Supporting Information

Extension on the Conjugated Framework of Non-fullerene Electron Acceptors

toward Highly Efficient Organic Photovoltaics

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Supplemental Experimental Procedures

Materials

D18 and PDINN and IC-Br were purchased from Solarmer Materials (Beijing) Inc. (China). Other reagents and solvents were purchased from commercial sources and used as received. Poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS, Clevios AI 4083) was purchased from Heraeus (Germany). Pre-patterned high-transmittance ITO-glass substrates (resistance ~12 Ω sq⁻¹, maximum transmittance ~94% at ~550 nm, size of 20 × 15 × 0.7 mm³) were purchased from You Xuan Ltd. (China). The synthesis and characterization details of BTP-4F-C5-16 (C5-16) can be found in our previous work.⁴ The synthesis and characterization details of B6F and C5Qx-B6F can be found below.

Synthesis of B6F and C5Qx-B6F



Compound 1. The Suzuki-Miyaura polymerization is used to prepare conjugated extended end groups ¹⁻³. A mixture of IC-Br (100 mg, 0.37 mmol), Pd(dppf)Cl₂ (14 mg, 0.019 mmol), CsCO₃ (597 mg, 1.84 mmol), 3,4,5-Trifluorophenylboronic acid (651 mg, 3.7 mmol) in DMSO (20 ml) and H₂O (5 ml) was reacted for 12 hours under Argon at 110 °C. After the reaction, the mixture was cooled to room temperature and then extracted with dichloromethane. The organic layer was washed with brine and dried over MgSO₄. After filtration, the crude product was purified by flash column chromatography with dichloromethane as the eluents to afford the final product as red solid (62 mg).



Synthesis of compound B6F: The synthesis route of compound 2 can be found our previous work ⁴. Under argon, compound 2 (141 mg, 0.13 mmol), compound 1 (169 mg, 0.52 mmol) and pyridine (0.5 mL) were dissolved in 30 mL chloroform, and stirred overnight at 65 °C. After cooling to room temperature, the solvent was removed and the mixture was poured into methanol and filtered. The residue was purified by silica gel column chromatography using petroleum ether/dichloromethane (1:1, ν/ν) as eluent to get a blue-black solid (167 mg, 76%). ¹H NMR (500 MHz, CDCl₃) δ 9.15, 8.74, 8.73, 8.05, 7.87, 7.87, 7.85, 7.85, 7.35, 7.34, 7.32, 7.26, 4.82, 4.81, 3.23, 3.21, 3.19, 2.23, 2.22, 2.20, 2.19, 2.18, 1.92, 1.91, 1.89, 1.87, 1.86, 1.55, 1.54, 1.51, 1.50, 1.49, 1.44, 1.43, 1.42, 1.40, 1.29, 1.26, 1.07, 1.06, 1.04, 1.02, 1.01, 1.00, 0.99, 0.96, 0.94, 0.93, 0.89, 0.88, 0.86, 0.76, 0.75, 0.73, 0.71, 0.70, 0.68. ¹³C NMR (126 MHz, CDCl₃) δ 187.85, 159.93, 153.41, 150.80, 147.41, 145.10, 143.73, 139.65, 137.86, 137.77, 135.77, 135.25, 134.01, 133.50, 132.96, 130.54, 125.91, 121.24, 120.77, 115.29, 114.92, 113.59, 111.58, 111.53, 111.44, 111.40, 77.26, 77.01, 76.75, 68.36, 55.84, 39.23, 31.95, 31.78, 31.62, 30.84, 30.69, 29.78, 29.69, 29.49, 29.34, 29.17, 25.67, 22.56, 22.51, 22.49, 14.08, 14.00, 13.94.



Compound 5. The synthesis route of compound 3 can be found our previous work ⁴. The synthesis of compound 5 refers to the previous work of Bi et al. ⁵ Under the protection of argon, LiAlH₄ (119 mg, 3.14 mmol) was added to a solution of compound 3 (647 mg, 0.63 mmol) in tetrahydrofuran (60 mL). The resulting mixture was stirred and heated to reflux for 10 h. After being cooled to 0 °C, water (20 mL) is slowly dropped into the reaction and extracted with dichloromethane. The organic layer was dried over anhydrous Na₂SO₄ for 0.5 h. After removal of solvent, the crude product was dissolved

