

Electronic Supplementary Information (ESI)

The alloy donor strategy leverages both complementary polymer donors to enable highly efficient and stable ternary organic solar cells

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1. Materials

The donor PBDTTS-2FQx with \bar{M}_w of ~1.4 kDa was synthesized according to the literature.¹ The donor J71 and acceptor IT-4F were purchased from Bide Pharmatech.

All solvents and other materials were purchased commercially and used as received without further purification.

2. Fabrication of organic solar cells

Organic solar cells were fabricated in a conventional device configuration of ITO/PEDOT:PSS(40 nm)/J71:PBDTTS-2FQx:IT-4F/PDIN(5 nm)/Ag(100 nm). The ITO substrates were first scrubbed by detergent and then ultrasonically cleaned with deionized water, acetone and isopropanol subsequently, and dried overnight in an oven. The cleaned ITO substrates were treated by UV-Ozone for 30 min before use. PEDOT:PSS (Clevios P VP AI 4083 from Heraeus) was spin-cast onto the ITO substrates at 4000 rpm for 30 s, and then dried at 150 °C for 15 min in air. The donor: acceptor blends (1.0:1.0 weight ratio) were dissolved in chloroform (the total concentration of blend solutions was 20 mg mL⁻¹), the mixture was stirred on a 50°C stirring heating table for 60 min at room temperature for 6 h in a nitrogen-filled glove box. The blend solution was spin-cast at 2500 rpm for 30 s. A thin PDIN layer was coated on the active layer, followed by the deposition of Ag (100 nm) (evaporated under 5×10⁻⁵ Pa through a shadow mask). The optimal active layer thickness measured by a Bruker Dektak XT stylus profilometer was about 105 nm. The current density-voltage (*J-V*) curves of all encapsulated devices were measured using a Keithley 2400 Source Meter in air under AM 1.5G (100 mW cm⁻²) using a Newport solar simulator. The light

intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement to bring spectral mismatch to unity). An optical microscope (Olympus BX51) was used to define the device area (6.0 mm²). EQEs were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300 W lamp source.

3. Instruments and measurements

UV-vis absorption spectra of polymer films were recorded on a Cary60 UV-Vis spectrophotometer. The external quantum efficiency (EQE) spectra of solar cells were recorded by a QE-R3011 measurement system (Enli Technology, Inc.). The electron and hole mobilities were measured by using the method of space-charge limited current (SCLC) for electron-only devices with the structure of ITO/ZnO/active layer/PNDIT-F3N/Ag and hole-only devices with the structure of ITO/PEDOT:PSS/active layer/MoO₃/Ag. The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the equation: $J = 9\epsilon_0\epsilon_r\mu V^2/8d^3$, where J is the current density, d is the film thickness of the active layer, μ is the charge carrier mobility, ϵ_r is the relative dielectric constant of the transport medium, and ϵ_0 is the permittivity of free space. $V = V_{\text{app}} - V_{\text{bi}}$, where V_{app} is the applied voltage, V_{bi} is the offset voltage. The carrier mobility was calculated from the slope of the $J^{1/2} \sim V$ curves. AFM measurements were obtained by using a Dimension Icon AFM (Bruker) in a tapping mode (2 × 2 μm²). The photoluminescence quenching effects of four devices (PBDTTS-2FQx, PBDTTS-2FQx:IT-4F, J71:IT-4F, and J71:PBDTTS-2FQx:IT-4F)

were tested at 620 nm and 740 nm using an Edinburgh FLS1000 steady-state/transient fluorescence spectrometer.

The carrier lifetime of organic solar cells was measured using the TPV module in Paios, an all-in-one characterization platform developed by Fluxim AG (Switzerland), with the device maintained in an open-circuit state. Under constant bias illumination, a light pulse was applied, and the voltage response was recorded and analyzed for decay. Similarly, the TPC module in Paios was employed to assess the charge extraction speed within the device by applying a light pulse and monitoring the resulting current response for decay. The data were fitted using the following exponential decay equation:

$$y = a \times e^{(-x/\tau)} + C$$

where a represents the constant corresponding to the peak height, x is time, and τ corresponds to the charge extraction time (TPC) or the carrier lifetime (TPV).

