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

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Abstract

The scaling transition of organic solar cells (OSCs) faces severe efficiency loss, with one key factor attributed to insufficient lateral charge transport. While electrode optimization has been well-established, the active layer's role remains underexplored. Departing from the conventional emphasis on out-of-plane π - π stacking, this work reveals that enhancing in-plane (IP) molecular packing is pivotal for achieving efficient large-area devices. By incorporating PTz-BO, a material featuring strong IP π - π stacking propensity, we achieve optimized IP structural order in ternary blend, facilitating superior lateral/vertical charge transport balance and minimizing fill factor loss during area upscaling. Notably, larger devices require progressively stronger IP molecular stacking in active layers to meet the increased demand for lateral charge transport. The small-area devices (0.04 cm²), medium-area modules (12.0 cm²), and large-area modules (101.9 cm²) achieve champion efficiencies of 20.59%, 17.56%, and 15.76% at increased PTz-BO contents of 10 wt%, 15 wt%, and 25 wt%, respectively, with the latter representing the highest efficiency for modules with an area exceeding 100 cm². The same principle applies to flexible modules fabricated by gravure printing. This study reshapes the paradigm of active layer optimization in upscaling and establishes IP molecular stacking as a fundamental design criterion for large-area organic photovoltaics.

Introduction

Organic solar cells (OSCs) have emerged as a promising next-generation photovoltaic technology, distinguished by their light weight, inherent flexibility, and compatibility with solution-processed manufacturing.¹⁻⁹ In the past years, continuous breakthroughs in photovoltaic materials and device engineering have progressively enhanced their power conversion efficiency (PCE) and operational stability,¹⁰⁻¹³ but a critical challenge impedes their path to commercialization, associated with a pronounced efficiency loss during the scale-up from laboratory-sized devices to industrially relevant modules.¹⁴⁻¹⁷

A primary contributor to this performance penalty is the dramatic increase in series resistance, stemming from insufficient lateral charge transport over extended distances.¹⁸ While increasing the number of sub-cells can shorten the lateral transport length of charges, this approach inevitably introduces risks of interconnection failure and enlarged dead area, ultimately limiting module performance. Alternative strategies have focused on the optimization of metal electrode grids and transparent conductive layers,¹⁹⁻²¹ but the critical role of photoactive layer morphology, particularly in governing lateral charge conduction, has remained largely unexplored. The conventional morphology optimization for OSCs predominantly focused on enhancing out-of-plane (OOP) π - π stacking between donor and acceptor molecules to improve vertical charge extraction.²²⁻²⁵ However, this paradigm often comes at the expense of in-plane (IP) molecular order, inadvertently exacerbating the lateral transport bottleneck in larger-area devices. This creates a critical materials design contradiction, in which the very strategy that benefits small-area cell efficiency may undermine scalability.

Herein, we present a counterintuitive yet effective strategy to specifically address the lateral transport challenge by deliberately enhancing the IP molecular packing within active layer. We design and synthesize PTz-BO, a triazole-based acceptor with strong IP π - π stacking capability, and incorporate it as a morphology regulator into PM6:L8-BO-X. Notably, PM6:PTz-BO OSCs can maintain astonishingly high efficiency retentions of nearly 100% during the device amplification process. The addition of PTz-BO progressively strengthens IP molecular packing in ternary blends, thereby improving lateral charge transport. Benefiting from the optimized IP/OOP molecular orientation balance, modules with increasing areas consistently achieve optimal performance at higher PTz-BO contents. Champion PCEs of 17.56%, 17.24%, and 15.76% are attained for devices with aperture areas of 12.0 cm², 24.0 cm², and 101.9 cm² at PTz-BO loadings of 15 wt%, 20 wt%, and 25 wt%, respectively, representing state-of-the-art performance for their respective area scales. The same principle is further validated in flexible modules fabricated by roll-to-roll gravure printing. On the other hand, incorporating a small amount of PTz-BO does not compromise OOP molecular stacking and vertical charge transport in ternary blends, but instead significantly reduces the proportion of amorphous domains. Enabled by cascade LUMO levels and an optimized fibrillar morphology, the resulting ternary OSCs deliver a leading efficiency of 20.59%, ranking among

the highest reported for non-halogenated solvent-processed devices to date. Finally, donor material L2, which also exhibits strong IP π - π stacking, is introduced as a third component into D18:L8-BO blend. Similarly improved efficiency retention during device amplification confirms the broad applicability of the IP stacking enhancement approach.