in chloroform (45 mL), then 3-dichloro-5, 6-dicyano-1, 4-benzoquinone (285 mg, 1.26 mmol) and 4, 5-difluorobenzene-1,2-diamine (452 mg, 3.14 mmol) were added to the solution in turn. The reaction was stirred at room temperature for 6 h, and the solvent was removed under vacuum. Finally, the residue was purified by column chromatography to give compound 4 as a red solid (571 mg, 82%). Under the protection of argon, phosphorus oxychloride (0.4 mL) was added to a solution of compound 4 (455 mg) and N, N-Dimethylformamide (0.3 mL) in 1, 2-dichloroethane (50 mL). The resulting mixture was stirred and heated to reflux for 12 h, then cooled to 0 °C. The resulting mixture was slowly added to a saturated solution of sodium acetate (40 mL), then stirred at room temperature for 2 h. The resulting mixture was extracted with dichloromethane and the organic layer was dried over anhydrous Na₂SO₄ for 1 h. After removal of solvent, the crude product was then purified by column chromatography on silica gel with hexanes/dichloromethane (v/v=1:2) as eluent to afford compound 5 as a red solid (382mg). ¹H NMR (500 MHz, CDCl₃) δ 10.16, 8.19, 8.17, 8.15, 7.26, 4.69, 4.68, 3.26, 3.25, 3.23, 2.15, 2.13, 2.12, 2.11, 2.10, 2.00, 1.99, 1.97, 1.95, 1.94, 1.55, 1.54, 1.53, 1.51, 1.44, 1.42, 1.42, 1.41, 1.39, 1.39, 1.37, 1.36, 1.34, 1.33, 1.25, 1.14, 1.12, 1.11, 1.10, 1.08, 1.07, 1.02, 1.01, 1.00, 0.98, 0.97, 0.94, 0.93, 0.91, 0.90, 0.79, 0.78, 0.76, 0.67, 0.66, 0.65. ¹³C NMR (126 MHz, CDCl₃) δ 181.71, 153.30, 153.16, 151.25, 151.10, 146.86, 144.24, 138.86, 138.15, 136.93, 136.81, 132.84, 129.54, 128.01, 117.61, 114.43, 114.32, 77.27, 77.01, 76.76, 55.42, 38.98, 31.73, 31.57, 31.51, 30.53, 30.47, 30.44, 29.65, 29.36, 29.25, 29.10, 28.20, 25.53, 22.57, 22.53, 22.43, 14.05, 14.02, 13.88.



Synthesis of C5Qx-B6F: Under argon, compound 5 (151 mg, 0.13 mmol), compound 1 (169 mg, 0.52 mmol) and pyridine (0.5 mL) were dissolved in 30 mL chloroform, and stirred overnight at 65 °C. After cooling to room temperature, the solvent was removed and the mixture was poured into methanol and filtered. The residue was purified by silica gel column chromatography using petroleum ether/dichloromethane (1:1, v/v) as eluent to get a blue-black solid (174 mg, 75%). ¹H NMR (500 MHz, CDCl₃) δ 9.19, 9.18, 8.79, 8.76, 8.07, 8.05, 8.03, 7.90, 7.89, 7.87, 7.36, 7.35, 7.34, 7.32, 7.30,

7.29, 7.26, 4.87, 4.86, 4.85, 4.84, 3.31, 3.29, 3.27, 2.27, 1.93, 1.92, 1.90, 1.61, 1.59, 1.58, 1.54, 1.43, 1.39, 1.37, 1.29, 1.29, 1.26, 1.15, 1.14, 1.13, 1.08, 1.07, 1.06, 1.05, 1.04, 1.01, 1.00, 0.95, 0.94, 0.92, 0.90, 0.88, 0.87, 0.75, 0.74, 0.72, 0.71, 0.69.

