^a Average values with standard deviation were obtained from 20 independent devices.

1 **Supplementary Table 28.** Photovoltaic parameters of 104.0 cm² R2R printed PM6:L8-BO-X:PTz-BO-based OSCs with
2 different PTz-BO contents.

PTz-BO content	V_{oc} (V)	J_{sc} (mA cm ⁻²)	FF (%)	PCE ^a (%)
0 wt%	10.037 (10.030 ± 0.007)	1.87 (1.82 ± 0.04)	63.29 (63.10 ± 0.15)	11.85 (11.59 ± 0.20)
10 wt%	10.250 (10.242 ± 0.007)	1.93 (1.91 ± 0.02)	64.52 (63.34 ± 0.15)	12.78 (12.54 ± 0.17)
15 wt%	10.274 (10.269 ± 0.005)	1.96 (1.93 ± 0.03)	64.93(64.75 ± 0.34)	13.09 (12.87 ± 0.14)
20 wt%	10.290 (10.282 ± 0.006)	1.96 (1.94 ± 0.02)	66.56 (66.35 ± 0.15)	13.44 (13.23 ± 0.12)
25 wt%	10.478 (10.477 ± 0.007)	1.92 (1.88 ± 0.04)	67.17 (67.05 ± 0.18)	13.54 (13.33 ± 0.14)
30 wt%	10.546 (10.538 ± 0.007)	1.91 (1.87 ± 0.03)	66.65 (66.48 ± 0.16)	13.45 (13.24 ± 0.14)

3 ^b Average values with standard deviation were obtained from 20 independent devices.

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