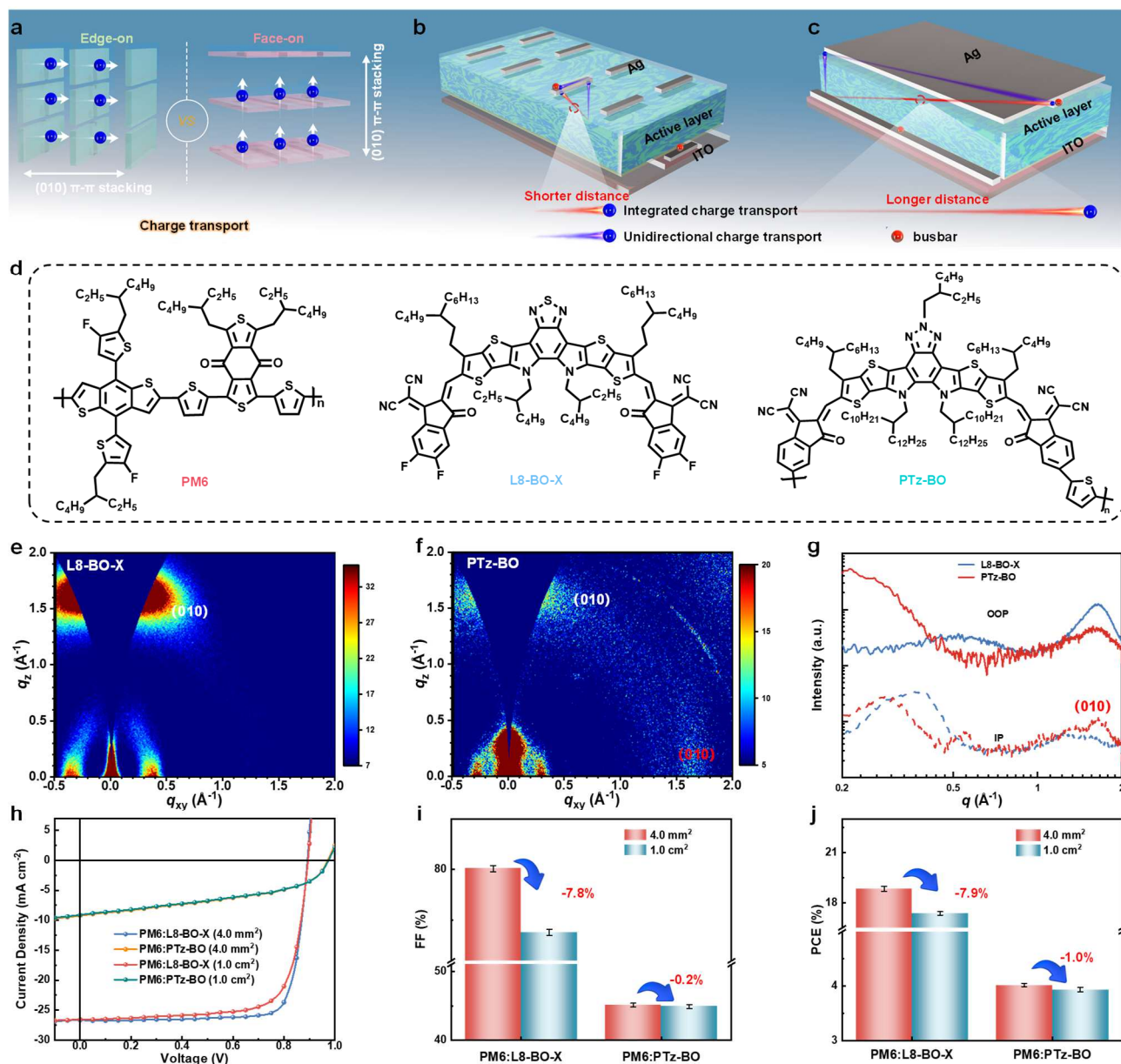
Result and discussion

Principle analysis and material selection

As shown in Fig. 1a,b, the charge transport distance (L) from device center (charge generation) to electrode edge (charge collection) is relatively short in small-area devices, resulting in a low lateral charge transport resistance R ($R = \rho \cdot L/A$, where ρ is lateral resistivity and A is cross-sectional area of device). Combined with the small total photocurrent (I) generated, the resulting voltage drop and power loss ($P_{\text{loss}} = I^2 R$) due to lateral transport are typically negligible. In this case, the electrodes can efficiently extract the majority of charges, enabling high-performance small-area OSCs to rely primarily on the favorable face-on orientation of photoactive materials. However, during the area upscaling process, the total photocurrent and the lateral transport distance required for charges from generation to extraction increase sharply (Fig. 1c), which always exacerbates charge recombination and results in poor fill factor (FF).^{15,16,26} Increasing electrode thickness to enlarge the cross-sectional area (Supplementary Fig. 1, Supplementary Tables 1 and 2), or designing multiple busbars to reduce the lateral transport distance (Supplementary Fig. 2 and Supplementary Table 3), can effectively reduce series resistance and thereby improve charge extraction, but the local performance gains from such optimizations have not fully met expectations. Moreover, increasing the thickness of a transparent electrode inevitably reduces its transparency and compromises light harvesting (Supplementary Fig. 3). Therefore, the further performance optimization of large-area OSCs necessitates enhancing the internal lateral charge migration within the photoactive layers, which can be achieved by promoting IP π - π stacking.

The chemical structures of main photovoltaic materials used in this work are shown in Fig. 1d, including the donor PM6, the small-molecule acceptor L8-BO-X and the polymer acceptor PTz-BO. PTz-BO has been reported by our group,²⁷ with the synthetic pathway shown schematically in Supplementary Fig. 4. Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements indicate that the neat L8-BO-X film maintains a dominant face-on orientation, while the neat PTz-BO film exhibits a mixed face-on/edge-on orientation with a significantly stronger π - π scattering peak in the IP direction compared to L8-BO-X (Fig. 1e-g and Supplementary Tables 4-6). Furthermore, PTz-BO displays a more compact and ordered molecular packing along the IP direction, as evidenced by its reduced π - π stacking d -spacing (3.77

1 Å vs. 4.18 Å) and longer coherence length (CCL; 20.78 Å vs. 12.91 Å). This exceptional IP stacking is well retained after
 2 blending with PM6, promising to enhance the lateral transport of photogenerated charges toward electrode collection
 3 regions in PM6:PTz-BO-based OSCs (Supplementary Fig. 5 and Supplementary Tables 7-9).



4
 5 **Fig. 1| Principle schematic and photovoltaic materials.** **a**, Schematic illustration of charge transport under different molecular orientation.
 6 **b,c**, Schematic diagrams comparing the lateral charge transport of small-area device (**b**) and large-area device (**c**). **d**, Molecular structures of
 7 PM6, L8-BO-X and PTz-BO. **e,f**, 2D GIWAXS diffraction patterns of neat L8-BO-X (**e**) and PTz-BO (**f**) films. **g**, GIWAXS in-plane and
 8 out-of-plane line-cut profiles of L8-BO-X and PTz-BO films. **h-j**, Current density-voltage (J - V) characteristics (**h**), and corresponding FF (**i**)
 9 and PCE (**j**) statistics of the optimized OSCs based on different areas. The error bars represent the standard deviations ($n = 20$).

10 To investigate the impact of dominant edge-on orientation on photovoltaic performance upon upscaling, OSCs with
 11 two active areas, 5.1 mm² and 1.1 cm² (aperture areas of 4.0 mm² and 1.0 cm²) were first fabricated using an
 12 ITO/2PACz/active layer/PNDIT-F3N/Ag structure. The electrode thicknesses and device configurations were carefully

optimized, and eco-friendly *o*-xylene (*o*-XY) was selected as the processing solvent to align with industrial requirements. It can be seen that the small-area PM6:L8-BO-X OSCs achieve a respectable efficiency of 19.12% with an open-circuit voltage (V_{oc}) of 0.890 V, short-circuit current density (J_{sc}) of 26.69 mA cm⁻² and FF of 80.5% (Fig. 1h and Table 1). Upon upscaling to 1.0 cm², however, the FF drops by ~7.8%, translating into a ~7.9% PCE loss and a final efficiency of 17.61% (Fig. 1h-j and Supplementary Table 10). In stark contrast, although the PM6:PTz-BO blend shows lower absolute efficiencies (4.06% and 4.02% for small- and large-area devices, respectively) due to suboptimal out-of-plane stacking and vertical charge transport (Supplementary Table 5), it exhibits exceptional performance retention upon upscaling, with nearly 100% FF and PCE preservation.

Table 1. Photovoltaic parameters of 4.0 mm² spin-coated binary and ternary OSCs with different PTz-BO contents.

PTz-BO content	V_{oc} (V)	J_{sc} (mA cm ⁻²)	J_{sc}^{cal} (mA cm ⁻²)	FF (%)	PCE ^a (%)
0 wt%	0.890 (0.888 ± 0.003)	26.69 (26.50 ± 0.11)	26.10	80.5 (80.1 ± 0.3)	19.12 (18.83 ± 0.14)
5 wt%	0.901 (0.899 ± 0.002)	27.14 (27.02 ± 0.09)	26.48	80.6 (80.4 ± 0.4)	19.71 (19.53 ± 0.13)
10 wt%	0.907 (0.904 ± 0.004)	27.68 (27.54 ± 0.12)	27.00	82.0 (81.7 ± 0.3)	20.59 (20.38 ± 0.16)
15 wt%	0.915 (0.912 ± 0.004)	27.35 (27.24 ± 0.10)	26.71	81.9 (81.5 ± 0.3)	20.50 (20.23 ± 0.17)
20 wt%	0.920 (0.917 ± 0.003)	27.05 (26.91 ± 0.11)	26.33	81.5 (81.1 ± 0.3)	20.28 (20.09 ± 0.12)
25 wt%	0.925 (0.918 ± 0.005)	26.71 (26.59 ± 0.11)	26.25	78.8 (78.4 ± 0.4)	19.47 (19.21 ± 0.19)
30 wt%	0.929 (0.922 ± 0.003)	26.19 (26.06 ± 0.10)	26.03	77.7 (77.3 ± 0.4)	18.91 (18.63 ± 0.14)
35 wt%	0.936 (0.931 ± 0.003)	26.05 (25.91 ± 0.10)	25.57	76.9 (76.6 ± 0.3)	18.75 (18.50 ± 0.16)
120 wt%	0.971 (0.969 ± 0.004)	9.25 (9.22 ± 0.07)	8.96	45.3 (45.1 ± 0.3)	4.06 (4.02 ± 0.03)

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

This trend is further corroborated by substituting the donor material with D18 and L2 (Supplementary Fig. 6), where L2 features strong IP π - π stacking. GIWAXS data are provided in Supplementary Figs. 7-8 and Tables 11-13. Notably, the D18:PTz-BO system yields nearly identical PCEs of 3.38% (small-area) and 3.35% (large-area), while the L2:L8-BO pair delivers comparable values of 6.95% and 6.86%, respectively (Supplementary Fig. 9 and Table 14). Conversely, the D18:L8-BO reference cells suffer a pronounced drop from 19.46% to 17.92% upon scaling, standing in sharp contrast to the stable system with enhanced IP molecular stacking. These results strongly indicate that promoting efficient lateral charge transport within the active layer is crucial for mitigating efficiency losses during the scaling-up of organic photovoltaics.

