Asymmetric Non-Fullerene Acceptors with Balanced crystallization Kinetics Enabling Trade-Off between Charge generation and Recombination in Ternary Organic Solar Cells

Xiaoqi Yu^{1,2}, Jintao Zhu³, Lin Xie^{1,4,*}, Haotian Hu¹, Tongqiang Liu¹, Pengfei Ding¹, Xueliang Yu¹, Jinfeng Ge¹, Chengcheng Han¹, Wei Song^{1,4*} and Ziyi Ge^{1,4},*

¹ Zhejiang Engineering Research Center for Energy Optoelectronic Materials and Devices, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China.

² School of Materials Science and Chemical Engineering, Ningbo University, Ningbo, Zhejiang 315211, P. R. China.

³ Key Laboratory of Flexible Electronics of Zhejiang Province, Ningbo Institute of Northwestern Polytechnical University, Ningbo 315100, China.

⁴ Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.

* E-mail: xielin@nimte.ac.cn; songwei@nimte.ac.cn; geziyi@nimte.ac.cn.

1. Detailed experimental section

Materials synthesis

All air and water-sensitive reactions were carried out under a nitrogen atmosphere. The other precursors were used at the common commercial level or purchased from Nanjing Zhiyan Technology Co.,Ltd and Derthon OPV Co., Ltd.

The synthetic route of YQX-1O and YQX-2O is shown in **Scheme S1** and detailed synthesis processes are described in the following. The corresponding nuclear magnetic resonance (NMR) and mass spectrometry (MS) data are provided in **Figures S13–S27**.



Scheme S1. Synthetic route of YQX-10.



Scheme S1. Synthetic route of YQX-2O.

YQX-10: The synthesis of YXQ-1O involves a statistical reaction. To minimize the generation of disubstituted by-products, this study employed an excess core strategy by increasing the molar ratio of the core to drive the reaction toward monosubstituted product **compound 3**. Compound 1(2.5g, 4mmol),compound 2(8g, 21 mmol) , $Pd_2(dba)_3$ (0.14g, 0.117mmol) and toluene (30 ml) were added under nitrogen atmosphere and the mixture was refluxed at 90°C for 5h. The aqueous phase was extracted with dichlorom-ethane for three times. The combined organic phase was dried over anhydrous Na₂SO₄, and then the solvent was removed by vacuum evaporation. Further

optimization of separation conditions via liquid chromatography using petroleum ether/dichloromethane (4:1, v/v) as mobile phase at 40 mL/min flow rate successfully achieved high-efficiency separation as the eluent to give a deep orange solid (2g,79.3%yield). ¹H NMR (400MHz,CDCl₃) δ :7.69(s,1H),7.28(s,1H),5.30(s,2H),2.78-2.75(m,1H),1.81-1.74(m, 2H) ,1.55(s, 1H),1.40-1.25(m,16H),0.89-0.84(m,4H).

Compound 3(2 g,3.2mmol), **compound 4**, (2.3g,4mmol) ,Pd₂(dba)₃(0.14 g,0.117 mmol) and toluene were (30 ml) added under nitrogen atmosphere and the mixture was refluxed at 90 °C for 5h. The aqueous phase was extracted with dichloromethane for three times. The combined organic phase was dried over anhydrous Na₂SO₄, and then the solvent was removed by vacuum evaporation. The compound was purified by column chromatography on silica gel using petroleum PE:DCM (2/1,v/v) as the eluent to give a deep orange solid(2.01g,74.4%yield). ¹H NMR (400 MHz,CDCl₃) δ : 7.69 (s,1H),7.58(s,2H),7.18(s,1H), 6.44(s,2H),3.99(d,J=4Hz,6H), 2.78-2.74(m,2H),1.85-1.25(m,28H),1.09-0.87 (m,10H).