2D-GIWAXS experiments were carried out on Xenocs 3.0 SAXS/WAXS laboratory beamline. The instrument was equipped with a Pilatus 300K detector. The X-ray source is a Genix 3D Microfocus Sealed Tube X-Ray Cu-source with integrated Monochromator (30 W). The wavelength is $\lambda = 1.54189 \text{ \AA}$. The film samples on the Si substrate were prepared under the same conditions as those used for device fabrication. The accumulation time was 30 minutes for each measurement. In-plane and out-of-plane line cuts were obtained using SAXSGUI program. GIWAXS characterizes the molecular packing and crystallinity of the organic active layer. The d-spacing

associated with the stacking peak indicates the molecular interlayer spacing, which can be calculated from the following equation:

$$d = \frac{2\pi}{q_z}$$

q_z is the position of the stacking peak in Q space. We further calculated the crystalline coherence length (CCL) using the Scherrer equation and quantitatively compared the crystallinity of the organic films:

$$CCL = \frac{2\pi k}{FWHM}$$

k is the shape factor (0.9) and FWHM is the full width at half maximum of the stacking peak.

The contact angles of J71, IT-4F, PBDTTS-2FQx, and J71:IT-4F blend films prepared with H₂O and CH₂I₂ were measured using a JC2000D1 contact angle goniometer. Their surface energies were calculated using the Owens-Wendt (OW) two-liquid method²:

$$\gamma_L(1 + \cos \theta) = 2(\sqrt{\gamma_L^D \times \gamma_S^D} + \sqrt{\gamma_L^P \times \gamma_S^P})$$

$$\gamma_S = \gamma_S^D + \gamma_S^P$$

where γ_L is the surface tension of a single liquid, θ is the measured contact angle of the liquid on the solid surface, γ_L^D is the dispersive component of the liquid surface tension, γ_L^P is the polar component of the liquid surface tension, γ_S^D is the dispersion component of solid surface tension (to be calculated); γ_S^P is the polar component of solid surface tension (to be calculated). The total surface tension, dispersion component and polar component of the two probe liquids were adopted as constant values. For water, γ_L , γ_L^D and γ_L^P are 72.8, 21.8 and 51.0 mN·m⁻¹, respectively. For diiodomethane, the corresponding values are 50.8, 50.8 and 0 mN·m⁻¹, respectively.

4. Changes in the device's PCE, V_{OC} , J_{SC} , and FF with increasing PBDTTS-2FQx content.

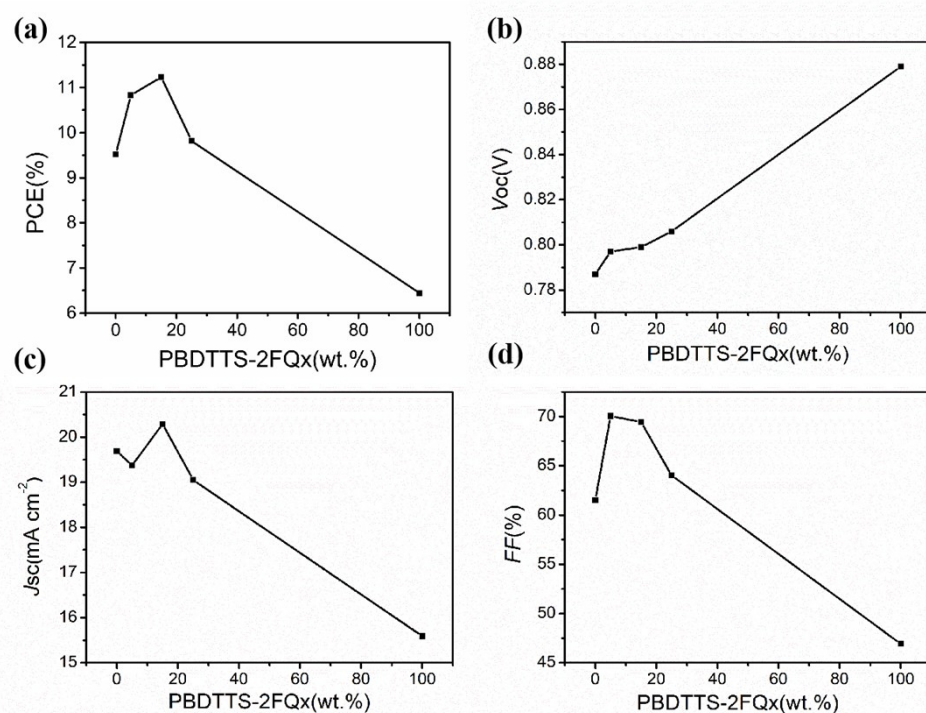


Fig. S1 Changes in the device's PCE, V_{OC} , J_{SC} , and FF with increasing PBDTTS-2FQx content.