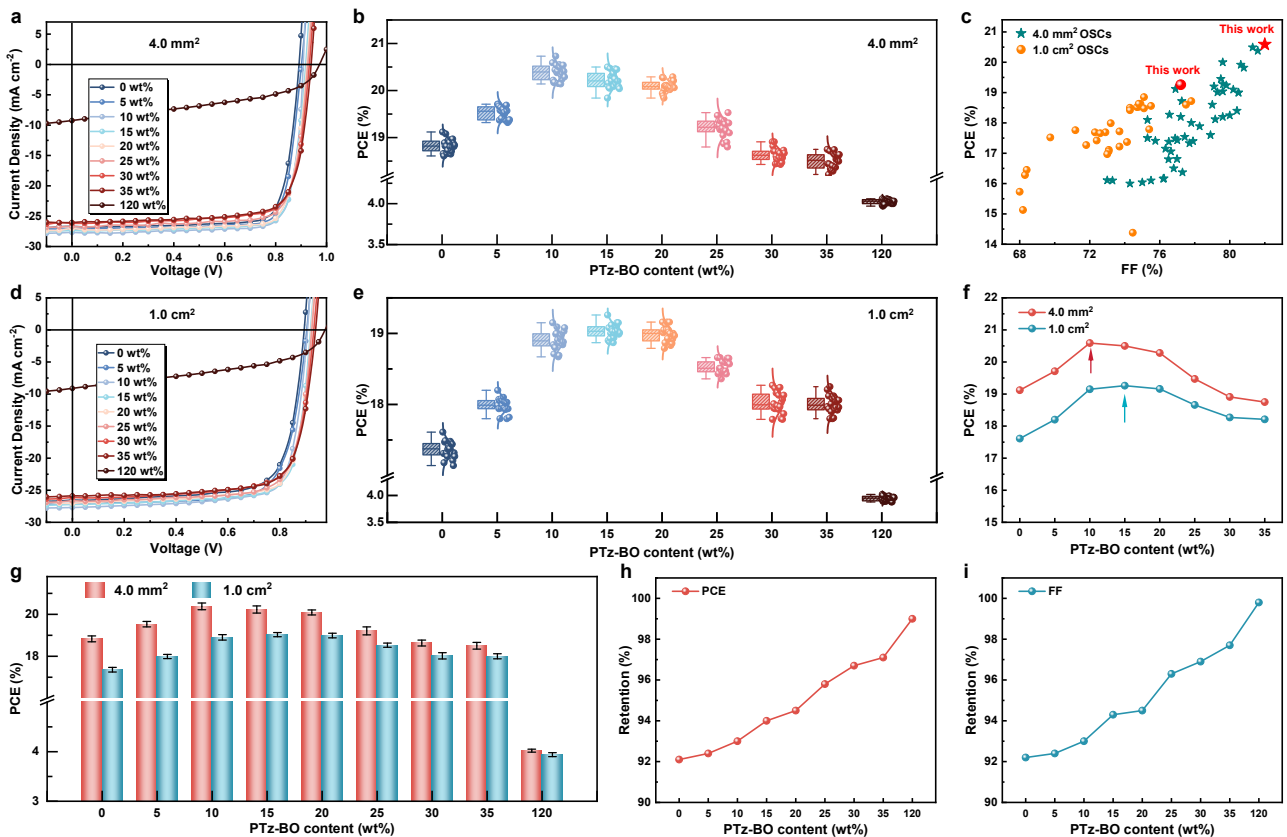
Ternary strategy and photovoltaic performance

To further boost the photovoltaic performance, we incorporated PTz-BO as a guest acceptor into the PM6:L8-BO-X host blend to optimize the molecular IP stacking. In terms of fundamental properties, PTz-BO exhibits an absorption peak at 832 nm, complementing the absorption spectra of PM6 and L8-BO-X well (Supplementary Fig. 10). Meanwhile, PTz-BO possesses a higher-lying lowest unoccupied molecular orbital (LUMO) level of -3.81 eV, compared to -3.99 eV for L8-BO-X, placing it intermediate between those of PM6 (-3.54 eV) and L8-BO-X (Supplementary Figs. 11 and 12). Such a cascade energy level alignment within the ternary blend is known to facilitate efficient exciton dissociation and charge transfer.^{28,29}

The small-area OSCs with an aperture area of 4.0 mm² were fabricated based on varied PM6:L8-BO-X:PTz-BO blends. The total weight of acceptors L8-BO-X and PTz-BO is always maintained at 120% of donor PM6, and the corresponding photovoltaic parameters are summarized in **Fig. 2a,b** and Table 1. As the PTz-BO content increases, the V_{oc} of ternary OSCs shows a continuous rise, whereas the J_{sc} first increases and then decreases, a trend that aligns closely with the variation in extinction coefficient of blend films (Supplementary Fig. 13). Consequently, the PCE reaches an optimum value of 20.59% at 10 wt% PTz-BO content, with a V_{oc} of 0.907 V, a J_{sc} of 27.68 mA cm⁻², and an FF of 82.0%. This efficiency was further certified as 20.16% by the National Institute of Metrology (NIM), China (Supplementary Fig. 14), ranking among the highest reported values to date for non-halogenated solvent-processed OSCs (Fig. 2c). External quantum efficiency (EQE) measurements (Supplementary Fig. 15) validate these results, as the integrated current densities from EQE spectra show excellent agreement with the J_{sc} values obtained from current density-voltage (J - V) characteristics. Meanwhile, remarkable PTz-BO content tolerance is observed, with ternary devices consistently achieving over 18.7% efficiency at PTz-BO loadings of 5~35 wt%. This indicates that the PM6:L8-BO-X:PTz-BO blends retain sufficient out-of-plane charge transport capability while enhancing in-plane transport, thereby laying the groundwork for the large-scale expansion of organic photovoltaics.

Similar performance enhancements are also observed in larger-area OSCs (1.0 cm²), with the highest-performing devices requiring a higher PTz-BO content of 15 wt% (Figs. 2d-f and Supplementary Table 10). Beyond improving V_{oc} s, the incorporation of PTz-BO significantly enhances the FFs in these devices, resulting in a record-breaking efficiency of 19.26%, markedly higher than that of PM6:L8-BO-X binary OSCs (Fig. 2d). Notably, the efficiency loss typically associated with device area upscaling progressively decreases from 7.9% to a negligible level as the PTz-BO content increases (Figs. 2g-i and Supplementary Fig. 16). Furthermore, across all enlarged devices, the PCE retention closely aligns with the FF retention (Fig. 2h,i). These results indicate that the ternary strategy effectively optimizes charge

1 OOP/IP transport and utilization to accommodate extended lateral transport distance while enhancing FF, representing a
 2 key strategy for achieving high-performance large-area OSCs.



3 **Fig. 2| Ternary strategy and photovoltaic performance.** **a,b,** $J-V$ characteristics (**a**) and efficiency-distributed histograms (**b**) of 4.0 mm²
 4 spin-coated devices based on PM6:L8-BO-X:PTz-BO blends with varied PTz-BO contents. The error bars represent the standard deviations
 5 ($n=20$). **c,** PCE comparison of OSCs processed with non-halogenated solvents. **d,e,** $J-V$ characteristics (**d**) and efficiency-distributed
 6 histograms (**e**) of 1.0 cm² spin-coated binary and ternary devices with different PTz-BO contents. **f,g,** PCE statistics of 1.0 cm² and 4.0 mm²
 7 devices with different PTz-BO contents. **h,i,** PCE (**h**) and FF (**i**) retention of devices upscaled from 4.0 mm² to 1.0 cm² with varied PTz-BO
 8 contents.
 9

10 Morphological and transport kinetics characterization

11 The self-assembly and stacking behavior of organic photovoltaic materials plays a critical role in the dissociation and
 12 directional transport of photogenerated charges within active-layer films. To probe the underlying film-formation kinetics,
 13 *in-situ* absorption spectroscopy measurements were conducted.³⁰⁻³² Time-dependent UV-vis absorption contour maps,
 14 corresponding 1D spectra, and acceptor peak position profiles for the binary and ternary blends are plotted in
 15 Supplementary Figs. 17-19. During solvent evaporation, the positional evolution of acceptor peak can be categorized into
 16 three distinct stages, corresponding to key physical transitions within the active layer: initial solvent removal in the wet-
 17 film state, solute precipitation following solution supersaturation, and the final stable dry-film state.^{31,33,34} Stage 2 (T2)
 18 is particularly significant, as it encompasses the primary processes of molecular aggregation and stacking. Analysis

reveals that the T2 duration for PM6:PTz-BO blend is markedly brief (0.6 s), considerably shorter than that of PM6:L8-BO-X blend (1.4 s). In high-boiling-point non-halogenated solvent systems, excessively slow solvent evaporation typically allows prolonged molecular aggregation, which always leads to oversized phase separation and degraded photovoltaic performance.^{25,35-39} Surprisingly, the introduction of PTz-BO into the ternary blends substantially accelerates the film-forming kinetics, reducing the T2 window to 0.7~1.1 s (Supplementary Fig. 19). This rapid film-forming process facilitates the suppression of excessive molecular aggregation, thereby optimizing charge separation and transport in OSCs.