Compound 5 (2 g,1.2 mmol) and PPh₃ (3.15 g,12 mmol) were dissolved in the 1,2dichlorobenzene (o-DCB,20 mL) under nitrogen. After being heated at 180°C for 24 h, the solvent was removed to get the crude product. The red residue was mixed with 5-(bromomethyl) undecane (3g,12mmol), potassium carbonate (0.5g,0.08mmol) and potassium iodide (1.6g,12mmol) in DMF (20mL) under N₂. The mixture was refluxed at 95°C overnight. After cooled down to room temperature, the residue was poured into water and extracted with, ethyl acetate three times. The combined organic phase was washed with water followed by brine. Then the solution was dried over Na₂SO₄ and concentrated under reduced pressure. The compound was purified by column chromatography on silica gel using petroleum PE:DCM (5/1,v/v) as the eluent to give a deep orange solid(500mg,33.3%yield). ¹H NMR (400MHz,CDCl₃) δ : 6.99 (s,1H),6.30(s,1H), 4.99 -4.55(m,4H),4.08-4.02(m,4H),2.84-2.80(m,2H)2.10-2.05(m,2H),1.91-1.82(m,2H),1.55-0.57(m,82H).

Zinc power (1g, 15.38mmol) was added into a solution of **compound 6** (500mg, 0.45mmol) in acetic acid (20ml) in three-necked flask under nitrogen. Then the mixture was heated to 110°C for

30 min. After the mixture was cooled to room temperature, the solid was removed by filtration. The mixture solution was extracted with dichloromethane. Then the organic phase was removed under reduced pressure and a dark green solid was obtained. The solid and **compound 7** (0.483mg,1mmol) was added into a mixed solution of EtOH:CH3COOH=1:1 without further purification. Then the mixture was heated to 110°C for 1 h. After the mixture solution was cooled to room temperature, it was extracted with dichloromethane. The solvent was removed under reduced pressure. Then the organic phase was purified by silica gel column chromatography (PE:DCM=10:1 v/v) to obtain an orange solid 3 (100 mg, 21%).¹H NMR (400MHz,CDCl₃) δ : 7.22 (s, 2H), 7.03 (s,1H), 6.29 (s,1H),4.63-4.05(m,4H),4.07(d,J=8Hz,2H),2.87-2.81(m,6H) 2.12-2.10(m,2H)1.94-1.84(m,2H)1.76-1.71(m,2H),1.55-0.65(m,114H).

Compound 8 (100mg,0.07mmol), 1,2-Dichloroethane (20ml), DMF (0.5ml) were mixed in threenecked flask under nitrogen. POCl₃ (0.5ml) was added drop wise slowly. After reacting at 80°C overnight, the mixture was transferred to a funnel. Then added into saturated Na₂CO₃solution slowly, and kept stirring. After no bubble, the mixture was extracted with dichloromethane. The organic phase was purified d by silica gel column chromatography (PE:DCM=1:2 v/v) to obtain a yellow solid 5(92mg, 88%).¹HNMR (400MHz,CDCl₃) δ:10.15 (s,1H),10.12(s,1H), 7.24(s,2H), 4.66-4.64(m,6H),3.26-3.22(m,2H),2.83-2.80(m,4H),2.08(s,2H),1.96-1.91(m,2H),1.74-1.70(m,2H),1.57-0.65(m,116H).

Compound 9 (92 mg, 0.058 mmol), $(CH_3CO)_2O$ (0.5 ml), toluene (20ml), BF₃.C₂H₅OC₂H₅ (0.5 ml), and **Compound 10** matrimonial (14.5 mg,0.189 mmol) were mixed in three-necked flask in the air. After reacting at 25°C 2h, the solvent was removed under reduced pressure. Then the organic phase was purified by silica gel column chromatography (PE:DCM=2:1v/v) to obtain an dark solid 6 (104mg, 86%).¹H NMR (400MHz,CDCl₃) δ :9.32(s,1H), 9.18(s,1H), 8.59-8.51 (m,2H),7.72-7.62(m,2H),7.28(s,2H)4.76-4.74(m,6H),33.30-3.26(m,2H)2.86-2.80(m,4H),2.15-2.09(m,2H),1.90-1.88(m,2H),1.75-1.70(m,2H),1.57-0.65(m,116H).