Fabrication of Organic Solar Cells

All solar cell devices were fabricated with a conventional structure (ITO/PEDOT:PSS/D18/NFAs/ PDINN/Ag). The ITO glass substrates were cleaned by sequential sonication in deionized water, ethanol, and isopropyl alcohol for 10 mins each. Then these ITO glass substrates were further treated with ultraviolet/ozone for another 30 mins after drying at 120 °C on a hotplate in air. PEDOT:PSS solution was spin-coated onto ITO glass substrates at a speed of 5000 rpm and annealed at 150 °C for 10 mins in air to get 20 nm PEDOT: PSS film. For the layer by layer active film, the donor layer was first spin coated from 4 mg/mL CF solution at 2,000 rpm, and the acceptor layer was deposited on the donor layer from an 8 mg/mL CF solution at 3,000 rpm; the optimal thicknesses of the donor layer and active layer were about 45 and 95 nm (with thickness error bar of about 2 nm), respectively. The solid additive DIB is added solely to the acceptor solution at a concentration of 100 %wt. The at-cast films were then thermally annealed at 80 °C for 5 min. PDINN (1 mg/mL) in MeOH solution was spin-coated at 3000 rpm onto the active layer to get 10 nm electron transport layer. Finally, devices were transferred to an evaporation chamber where 100 nm Ag was thermally evaporated through a shadow mask under high vacuum to form the anode. The size of the active area of OSCs is defined by the overlapping of anode and cathode and given to be 6.625 mm².

Characterization

Film absorption spectra were obtained by using a UV-visible spectrophotometer (HITACHI, Japan). The thickness of film was obtained by using a spectroscopic ellipsometer (J. A. Woollam, USA). Current density-voltage (*J-V*) measurements were performed under AM 1.5G (100 mW cm⁻²) using a Newport 3A solar simulator (Newport, USA) at room temperature in air, and the light intensity was calibrated using a standard silicon reference cell certified by the National Renewable Energy Laboratory (NREL, USA). *J-V* characteristics were measured with a programmed software developed by Ossila Ltd. (UK) and a source meter unit (2612B, Keithley, USA). An aperture mask was placed over the device to define an area of 4 mm² for each pixel. External quantum efficiency (EQE) was measured with an EQE system (Zolix, China) equipped with a standard Si diode. GIWAXS measurements were conducted at beamline BL14B1 at the Shanghai Synchrotron Radiation Facility

in China. Grazing-incidence small-angle X-ray scattering (GISAXS) were conducted using the beamline BL16B1 at the Shanghai Synchrotron Radiation Facility in China. Water contact angle and surface energy was performed using a water contact angle measurement system (Attension Theta Lite).

Charge Mobility Measurements of Devices

The hole and electron mobilities of binary and ternary devices were obtained by using the space charge limited current (SCLC) method. The device structures for hole- and electron- only devices are ITO/ZnO/active layer/PDINN/Ag and ITO/PEDOT:PSS/active layer/MoO₃/Ag, respectively. Mobilities were obtained by fitting the current-voltage curves in the space charge limited range, where the SCLC is described following the equation below:

$$J = \frac{9\varepsilon_r \varepsilon_0 \mu_0 (V - V_{bi})^2}{8L^3}$$

Here ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, μ_0 is the hole or electron mobility, V is the applied voltage, V_{bi} is the built-in voltage.

GISAXS Modelling

1D GISAXS profiles of pure films were simulated *via* a versatile Fractal model according to previous work, which was used to quantify the fractal-like aggregation formed by NFA crystallites. The scattering intensity of NFA films can be expressed as **equation 1**, where P(q) and S(q) are the form factor and fractal structure factor, respectively, constant B is the incoherent scattering background. P(q) includes the product of particle volume fraction ϕ , the square of scattering length density difference between crystalline and amorphous polymers $\Delta \rho^2$ and the crystalline particle volume $V_{\rm P}$. S(q) is given by **equation 2**, where ϕ refers to the relative volume fraction of crystallites, 2*R* refers to the size of the primary crystalline particle, ξ and D represent the correlation length and fractal dimension of the crystalline domain, and $R_{\rm g}$ is the size of the crystalline domain (**equation 3**).

$$I(q) = P(q)S(q) + B \tag{1}$$

$$S(q) = 1 + \frac{\sin[m][(D-1)tan^{-1}(q\xi)]}{(qR)^{D}} \frac{D\Gamma(D-1)}{\left[1 + \frac{1}{(q\xi)^{2}}\right]^{\frac{D-1}{2}}}$$
(2)

$$R_g = \sqrt{\frac{D(D+1)}{2}}\eta \tag{3}$$

To quantify and compare the phase separation in photovoltaic LBL film, the 1D GISAXS profiles were fitted by using a DAB+Fractal model expressed in **equation 4** via the fitting software SASView (Version 4.2.2). The first term of the equation is the so-called Debye-Anderson-Brumberger (DAB) term, where q is the scattering wave vector, A_1 is an independent fitting parameter, and ξ is the average correlation length of the polymer domain. The second term of the equation is assigned to the Fractal model, which means the occupation of fractal-like structure of the non-fullerene acceptor. P (q, *R*) and S (q, *R*) are the form factor and fractal structure factor, respectively. The correlation length of the fractal-like structure is represented by η and D is the fractal dimension.