5. TPV and TPC curves of optimized binary and ternary devices

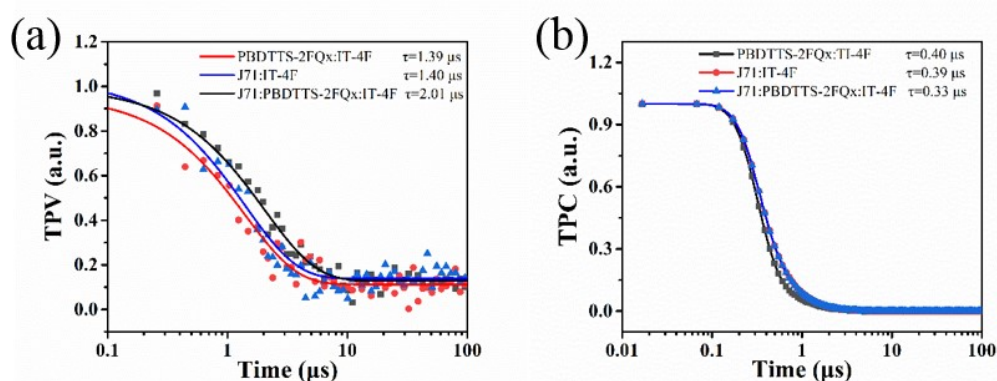


Fig.S2 (a) TPV and (b) TPC curves of optimized binary and ternary devices

6. IP and OOP extracted line-cut profiles of the corresponding blend films

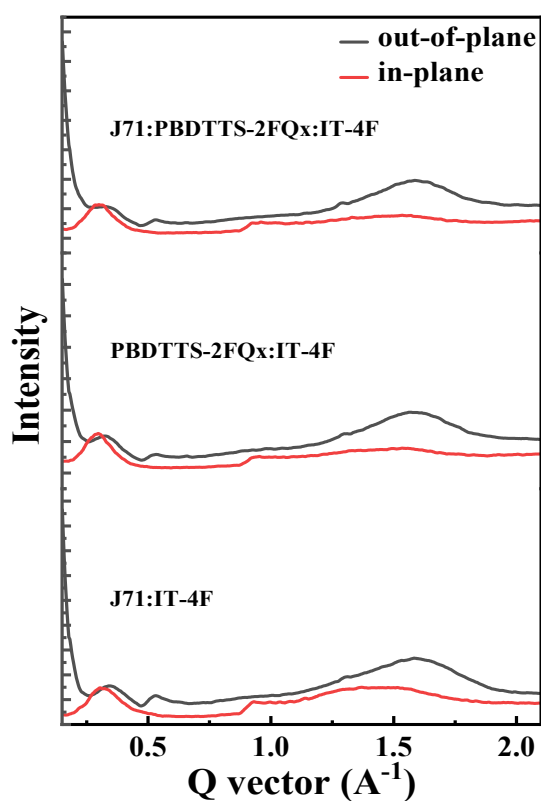


Fig.S3 1D line-cuts of the corresponding blend films along the in-plane (IP) and out-of-plane (OOP) directions

7. Contact angles and calculated surface energy parameters of the prepared films

Table S1. Contact angles and calculated surface energy parameters of the prepared films³

Active layer materials	$\theta_{\text{Water}} (^{\circ})$	$\theta_{\text{diiodomethane}} (^{\circ})$	$\gamma_s (\text{mN m}^{-1})$
J71	94.6	48.7	35.68
IT-4F	81.6	43.6	41.27
PBDTTS-2FQx	92.8	47.8	36.41
J71:IT-4F	90.0	45.4	37.82

References

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