YQX-20: Zinc power (1g, 15.38mmol) was added into a solution of **compound 12** (500mg, 0.44mmol) in acetic acid (20 ml) in three-necked flask under nitrogen. Then the mixture was

heated to 110°C for 30 min. After the mixture was cooled to room temperature, the solid was removed by filtration. The mixture solution was extracted with dichloromethane. Then the organic phase was removed under reduced pressure and a dark green solid was obtained. The solid and **compound 7** (0.483mg,1mmol) was added into a mixed solution of EtOH:CH₃COOH=1:1 without further purification. Then the mixture was heated to 110°C for 1h. After the mixture solution was cooled to room temperature, it was extracted with dichloromethane. The solvent was removed under reduced pressure. Then the organic phase was purified by silica gel column chromatography (PE:DCM=10:1v/v) to obtain an orange solid3(120mg, 25%). ¹H NMR (400MHz, CDCl₃) δ :7.22(s,2H), 6.30(s,2H), 4.61 (d,J =8Hz,4H),4.07(d,J=8Hz,4H),2.83(d,J=4Hz,4H) 2.16-2.11(m,2H),1.96-1.90(m,2H),1.78-1.72(m,2H),1.53-0.65(m,114H).

Compound 13 (120mg,0.08mmol), 1,2-Dichloroethane (20ml), DMF (0.5 ml) were mixed in three-necked flask under nitrogen. POCl₃ (0.5ml) was added dropwise slowly. After reacting at 80°C overnight, the mixture was transferred to a funnel. Then added into saturated Na₂CO₃solution slowly, and kept stirring. After no bubble, the mixture was extracted with dichloromethane. The organic phase was purified d by silica gel column chromatography (PE:DCM=1:2 v/v) to obtain a yellow solid 5 (100mg, 92%). ¹H NMR (400MHz, CDCl₃) δ :10.12(s,2H), 7.24(s,2H), 4.66-4.59(m,8H),2.81(d,J=4Hz,4H),2.10-2.05(m,2H),1.96-1.92(m,2H),1.74-1.7(m,2H),1.52-0.65(m,114H).

Compound 14 (100mg, 0.06mmol), (CH₃CO)₂O (0.5 ml), toluene (20 ml), BF₃. C₂H₅OC₂H₅(0.5 ml), and 2-(5,6-dibromo-3-oxo-2,3-dihydro-1H-inden-1-ylidene) malononitrile. (15 mg, 0.2 mmol) were mixed in three-necked flask in the air. After reacting at 25°C 2h, the solvent was removed under reduced pressure. Then the organic phase was purified by silica gel column chromatography (PE:DCM=2:1v/v) to obtain an dark solid 6 (108mg, 88%). ¹H NMR (400 MHz,CDCl₃, ppm) δ : (9.32,s,2H),8.55-8.50(m,2H),7.66-7.63(m,2H),7.26(s,2H),4.76-4.74(m,8H),2.82-

2.80(d,J=8Hz,4H),2.15-2.07(m,4H),1.73-0.65(m,118H).

Device fabrication

Small-area devices: The ITO substrates were purchased from szsunytech Inc. The anti-flection coating was not applied in this work. Devices were fabricated with the conventional device structure of glass/ITO/2PACz/Active layer/PDINN/Ag. ITO-coated glass substrates were cleaned

with detergent and ultrasonicated in deionized water, acetone and ethyl alcohol for 20 min each and subsequently blow-dried by nitrogen. The 2PACz (0.2 mg/ml in ethanol) was spin-cast onto the ITO surface at 3000 r.p.m. for 30 s and baked at 100°C for 10 min in the air. For binary devices, the PM6:BTP-eC9 (1:1.2 weight ratio, the concentration of PM6 is 7.5 mg/ml with 0.5wt% 1,8-diiodooctane (DIO)) were dissolved in chloroform in a nitrogen-filled glove box and stirred overnight and heated at 40°C for 30min before fabrication. For ternary devices, PM6:BTPeC9:YQX-10 and PM6:BTP-eC9: YQX-20 (1:1.05:0.15 weight ratio, the concentration of PM6 is 7.5 mg/ml with 0.5wt% 1,8-diiodooctane (DIO)) were dissolved in chloroform in a nitrogenfilled glove box and stirred overnight and heated at 40°C for 30min before fabrication. The blended solutions were spincast at 4000 rpm for 30 s followed by 10mins thermal annealing. For the cathode interlayer, PDINN was dissolved in methanol at the concentration of 1 mg/ml and spin-coated onto the photoactive layer at 2000 r.p.m. for 1 min. Finally, a 150nm Ag electrode were deposited on top of the active layers through a shadow mask under a vacuum about 1×10-5 Pa. The active area was 0.04 cm².