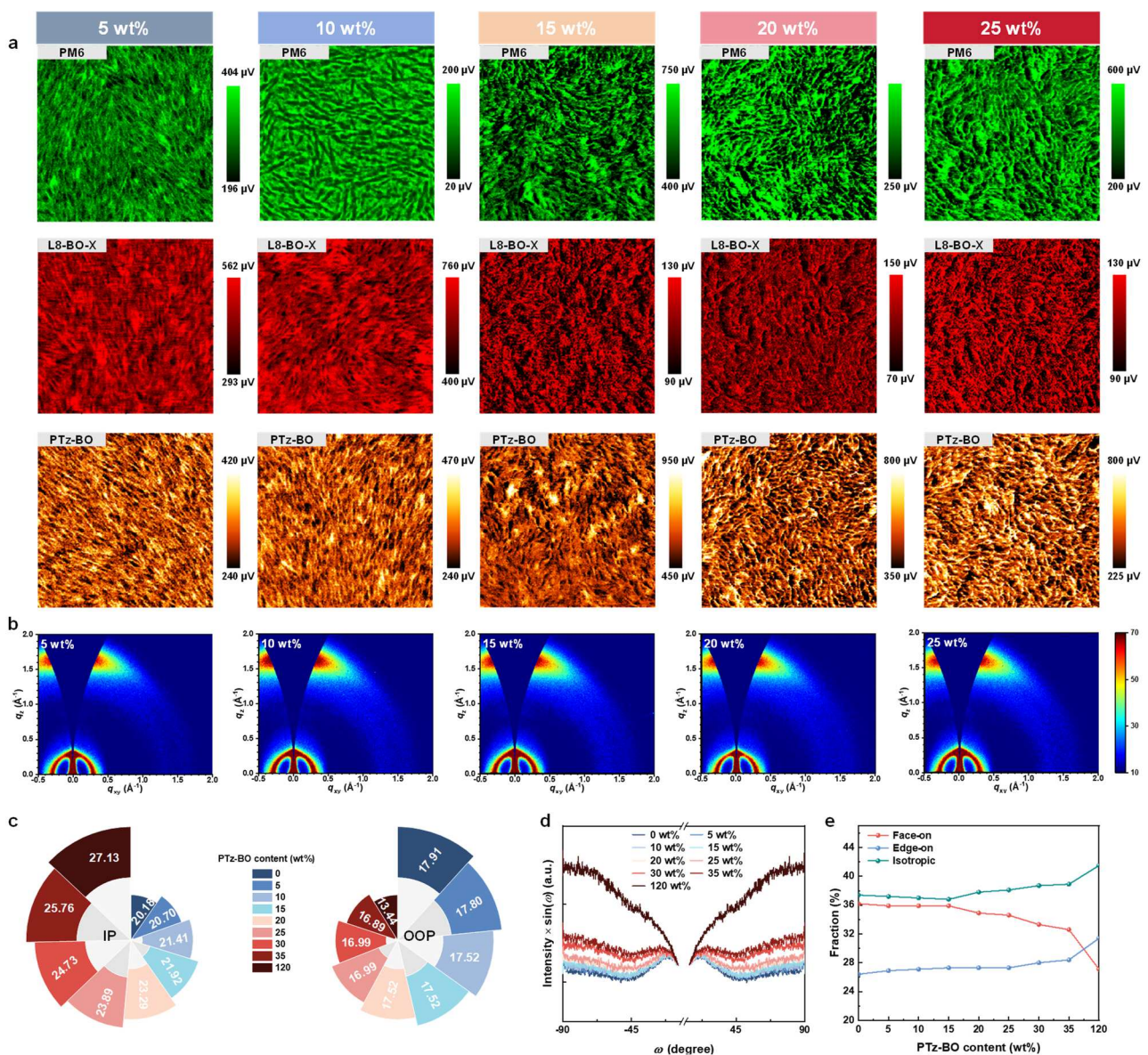


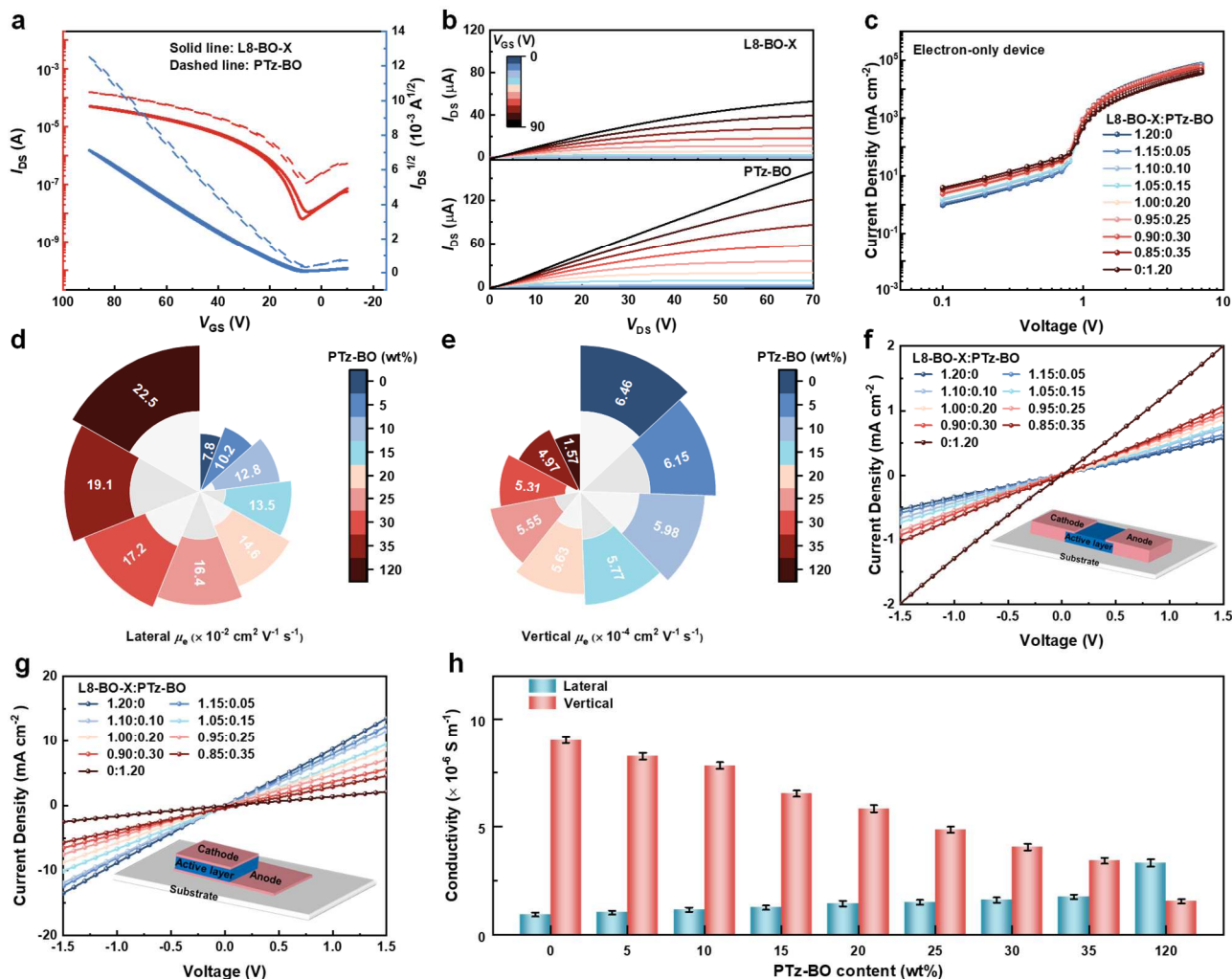
Fig. 3| Morphological characterization. **a,b**, PiFM images (**a**) and 2D GIWAXS patterns (**b**) of the ternary blends with varied PTz-BO contents. **c**, CCL statistics of the (010) peaks in the IP and OOP direction. **d**, Pole figure extracted from the (010) diffraction of 2D GIWAXS patterns. **e**, Comparison of molecular orientation fractions across binary and ternary blends with varied PTz-BO contents.