$$I(q) = \frac{A_1}{\left[1 + (q\xi)^2\right]^2} + A_2(P(q,R)S(q,R,\eta,D) + B$$
(4)

In Situ Spectroscopic Ellipsometry of molecular aggregation dynamics

In situ spectroscopic ellipsometry measurements were conducted to probe the molecular aggregation dynamics of NFAs through mapping their extinction coefficient (k) evolutions during the film formation process, which were extracted using a Kramers–Kronig consistent B-spline model where k locating at refer to the systems characteristic absorption peak. All films experience a thickness reduction from wet to dry within 2.5 s duration, and the corresponding optical parameters of films were recorded by ellipsometry at an interval of 0.05 s. The film thicknesses were further simulated and calculated by a B-Spline model and further verified by Cauchy model. The confirmation of t=0 starts at the moment when the active layer film preparation ends.

In Situ Spectroscopic Ellipsometry of structural relaxation

Film thickness was measured through ellipsometry using the Cauchy model. The roughness was first fitted during iso-hold and then the roughness value was fixed during the global fitting of thickness, which substantially reduces the deviations during fitting. The thickness and roughness were fitted in the wavelength range of 950-1000 nm. All films were coated on silicon substrate. For each system, three films were utilized to verify the effectiveness of measurements. For relaxation behavior measurement, samples were in-situ heated in a chamber filled with N_2 , and the film thickness was collected at the initial temperature of 30 °C, with the ramp rate of 0.6 °C s⁻¹. Once the temperature has reached 150 °C, this temperature was kept constant for 30 mins to study structural relaxation.

Molecular Dynamics Simulations

Geometry optimization and Polymorph. The geometry of the molecules was sequentially optimized using the Forcite and DMol3 modules. The Compass II forcefield was used to assign charges in the Forcite module, then the atom-based summation method was used to determine the electrostatic and van der Waals interactions. Next, the results from Forcite were performed to obtain geometry optimization in the DMol3 module through the Perdew-Burke-Ernzerhof (PBE) and generalized gradient approximation (GGA) functions, with the basis set as DNP. Finally, the optimized B6Cl molecules were placed in the Polymorph module to predict the crystal structures and the intermolecular packing of the given molecular structure. The forcefield and summation steps in the Polymorph module are the same as that in Forcite.

Adsorption Simulations. By taking one molecule as the substrate to allow another molecule as the adsorbate, we can simulate the interactions between two molecules. The geometry optimization and energy tasks in the Forcite module were used to gain the adsorption energy between NFA molecules.

Energy Loss

Non-radiative Energy Losses. The non-radiative energy losses were analyzed and calculated by the equations following: $E_{loss} = E_g - q V_{OC}$,

$$E^{non-rad}_{loss} = qV^{rad}_{oc} - qV_{OC}, \ V^{rad}_{oc} = \frac{kT}{q} \ln\left(\frac{J_{SC}}{J^{rad}_{0}} + 1\right) \cong \frac{kT}{q} \ln\left(\frac{q \cdot \int_{0}^{+\infty} EQE(E) \cdot \phi_{AM \ 1.5G}(E) \cdot dE}{q \cdot \int_{0}^{+\infty} EQE(E) \cdot \phi_{BB}(E) \cdot dE}\right),$$

where *T* is the temperature of the solar cell (T = 300 K is used in this work), *q* is elementary charge, $\emptyset_{AM 1.5G}(E)$ and $\emptyset_{BB}(E)$ are the standard solar spectrum under AM 1.5G (100 mW cm⁻²) and black body spectrum at the temperature *T* of the solar cell.

Reorganization Energy. The variation in reorganization energy can be quantified by the Stokes shift $(\Delta \lambda)$, which represents the gap between absorption and photoluminescence peaks.

Transient Photovoltage Decays

The photovoltage decays were measured using PD-RS from ENLITECH with a laser pulse excitation at 633 nm, with a pulse duration of 10 ns and a repetition rate of 50 Hz. The carrier lifetimes were deduced by fitting the photovoltage decay curves using a stretched-exponential function. The fitting function is given by:

$$V(t) = V_0 * \exp(-(t/\tau)^{\beta})$$

where V(t) is the photovoltage at time t, V_0 is the initial photovoltage, τ is the characteristic lifetime, and β is the stretching exponent. The fitting parameters, including the characteristic lifetime (τ) and the stretching exponent (β), were obtained from the equation shown in **Table S9**.