Small-area inverted devices: Devices were fabricated with the conventional device structure of glass/ITO/ ZnO / active layer/ MnO_3 /Ag. The processing of ITO and the active layer followed the same methodology as small-area devices. Zinc acetate dihydrate and ethanolamine were dissolved in 2-methoxyethanol, and the mixture was heated at 60°C under continuous stirring for 2 hours. The ZnO (0.45M) was spin-cast onto the ITO surface at 5000 r.p.m. for 30 s and baked at 200°C for 15 min in the air. A 8nm MnO_3 and a 120nm Ag electrode were deposited on top of the active layers through a shadow mask under a vacuum about 1×10-5 Pa. The active area was 0.0484 cm².

Device characterization and measurement

The *J-V* measurement was performed via the solar simulator (Newport-Oriel® Sol3A 450W). The intensity of the AM 1.5G spectra was calibrated by a certified standard silicon solar cell. The area of the tested solar cells was determined by an optical microscope. The effective areas of the cells were 0.04 cm². PYS is a surface-sensitive technique used to measure the HOMO (Highest Occupied Molecular Orbital) energy levels of solids or thin film materials, and to determine the work function or energy level distribution relative to the vacuum level. The intensity of the photo electron yield is plotted against the incident photon energy. The threshold at which the photo electron yield rapidly increases (the onset) is mapped to the HOMO corresponding to the sample's vacuum level. By combining this with the material's optical band gap, the LUMO (Lowest Unoccupied Molecular Orbital) position can be further estimated. A solar cell QE tester (QE-R, Enli Technology Co., Ltd) calibrated with a 75W xenon lamp source standard probe was be utilized to obtain the external quantum efficiency (EQE) spectra. In order to study the dependence of devices properties on light intensity, neutral density filters were used to tune the light intensity, which were calibrated by the standard Si solar cell. Surface morphology and phase diagram were performed by Veeco Dimension 3100V atomic force microscope. The atomic force microscopic (AFM) images were acquired using a Bruker Dimension EDGE in tapping mode. Grazingincidence wide-angle X-ray scattering (GIWAXS) and the grazing-incidence small-angle X-ray scattering (GISAXS) analyses were conducted by Xeuss 3.0 UHR SAXS/WAXS equipment. EL and EQE_{EL} measurements were performed by applying external voltage/current sources through the OSCs (REPS, Enlitech) which consists of a monochromator in combination with a Si-CCD detector. Highly sensitive EQE was measured using an integrated system (PECT-600, Enlitech), where the photocurrent was amplified and modulated by a lock-in instrument. Time resolved femtosecond transient absorption (TA) spectroscopy was performed on an Ultrafast Helios pumpprobe system in collaboration with a regenerative amplified laser system from Coherent.

Table S1 Photovoltaic parameter of OSCs.

Blends	$V_{\rm OC}({ m V})$	J _{SC} (mA cm ⁻²)	FF(%)	PCE(%)
PM6:YQX-1O	0.97	20.34	55.51	10.94
PM6:YQX-2O	1.02	14.85	49.55	7.50

UV-Vis absorption spectroscopy



Figure S1. Normalized absorption spectra of neat BTP-eC9, YQX-1O and YQX-2O in the film. Photoelectron Yield Spectroscopy (PYS)

The HOMO (Highest Occupied Molecular Orbital) of compound PM6, BTP-eC9, YQX-1O and YQX-2O was determined using the Inverse Photoemission Spectroscopy (IPS) method. The intensity of the photoelectron yield was plotted as a function of the incident photon energy. The onset, at which the photoelectron yield exhibits a rapid increase, was identified and correlated with the vacuum energy level of the sample, thereby mapping the corresponding electronic state to the HOMO.

$$\begin{array}{c} 0.03 \\ 0.02 \\ 0.02 \\ 0.00 \\ 0.$$

$$LUMO = E_g - HOMO$$

Figure S2. PYS curves for PM6, BTP-eC9, YQX-10, and YQX-20 under N2.