To investigate the influence of accelerated film-forming process on film morphology and molecular orientation, we conducted photo-induced force microscopy (PiFM), atomic force microscopy (AFM) and GIWAXS analyses. According

1 to the characteristic peaks identified by Fourier Transform Infrared (FT-IR) spectroscopy (Supplementary Fig. 20), all
2 blend films were imaged at specific infrared absorption wavenumbers: 1650 cm^{-1} for PM6 (green images), 1230 cm^{-1} for
3 L8-BO-X (red images) and 1580 cm^{-1} for PTz-BO (orange images). As shown in **Fig. 3a**, the ternary blends exhibit a
4 well-defined interpenetrating fibrillar network, a morphology conducive to efficient exciton dissociation and charge
5 transport.^{5,40} With increasing PTz-BO content, the fibrillar structures become more prominent and coarser, which is
6 quantitatively supported by the larger full width at half maximum values of fibril size distributions for PM6, L8-BO-X,
7 and PTz-BO phases (Supplementary Figs. 21-30). Moreover, AFM height images in Supplementary Fig. 31 corroborate
8 the PiFM observations, showing a progressive increase in root-mean-square (RMS) roughness from 1.05 nm to 1.56 nm
9 as PTz-BO content rises. This trend aligns with the enhanced perpendicular lamellar ordering observed in ternary films
10 (Supplementary Fig. 32).

11 GIWAXS measurements provide additional morphological information as detailed in Fig. 3b, Supplementary Fig.
12 32 and Supplementary Tables 7-9. All ternary blends exhibit a mixed face-on/edge-on molecular orientation. The distinct
13 diffraction peaks observed in both IP and OOP directions around $q_{xy} = 1.64 \text{ \AA}^{-1}$ originate from the combined (010)
14 diffraction signals of PM6, L8-BO-X and PTz-BO. As the PTz-BO content increases from 0% to 35%, the (010) peak in
15 IP direction associated with π - π stacking shows slightly tighter packing, with its CCL increasing markedly from 20.18 $\text{\AA}$
16 to 25.76 $\text{\AA}$ (Fig. 3c, Supplementary Fig. 33 and Supplementary Table 7). This structural evolution indicates that PTz-BO
17 incorporation effectively enhances in-plane molecular ordering of ternary blends, aligning with the improved FF and PCE
18 in large-area OSCs (Fig. 2d). Simultaneously, the (010) peak in the OOP direction and the (100) peak in the IP direction
19 jointly demonstrate a reduction in out-of-plane structural order, evidenced by increased d -spacings and decreased CCLs
20 (Fig. 3c, Supplementary Fig. 33, Supplementary Tables 8 and 9). It is important to note that the enhancement of edge-on
21 molecular orientation in ternary blends does not occur solely at the expense of face-on orientation, but is also facilitated
22 by the suppression of amorphous domains. As shown in Fig. 3d,e and Supplementary Fig. 34, the proportion of
23 amorphous domains in ternary blends is highly sensitive to PTz-BO content and decreases significantly when 5~15 wt%
24 PTz-BO is incorporated, which helps improve overall charge transport within the solar cells. In particular, with 10 wt%
25 PTz-BO, the face-on orientation fraction of ternary blend remains comparable to that of binary PM6:L8-BO-X film, while
26 the edge-on orientation fraction rises noticeably from 26.4% to 27.1%. This balanced improvement stems from the
27 effective suppression of isotropic molecular packing, which enables efficient bidirectional charge transport and
28 contributes to the record-high device efficiencies achieved in this work (Fig. 2c). In addition, more orderly molecular
29 packing also enhances the morphological stability of active layer films, extending the T_{80} lifetime (the time required for

1 PCE to decline to 80% of its initial value) under continuous sunlight exposure from 1450 h (0 wt%) to 2190 h (15 wt%),
 2 and thus facilitates commercial application (Supplementary Fig. 35).



3
 4 **Fig. 4| Charge transport properties.** a,b, Typical transfer (a) and output (b) characteristics of OFET devices based on neat L8-BO-X and
 5 PTz-BO films. c, J - V characteristics of electron-only devices based on L8-BO-X:PTz-BO blends with different ratios. d,e, lateral (d) and
 6 vertical (e) electron mobility statistics of devices based on L8-BO-X:PTz-BO blends with different ratios. f,g, J - V characteristics of the
 7 Ag/Acceptors/Ag-based devices for calculating lateral (f) and vertical (g) conductivities, respectively. The illustration shows the specific
 8 device structure used in the conductivity measurements. h, Lateral and vertical conductivity statistics of the varied acceptor blends. The error
 9 bars represent the standard deviations ($n = 5$).

10 In order to deeply study the effect of PTz-BO incorporation on charge transport, we evaluated the electron mobility
 11 (μ_e) using an organic field-effect transistor (OFET) structure and space-charge-limited current (SCLC) method,
 12 respectively (Figs. 4a-e).^{41,42} Field-effect mobilities from OFET measurements represent in-plane (lateral) charge
 13 transport along the film, while mobilities acquired via SCLC correspond to vertical carrier transport across the thin-film
 14 thickness. OFET device structure is illustrated in Supplementary Fig. 36, with corresponding transfer and output
 15 characteristics shown in Fig. 4a,b and Supplementary Figs. 37-39. The lateral electron mobility of neat L8-BO is

1 measured as $0.078 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, while that of neat PTz-BO reaches $0.225 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Supplementary Table 15). For the
2 blends of two acceptors, the lateral electron mobilities fall between those of the individual components and increase
3 progressively with higher PTz-BO content. In contrast, the vertical electron mobility of acceptor blends exhibits an
4 opposite trend, decreasing gradually from $6.46 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $1.57 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ as the PTz-BO content increases
5 (Fig. 4c and Supplementary Table 16). We further measured the lateral and vertical conductivities of acceptor blends
6 based on the Ag/Acceptors/Ag device structure. As anticipated, the lateral conductivity of L8-BO-X:PTz-BO blends
7 gradually increases from $9.30 \times 10^{-7} \text{ S m}^{-1}$ (L8-BO-X) to $3.32 \times 10^{-6} \text{ S m}^{-1}$ (PTz-BO) with rising PTz-BO content, while
8 the vertical conductivity decreases from $9.02 \times 10^{-6} \text{ S m}^{-1}$ to $1.54 \times 10^{-6} \text{ S m}^{-1}$ (Figs. 4f-h and Supplementary Table 17).
9 After blending with the donor PM6, a similar conductivity trend is observed in PM6:L8-BO-X:PTz-BO ternary blends
10 (Supplementary Fig. 40 and Supplementary Table 18), consistent with the GIWAXS findings. These results provide
11 compelling evidence for the feasibility of utilizing third-component materials to regulate molecular stacking orientation,
12 thereby fine-tuning the balance between vertical and lateral charge transport to accommodate extended lateral transport
13 distances.