Excitonic Static Disorder Value

The static disorder of organic semiconductor can be obtained from its photovoltaic external quantum efficiency spectrum at wavelengths near the absorption onset. The fitting of exciton static disorder values was achieved by applying a modified sub-gap singlet exciton (SE) absorption coefficient model (with the MATLAB Script shown in Adv. Funct. Mater. 2022, 32, 2113181) to simulate the external quantum efficiency spectra of the photovoltaic device (**Figure S16**). Note that the relevant fitting scripts can be found in our previous work. ⁶



Figure S1. Energy levels of D18, C5Qx-B6F, B6F and C5-16. The cyclic voltammetry curves of C516, B6F and C5Qx-B6F films. The corresponding potential values are extracted by the crossing points of the two tangent lines. The energy levels of the molecules were calculated from the equation: HOMO/LUMO = $-(E_{ox}/E_{red}+ 4.41)$ eV.



Figure S2. The dihedral angles between the central core and terminal units of C5-16, B6F and C5Qx-B6F.



Figure S3. The top views of the π - π stacking patterns of C5-16 dimers with the interaction energy (E_{ad}) depict below.



Figure S4. The top views of the π - π stacking patterns of B6F dimers with the interaction energy (E_{ad}) depict below.



Figure S5. The top views of the π - π stacking patterns of C5Qx-B6F dimers with the interaction energy (E_{ad}) depict below.



Figure S6. The top views of the π - π stacking patterns of C5-16:C5Qx-B6F dimers with the interaction energy (E_{ad}) depict below.



Figure S7. Normalized absorption spectra of C5-16, B6F, C5Qx-B6F and C5-16:C5Qx-B6F (1:1) in solution and films.



Figure S8. Normalized PL of C5-16, B6F, C5Qx-B6F and C5-16:C5Qx-B6F (1:1) films.



Figure S9. Schematic of in-situ testing for C516 and C516:C5QXx-B6F films during film formation.



Figure S10. 2D GISAXS patterns of D18/C5-16, D18/B6F, D18/C5Qx-B6F, D18/C5-16:C5Qx-B6F, and aged D18/C5-16:C5Qx-B6F films.



Figure S11. Normalized absorption of D18 with 1% acceptors, D18/C516 and D18/C5Qx-B6F:C516 films.



Figure S12. AFM images of D18/C5-16, D18/B6F, D18/C5Qx-B6F and D18/C5-16:C5Qx-B6F films.



Figure S13. Statistics of relaxation behavior of D18/C5-16, D18/B6F, D18/C5Qx-B6F, D18/C5-16:C5Qx-B6F films measured from multiple samples, demonstrating good reproducibility



Figure S14. Charge transport properties of D18/C5-16, D18/B6F, D18/C5Qx-B6F, D18/C5-16:C5Qx-B6F.



Figure S15. The original data of TPV and the fitted lines.



Figure S16. The data of the FTPS-EQE required for the fitting of excitonic static disorder value of binary and ternary devices.



Figure S17. Dark J-V curves of D18/C516, D18/B6F, D18/C5Qx-B6F and D18/C5Qx-B6F:C516.



Figure S18. The spectrum of the LED for stability testing



Figure S19. Normalized PCE of ITO/PEDOT:PSS/Active layer/PDINN/Ag devices. Operational measurements performed under continuous illumination equivalent to one sun in air.



Figure S20. Normalized PCE (the maximum values are represented by points, while the average values are shown as the filled areas) of ITO/PEDOT:PSS/Active layer/PDINN/Ag devices.



re S21. Normalized FF, J_{SC} and V_{OC} of ITO/PEDOT:PSS/Active layer/PDINN/Ag devices. Operational measurements performed under continuous illumination equivalent to one sun in air.



Figure S22. The ¹H NMR (500 MHz CDCl₃) spectrum of B6F.



Figure S23. The ¹³C NMR (500 MHz CDCl₃) spectrum of B6F.



Figure S24. The ¹H NMR (500 MHz CDCl₃) spectrum of compound 5.