14 We also used the SCLC measurements to determine vertical electron (μ_e) and hole mobilities (μ_h) of PM6:L8-BO-
15 X:PTz-BO-based devices. As shown in Supplementary Fig. 41 and Supplementary Table 19, the vertical μ_h decreases
16 gradually with increasing PTz-BO content, whereas the μ_e first increases and then decreases. When the PTz-BO content
17 reaches 10 wt%, the ternary blend exhibits the most balanced electron and hole transport ($\mu_h/\mu_e = 1.15$), which favours
18 reducing charge recombination caused by localized charge accumulation and is consistent with the highest FF and J_{sc}
19 among ternary OSCs (Table 1). The fluctuations of electron mobility can be explained by combining the vertical phase
20 distribution and molecular orientation within the ternary blends. Supplementary Figs. 42 and 43 collected the film-depth-
21 dependent light absorption spectroscopy (FLAS) and calculated donor/acceptor composition distribution profiles.⁴³⁻⁴⁷ For
22 the binary PM6:L8-BO-X blend, donor molecules are overly enriched near the cathode, which typically acts as a barrier
23 hindering the electron extraction by electrodes. The incorporation of PTz-BO induces a progressive L8-BO-X
24 accumulation at the film surface, while more PM6 is deposited near anode, facilitating the formation of more effective
25 charge transport pathways. The balance between optimized vertical phase distributions and gradually weakened
26 molecular out-of-plane orientations leads to a normal distribution in electron mobility (Supplementary Table 19).

27 The exciton generation contours of blend films were calculated via numerical simulations using the optical transfer
28 matrix method from the FLAS profiles (Supplementary Figs. 44 and 45). The ternary blends exhibit a faster exciton
29 generation and a broader exciton generation contours than PM6:L8-BO-X-based film, with this effect being particularly

pronounced at 10 wt% and 15 wt% PTz-BO additions. Furthermore, the exciton generation centers in these two ternary films are located closer to the middle of the active layer, specifically at depths of 56.4 nm and 50.4 nm, respectively. This positioning shortens the travel distance for separated charges before collection by their respective electrodes, thereby significantly reducing the risk of charge recombination and leading to the highest FF and J_{sc} values in the resulting devices (Table 1). Notably, although the PM6:PTz-BO film shows faster exciton generation than PM6:L8-BO-X, its J_{sc} is considerably lower, which is mainly due to severe bimolecular recombination ($\alpha = 0.89$) and trap-assisted recombination ($\beta = 1.77$; Supplementary Fig. 46a,b). Here, α and β represent exponential factors for the power-law relationships between J_{sc} and P_{light} ($J_{sc} \propto (P_{light})^\alpha$), and between V_{oc} and $\ln(P_{light})$ ($V_{oc} \propto \ln(P_{light})^\beta$), respectively, where P_{light} represents light intensity.^{33,48,49} Deviation of $\alpha(\beta)$ from the unit slope 1(kT/q) indicates the degree of recombination. The markedly increased α values and reduced β values observed in ternary devices reflect the effective suppression of charge recombination. Another key factor contributing to the poor photovoltaic performance of PM6:PTz-BO-based OSCs is its limited charge dissociation probability ($P(E,T)$).⁵⁰ As shown in Supplementary Fig. 46c, the photocurrent failing to saturate even at an effective voltage of 2.5 V, which can likely be attributed to its unfavorable phase-separated morphology. In contrast, the $P(E,T)$ increases from 98.3% for PM6:L8-BO-X device to 99.1% for ternary OSCs containing 10 wt% PTz-BO, correlating with the record-breaking efficiency.

Large-scale modules

To further investigate the optimal balance between lateral (IP molecular packing) and vertical (OOP molecular packing) charge transport in larger active layers, we fabricated rigid OSC modules with scaled areas of 12.0 cm², 24.0 cm², 45.6 cm² and 101.9 cm² (Supplementary Fig. 47). All fully optimized modules adopt a traditional device architecture of ITO/2PACz/Active Layer/C₆₀/BCP/Ag. For these four module sizes, the corresponding sub-cell widths are 4.0, 5.0, 6.0, and 6.5 mm, with sub-cell counts of 12, 15, 16, and 28, respectively. As the active area increases, both the number and the width of the sub-cells are progressively scaled up. This structural scaling implies higher series resistance and more pronounced challenges in lateral charge transport for larger modules. Notably, enhanced lateral transport offers an additional advantage in large-area OSC modules: the "L-shaped" electrode design enables efficient collection of photogenerated charges not only through vertical transport but also via direct lateral extraction at the side interface of Ag electrode and active layer (Fig. 5a and Supplementary Fig. 48). This improved charge collection is preliminarily supported by the higher FF observed in simplified test structures (74.2% vs. 73.8%; Supplementary Table 20).

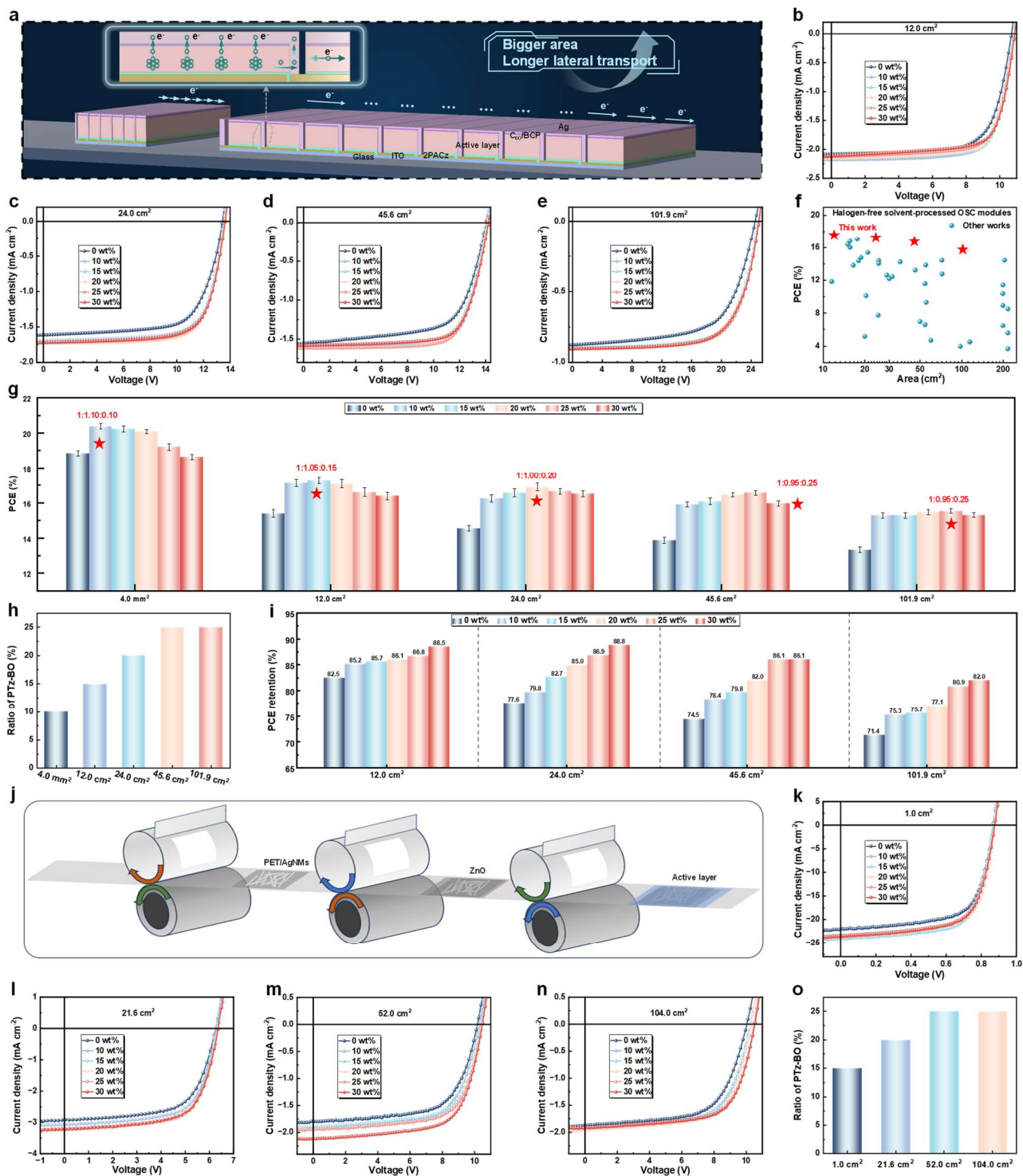


Fig. 5 | Large-scale organic modules. **a**, Schematic illustration of rigid OSC module structure and charge transport pathways. **b-e**, $J-V$ characteristics of the rigid modules of 12.0 cm² (**b**), 24.0 cm² (**c**), 45.6 cm² (**d**) and 101.9 cm² (**e**). **f**, PCE comparison of OSC modules. **g**, PCE statistics for OSCs with varying PTz-BO contents across different areas in rigid devices. **h**, Optimal PTz-BO content for champion efficiency across different areas in rigid devices. **i**, PCE retention statistics for rigid OSCs with varying PTz-BO contents across different areas. **j**, Schematic diagram of R2R gravure printing. **k-n**, $J-V$ characteristics of the R2R printed flexible OSCs with active area of 1.0 cm² (**k**), 21.6 cm² (**l**), 52.0 cm² (**m**) and 104.0 cm² (**n**). **o**, Optimal PTz-BO content for champion efficiency across different areas in R2R printed flexible devices.