Figure S25. The ¹³C NMR (126 MHz CDCl₃) spectrum of compound 5.



Figure S26. The ¹H NMR (500 MHz CDCl₃) spectrum of C5qx-B6F.

Acceptors	A to A Stacking	A to D Stacking	D to D Stacking	π–π Stacking	alkyl chain stacking	others
C5-16 & C5- 16	35%	19%	15%	69%	15%	16%
B6F & B6F	23%	18%	9%	50%	11%	39%
C5Qx-B6F & C5Qx-B6F	17%	15%	51%	83%	6%	11%
C5Qx-B6F & C5-16	23%	41%	24%	88%	7%	5%

Table S1. Summary of π - π stacking, A-to-A, A-to-D and D-to-D packing among NFAs from molecular dynamics simulations.

Table S2. $\Delta\lambda$ values of the peak position shifts across different stages.

System	$\Delta\lambda_{\text{stage1}}(s)$	early $\Delta\lambda_{stage2}(s)$	later $\Delta\lambda_{stage2}$ (s)	$\Delta\lambda_{\text{stage3}}(s)$
C516	4.8 nm (0-1.0 s)	77.2 nm (0.9-1.4 s)	1.6 nm (1.4-1.7 s)	1.6 nm (>1.7 s)
B6F	4.0 nm (0-0.9 s)	55.3 nm (1.0-1.4 s)	3.5 nm (1.4-1.7 s)	1.6 nm(>1.7 s)
C5Qx-B6F	8.3 nm (0-0.6 s)	45.1 nm (0.6-0.75 s)	1.7 nm (0.75-1.65 s)	1.7 nm(>1.65 s)
C516:C5Qx-B6F	13.4 nm (0-0.45 s)	30.2 nm (0.45-0.7 s)	1.7 nm (0.7-1.65 s)	1.7 nm(>1.65 s)

Table S3. Fitting parameters of 1D GISAXS profiles of C5-16, B6F, C5Qx-B6F and C5-16:C5Qx-B6F, where ϕ refers to the relative volume fraction of crystallites, 2R refers to the size of the primary crystalline particle, ξ and D represent the correlation length and fractal dimension of the crystalline domain, and R_g is the size of the crystalline domain.

System	φ (%)	2R (nm)	ξ (nm)	D	R _g (nm)
C5-16	23.1	7.2	18.6	2.9	44.8
B6F	22.5	7.9	18.5	2.9	44.6
C5Qx-B6F	39.1	13.4	24.6	3.0	60.3
C5-16:C5Qx-B6F	33.9	12.1	22.8	3.0	55.8

Table S4. Detailed GIWAXS data of C5-16, B6F, C5Qx-B6F, C5-16:C5Qx-B6F films.

	In plane				Out of plane			
System	q (Å-1)	d (Å-1)	FWHM (Å ⁻¹)	CCL (Å)	q (Å-1)	d (Å-1)	FWHM (Å-1)	CCL (Å)
C5-16	0.39	16.11	0.09	62.83	1.75	3.59	0.28	20.20
B6F	0.38	16.53	0.12	47.12	1.72	3.65	0.30	18.85
C5Qx-B6F	0.35	17.95	0.10	56.55	1.74	3.61	0.26	21.75
C5-16:C5Qx-B6F	0.40	16.11	0.08	70.69	1.78	3.53	0.24	23.56

	In plane				Out of plane			
System	q (Å-1)	d (Å-1)	FWHM (Å ⁻¹)	CCL (Å)	q (Å-1)	d (Å-1)	FWHM (Å ⁻¹)	CCL (Å)
D18/C5-16	0.32	19.63	0.08	70.69	1.76	3.57	0.26	21.75
D18/B6F	0.33	19.04	0.10	56.55	1.74	3.61	0.28	20.20
D18/C5Qx-B6F	0.32	19.63	0.06	94.25	1.75	3.59	0.24	23.56
D18/C5-16:C5Qx-B6F	0.33	19.04	0.06	94.25	1.79	3.51	0.24	23.56

Table S5. Detailed GIWAXS data of C5-16, B6F, C5Qx-B6F, C5-16:C5Qx-B6F films.

Table S6. GISAXS fitting parameters via a DAB+Fractal model, where the correlation length ξ refers to the domain size of the donor-rich phase, η and D represent the correlation length and fractal dimension of acceptors, and $2R_g$ is regarded as the domain size of the acceptor domain.

System	<i>§</i> (nm)	7 (nm)	D	2R _g (nm)
D18/C5-16	24.9	4.1	2.8	18.9
D18/B6F	24.1	3.9	2.8	18.0
D18/C5Qx-B6F	36.2	7.8	3.0	38.2
Ternary	29.8	5.2	2.9	24.7
Ternary aged	30.1	5.4	2.9	25.7

Table S7. Summary of photovoltaic parameters of devices based on D18/C516:C5Qx-B6F system.

Active layer	PCE (a.u.)	FF	$J_{\rm SC}~({\rm mA/cm^2})$	$V_{\rm OC}$ (V)
D18/C5Qx-B6F:C516 (0:100)	$18.6 \pm 0.4 \; (19.0)$	$79.9 \pm 0.5 \; (80.4)$	$27.3 \pm 0.6 \ (27.8)$	$0.844 \pm 0.002 \; (0.847)$
D18/C5Qx-B6F:C516 (10:90)	$18.7\pm 0.4\;(19.1)$	$79.4 \pm 0.7 \ (80.1)$	$27.4 \pm 0.4 \; (27.9)$	$0.855 \pm 0.001 \; (0.856)$
D18/C5Qx-B6F:C516 (25:75)	$18.5\pm 0.6\;(19.1)$	80.0 ± 0.4 (80.4)	$27.0 \pm 0.4 \; (27.4)$	$0.866 \pm 0.002 \; (0.868)$
D18/C5Qx-B6F:C516 (50:50)	$19.4 \pm 0.5 \; (20.0)$	80.4 ± 0.6 (81.1)	27.1 ± 0.4 (27.5)	$0.893 \pm 0.003 \; (0.897)$
D18/C5Qx-B6F:C516 (75:25)	19.0 ± 0.5 (19.6)	$79.1 \pm 0.9 \ (80.0)$	$26.5 \pm 0.4 \ (27.0)$	$0.902 \pm 0.004 \; (0.906)$
D18/C5Qx-B6F:C516 (90:10)	18.7 ± 0.5 (19.3)	$78.9 \pm 0.6 \ (79.6)$	27.1 ± 0.4 (26.7)	$0.906 \pm 0.002 \; (0.909)$
D18/C5Qx-B6F:C516 (100:0)	$18.2\pm 0.9\ (19.1)$	$78.0 \pm 1.4 \ (79.4)$	$25.4 \pm 0.7 \ (26.1)$	$0.919 \pm 0.004 \; (0.923)$

The device structure is ITO/PEDOT:PSS/Active layer/PDINN/Ag.

Table S8. Charge transport properties of D18/B6F, D18/C5-16, D18/C5Qx-B6F and D18/C5-16:C5Qx-B6F (1:1) films measured via SCLC.

Active layer	$\mu_{\rm h}~(10^{-4}~{\rm cm}^{-1}{\rm V}^{-1}{\rm s}^{-1})$	$\mu_{\rm e}$ (10 ⁻⁴ cm ⁻¹ V ⁻¹ s ⁻¹)	$\mu_{ m e}/\mu_{ m h}$
D18/C5-16	6.1	6.3	1.03
D18/B6F	3.0	4.3	1.43
D18/C5Qx-B6F	3.4	4.5	1.32
D18/C5Qx-B6F:C5-16	6.6	6.9	1.05

Active layer	$\boldsymbol{\tau}\left(\mathrm{s}\right)$	a ₁	t ₁ (s)	a ₂	$t_2(s)$	$V_0(\mathbf{V})$
D18/B6F	4.08E-05	1.00E-01	1.60E-05	8.84E-02	6.88E-05	8.01E-01
D18/C5Qx-B6F	4.38E-05	1.07E-01	1.65E-05	9.34E-02	7.49E-05	8.05E-01
D18/C5Qx-B6F:C516	5.20E-05	1.09E-01	2.12E-05	9.22E-02	8.85E-05	8.02E-01
D18/C516	5.47E-05	1.00E-01	2.47E-05	6.51E-02	1.01E-04	7.98E-01

Table S9. The parameters of the TPV fitting

 $V(t) = V_0 + a_1 \exp[-(t/t_1)^{\beta 1}] + a_2 \exp[-(t/t_2)^{\beta 2}].$

stretching exponent $\beta_1 = \beta_2 = 1$; $\tau = (a_1t_1 + a_2t_2) / (a_1 + a_2)$

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