1 The J - V characteristics and efficiency distribution statistics of modules are summarized in Fig. 5b-e and
 2 Supplementary Fig. 49. Champion PCEs of 17.56%, 17.24%, 16.77%, and 15.76% are obtained for devices with aperture
 3 areas of 12.0 cm², 24.0 cm², 45.6 cm², and 101.9 cm², at PTz-BO contents of 15 wt%, 20 wt%, 25 wt%, and 25 wt%,
 4 respectively (Supplementary Tables 21-24). These efficiencies significantly outperform those of binary PM6:L8-BO-X
 5 devices and represent one of the highest reported values for modules of corresponding sizes (Fig. 5f). As shown in Fig.
 6 5g,h and Supplementary Fig. 50, scaling the OSC area from 4.0 mm² to 45.6 cm² consistently requires higher PTz-BO
 7 content, which mirrors the growing requirement for in-plane molecular packing (Fig. 3c) and enhanced lateral charge
 8 transport (Fig. 4d). Specifically, the 12.0 cm² module achieves the highest PCE of 17.56% with 15 wt% PTz-BO,
 9 exhibiting a V_{oc} of 10.862 V, a J_{sc} of 2.16 mA cm⁻², and an FF of 74.9%, while the 24.0 cm² module delivers a champion
 10 PCE of 17.24% with 20 wt% PTz-BO, showing a V_{oc} of 13.572 V, a J_{sc} of 1.73 mA cm⁻², and an FF of 73.5%. The 45.6
 11 cm² module with an increased sub-cell width of 6 mm reaches its peak PCE of 16.77% at 25 wt% PTz-BO (V_{oc} = 14.205
 12 V, J_{sc} = 1.62 mA cm⁻², and FF = 73.0%.), while the 101.9 cm² module (6.5 mm sub-cell width) also attains its best
 13 performance at 25 wt% PTz-BO with a champion efficiency of 15.76%. Notably, this strategy proves particularly
 14 effective for larger-area devices, as both efficiencies (16.77% and 15.76%) represent record values to date for their
 15 respective area scales. Overall, OSC devices with different active areas follow a consistent trend: as the PTz-BO content
 16 rises, the retention of both FF and PCE after area upscaling steadily improves (Fig. 5i and Supplementary Fig. 51), even
 17 though the overall device performance starts to decline at high PTz-BO concentrations due to compromised out-of-plane
 18 transport.

19 In addition, we fabricated flexible OSC devices and modules via roll-to-roll (R2R) gravure printing, with active
 20 areas ranging from 1.0 cm² to 21.6, 52.0, and 104 cm². These devices adopt an inverted architecture of
 21 PET/AgNWs/ZnO/Active Layer/MoO₃/Al (Fig. 5j). As shown in Supplementary Fig. 52, with the increase in active area,
 22 not only does the number of sub-cells rise from eight to thirteen, but the width of each sub-cell also expands gradually.
 23 When the PTz-BO content is 15 wt%, 20 wt%, 25 wt%, and 25 wt%, respectively, the champion PCEs of flexible OSCs
 24 with active areas of 1.0 cm², 21.6 cm², 52.0 cm², and 104.0 cm² reach 14.20%, 13.72%, 13.68%, and 13.54%, respectively
 25 (Figs. 5k-n, Supplementary Fig. 53 and Supplementary Tables 25-28). These results further confirm that larger active
 26 areas demand enhanced in-plane molecular stacking and lateral charge transport, which are enabled by higher PTz-BO
 27 loadings. These findings underscores the critical importance of enhancing in-plane molecular stacking in balancing IP
 28 and OOP charge transport for high-performance organic modules, providing a strategic molecular-design guideline for
 29 photovoltaic materials tailored to large-scale applications.

Conclusion

In summary, we establish enhanced in-plane molecular packing as a key design criterion to overcome the lateral charge-transport bottleneck that limits the scale-up of organic solar cells. By incorporating PTz-BO, a material with a strong IP π - π stacking propensity, into PM6:L8-BO-X blend, we systematically manipulate molecular orientation to rebalance lateral and vertical charge transport. This structural regulation effectively mitigates FF losses upon device upscaling, demonstrating that tailoring IP packing directly addresses the increasingly stringent lateral transport demands as active areas expand. The successful application of donor L2, another IP-stacking material, further demonstrates the generality of this approach. Notably, this strategy yields superior efficiencies consistently across all scales, from millimetre-scale devices to hundred-square-centimetre modules, establishing top-tier performance for non-halogenated solvent-processed organic photovoltaics. Collectively, our findings suggest that active-layer molecular design should move beyond the conventional out-of-plane perspective and fully incorporate the in-plane dimension, offering a new route for efficient upscaling of organic photovoltaics.

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Methods

Materials

PM6, D18, L8-BO and L8-BO-X were purchased from Solarmer Materials Inc. PTz-BO and L2 were synthesized in our group according to the reported literature^{27,51}. CF and *o*-XY were purchased from Energy Chemical. 1,4-Diiodobenzene (DIB) was purchased from J&K. Acetic acid was purchased from Macklin. Hole-transport material 2-(9H-Carbazol-9-yl)ethylphosphonic acid was purchased from Shanghai Haohong Scientific Co., Ltd (Cat No. 1444462, Leyan, Shanghai, China). The silver for electrodes was purchased from ZhongNuo Advanced Material (Beijing) Technology Co., Ltd. The ITO electrodes were purchased from Advanced Election Technology Co., Ltd. All purchased materials were used without further purification.

Device fabrication and characterization

Preparation of rigid OSCs: Rigid OSCs were fabricated using a conventional device structure of ITO/2PACz/active layer/PNDIT-F3N/Ag. ITO-coated substrates were first cleaned sequentially with detergent, deionized water, acetone,

1 and isopropanol in an ultrasonic bath, each for 20 minutes. After cleaning, the substrates were dried overnight in an
2 oven at 100°C. Before used, they were further treated with plasma cleaning for 2 min under vacuum below 100 Pa. A
3 layer of 2PACz was spin-coated onto the ITO surface at 3000 rpm for 30 s and then thermally annealed at 100 °C for
4 10 min in a N₂-filled glove box. Then the active layers with different contents of PTz-BO were spin-cast on the 2PACz
5 surface in a N₂-filled glove box at 2800 rpm for 40 s with the PM6 concentration of 12 mg mL⁻¹ in *o*-XY and with DIB
6 (150 wt%) added as additives. The weight ratio of the donor and acceptor was kept at 1:1.2. Then, the active layers were
7 thermally annealed at 100 °C for 10 min. Next, a methanol-based solution of PNDIT-F3N (1.2 mg mL⁻¹, with 0.5 vol%
8 acetic acid) was spin-coated at 4200 rpm for 30 s as the electron-transport layer. Finally, a 140 nm-thick silver layer
9 was thermally deposited under a vacuum condition of 3×10⁻⁴ Pa. The active areas of the small-area and large-area rigid
10 devices are 5.1 mm² and 1.1 cm², respectively. The performance of all OSCs was characterized under standard AM1.5G
11 illumination (100 mW cm⁻²), provided by an Enlitech SS-F5-3A solar simulator and calibrated with a reference silicon
12 cell (Enlitech SRC2020). *J-V* measurements were conducted using a Keithley 2400 Source Meter. EQE spectra were
13 acquired with an Enlitech QE-R3011 system. For devices with active areas of 5.1 mm² and 1.1 cm², measurement masks
14 with aperture areas of 4.0 mm² and 1.0 cm² were employed, respectively.

15 **Preparation of rigid modules:** Rigid modules were fabricated with a conventional architecture of
16 glass/ITO/HTL/active layer/C₆₀/BCP/Ag. P1 line was first laser-patterned on ITO substrates using a laser at 0.375 W
17 for large-area modules. Substrates were sequentially cleaned in an ultrasonic bath using detergent, deionized water,
18 acetone, and isopropanol (20 minutes each), followed by drying in an oven at 100°C overnight. Before film deposition,
19 a 30-minute UV-ozone treatment was applied to improve substrate wettability. The HTL (2PACz at 0.5 mg ml⁻¹ in
20 methanol) was blade-coated in glovebox at 10 mm s⁻¹ with a gap of 200 μm, followed by thermal annealing at 65 °C for
21 5 minutes. The active layer solution was prepared with PM6:L8-BO-X:PTz-BO, with DIB (150 wt%) added as additives.
22 The precursor solution was stirred at 60°C for 30 minutes before blade-coating onto the HTL-coated substrates in
23 glovebox at 50 mm s⁻¹ with a 250 μm blade gap. The films were thermally annealed at 100 °C for 10 minutes in ambient
24 and subsequently transferred to a vacuum thermal evaporator for cathode deposition. Then, C₆₀ (1 nm, 0.1 Å s⁻¹), BCP
25 (5 nm, 0.1 Å s⁻¹), and Ag (50 nm, 1 Å s⁻¹) were sequentially deposited. Then P2 lines were patterned next to P1 using the
26 same laser parameters (0.375 W). After the second layer of 50 nm Ag was thermally evaporated over the scribed P2
27 region, P3 lines were scribed beside P2 to complete the cell interconnections. Four modules with aperture areas of 12.0,
28 24.0, 45.6, and 101.9 cm² were fabricated, comprising 12, 15, 16, and 28 subcells, respectively, with corresponding

subcell widths of 4.0, 5.0, 6.0, and 6.5 mm. The geometric fill factors (GFF) were 97.5%, 98.0%, 98.3%, and 98.5% for the four modules, respectively, increasing with aperture area.

Preparation of flexible OSCs and modules: The AgNW ink with a concentration of 5 mg mL⁻¹ was prepared by blending water-dispersed and IPA-dispersed AgNW inks in a mixed solvent (IPA:H₂O = 7:3, v/v). This ink was then gravure-printed onto PET substrates using a lab-scale printer (D&R Lab Gravure Printer G-1100S; Suzhou D&R Instrum Co., Ltd.) at a speed of 50 m min⁻¹. The gravure roller had a cavity volume of 13 mL m⁻² and a line density of 50 lines cm⁻¹. After printing, the AgNW electrodes were annealed at 120 °C for 10 min. For the ZnO:PVP composite ink, ZnO nanoparticles were first dispersed separately in butanol and ethanol, then mixed to form composite solvent-based inks. These were subsequently blended with an ethanolic PVP solution (10 mg mL⁻¹) to obtain ZnO:PVP inks. To fabricate PET/AgNWs/ZnO:PVP films, the printed AgNW electrode was first treated with oxygen plasma for 2 min. The ZnO:PVP ink was then printed over it using the same gravure printer and parameters as above, followed by annealing at 120 °C for 10 min. The active layers were prepared following the same procedure as that for the rigid devices. The solution was stirred at 80 °C overnight and then cooled to room temperature prior to printing. Using the same strip pattern, the AgNWs, ZnO:PVP, and active layer were sequentially deposited via gravure printing. The printed wet film was then transferred to an oven and annealed at 100 °C for 10 min. Finally, a MoO₃ layer (10 nm) and an Al layer (200 nm) were deposited on the active layer under a vacuum of 3×10⁻⁴ Pa. The module's series interconnection was defined through three patterning steps: the P1 line (width: 1.5 mm) was formed by patterned printing, while the P2 and P3 lines (widths: 1.5 mm and 0.5 mm, respectively) were deposited via vacuum evaporation. Three modules with active areas of 21.6, 52.0, and 104.0 cm² were fabricated, comprising 8, 13, and 13 subcells with widths of 5.0, 6.0, and 7.5 mm, respectively. All measurements were performed without shadow masks.

Ultraviolet-visible (UV-vis) spectroscopy measurements

The UV-vis absorption spectra of pristine and blend films were characterized using a Shimadzu UV-3700 spectrophotometer.

Space-charge-limited current (SCLC) measurements

The vertical charge transport properties of both pristine and blend films were investigated using the space-charge-limited current (SCLC) method. Hole-only and electron-only devices were fabricated with the respective architectures of ITO/PEDOT:PSS/Active Layer/MoO₃/Ag and ITO/ZnO/Active Layer/PNDIT-F3N/Ag. The vertical charge carrier mobility was obtained by fitting the corresponding J - V characteristics using the equation of $J=9\epsilon_0\epsilon_r\mu V^2/8L^3$, where J is the current density, ϵ_0 is the vacuum permittivity, ϵ_r is the relative permittivity of the active layer, μ is the hole or electron

carrier mobility, V is the effective voltage ($V=V_{\text{appl}}-V_{\text{bi}}$, where V_{appl} is the applied voltage, V_{bi} is the built-in potential) and L is the film thickness of the pristine film or blend film.

Photo-induced force microscope (PiFM)

A VistaScope microscope (Molecular Vista Inc.) was coupled to a quantum cascade laser (LaserTune QCL, Block Engineering) with a wavenumber resolution of 0.5 cm^{-1} and a tuning range of $800\text{--}1800\text{ cm}^{-1}$. All measurements were performed in the dynamic mode using NCH-Au 300 kHz non-contact cantilevers (Nanosensors).

***In-situ* absorption measurements**

The *in-situ* absorption measurements were performed using a DU-200 spectrophotometer (Shaanxi Puguang Weishi, Co. Ltd), which offers a detection range of $186\text{ to }1026\text{ nm}$ with spectral and temporal resolutions of 0.01 nm and 1 ms , respectively.

Atomic force microscopy (AFM)

AFM measurements were carried out on a Bruker Dimension Icon system operated in tapping mode.

Grazing-incidence wide-angle X-ray scattering (GIWAXS)

GIWAXS characterization was performed on a GANESHA 300XL+ system from JJ X-ray equipped with a Genix 3D Microfocus sealed tube Cu X-ray source with an integrated monochromator (30 W , $\lambda=1.5418\text{ \AA}$). Samples were vertically positioned on the goniometer with the incident beam set at a grazing angle of 0.2° .

Film-depth-dependent light absorption spectroscopy (FLAS)

FLAS characterization was acquired using an *in-situ* spectrometer (PU100, Shaanxi Puguang Weishi Co. Ltd.). The system was equipped with a soft plasma-ion source operating at 100 W and an oxygen pressure of $\sim 10\text{ Pa}$. The film surface was progressively etched by this gentle ion source avoiding damage to the sublayers, while the process was *in-situ* monitored by the spectrometer. By tracking the spectral evolution and applying the Beer-Lambert law, depth-resolved absorption profiles were extracted. Finally, the exciton generation profile was numerically simulated by feeding these sublayer absorption spectra into a modified optical transfer-matrix model.

Data availability

Source data are provided with this paper. The remaining data are available from the corresponding authors upon reasonable request.

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7 **Author contributions**

8 J. Z., X. D. and Y. S. conceived the idea. X. L. and J. L. synthesized PTz-BO and L2, respectively. J. Z., X. D., J. D. and
9 Z. Z. were involved in rigid device fabrication and characterization. J. S. was responsible for the certification. S. L., X.
10 P., and S. C. fabricated the rigid modules. W. X. and Q. L. prepared the flexible OSCs. X. W. and R. Y. conducted the
11 GIWAXS characterizations and subsequent data analysis. H. X. and G. L. conducted FLAS measurement and analysed
12 the corresponding data. X. D., S. C. and Y. S. supervised and directed this project. J. Z., X. D., S.C. and Y. S. wrote the
13 manuscript. All authors discussed the results and commented on the manuscript.

14 **Competing interests**

15 The authors declare no competing interests.
16
17
18

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