Table S2. Optical properties in film and the electronic energy levels of PM6, BTP-eC9, YQX-10

and	Y	O	X.	-2	Ο	۱.
unu		\sim	x x	-	\sim	٠

System	λ _{onset}	$E_{ m g}^{ m opt}$ a)	E _{HOMO}	ELUMO
System	(nm)	(eV)	(eV)	(eV)
PM6	674.1	1.84	-5.43	-3.59
BTP-eC9	938.4	1.32	-5.87	-4.55
YQX-10	867.5	1.43	-5.80	-4.37
YQX-20	851.8	1.46	-5.87	-4.41

^{a)} The optical gap calculated from the absorption onset of films by the equation: $E_g^{opt} = \frac{1240}{\lambda_{film\,onset}}$

Angle measurement.

Contact angles were measured from spin-coated films by an optical contact angle meter(CAM 200). The surface energy was estimated by the Harmonic mean equations:

$$(1 + \cos\theta_{1})\gamma_{1} = 4(\frac{\gamma_{1}^{d}\gamma_{s}^{d}}{\gamma_{1}^{d} + \gamma_{s}^{d}} + \frac{\gamma_{1}^{p}\gamma_{s}^{p}}{\gamma_{1}^{p} + \gamma_{s}^{p}})$$
$$(1 + \cos\theta_{2})\gamma_{2} = 4(\frac{\gamma_{2}^{d}\gamma_{2}^{d}}{\gamma_{2}^{d} + \gamma_{2}^{d}} + \frac{\gamma_{2}^{p}\gamma_{s}^{p}}{\gamma_{2}^{p} + \gamma_{s}^{p}})$$
$$\gamma_{s=}\gamma_{s}^{d} + \gamma_{s}^{p}$$

where γ_s^d represents the dispersive components, γ_s^p is the polar component. θ_{1} and θ_{2} are the contact angles of pure water and diiodomethane, respectively. H₂O: $\gamma_1 = 72.8 \text{ mJ} m^{-2}$, $\gamma_1^d = 21.8 \text{ mJ} m^{-2}$, $\gamma_{1=51.0}^p \text{ mJ} m^{-2}$; diiodomethane: $\gamma_2 = 50.8 \text{ mJ} m^{-2}$, $\gamma_2^d = 48.5 \text{ mJ} m^{-2}$, $\gamma_{2=2.3 \text{mJ}}^p m^{-2}$, γ_s is the surface energy.



Figure S3. Contact angle images of PM6, BTP-eC9, YQX-10 and YQX-20 films with water and diiodomethane droplet on top.

Sample	Contact Angle 1 (°)	Contact Angle 2 (°)	Contact Angle 3 (°)	Mean ± SD (°)
PM6	105.009	98.902	95.424	99.778±4.852
BTP-eC9	93.145	94.859	93.719	93.908±0.872
YQX-10	95.426	95.428	95.428	95.427±0.001
YQX-20	94.854	94.862	94.862	94.859±0.005

Table S3. Contact angle of PM6, BTP-eC9, YQX-1O and YQX-2O films with water.

Table S4. Contact angle of PM6, BTP-eC9, YQX-1O and YQX-2O films with Diiodomethane.

Sample	Contact Angle 1 (°)	Contact Angle 2 (°)	Contact Angle 3 (°)	Mean ± SD (°)
PM6	59.983	60.024	60.032	60.013±0.0262
BTP-eC9	49.242	45.032	56.234	50.169±5.658
YQX-10	49.246	42.174	47.426	46.282±3.672
YQX-20	42.779	44.981	48.436	45.399±2.851

Table S5. Summary of contact angles, surface tensions, and Flory-Huggins interactionparameters for PM6, BTP-eC9, YQX-10 and YQX-20.

System	θ _{water} (°)	θ _{diiodomethane} (°)	γa (mN/m)	γ _p (mN/m)	γ _{tot} (mN/m)	χd-а (K)	Ха-а' (K)
PM6	99.778	60.013	28.13	0.583	28.714	-	-
BTP-eC9	93.908	50.169	33.3	0.954	34.255	0.244	-

YQX-10	95.427	46.282	36.24	0.461	36.701	0.489	0.0422
YQX-2O	94.859	45.399	36.653	0.500	37.153	0.543	0.0588

TA measurements



Figure S4. TA spectra in the range of 500-1100 nm for PM6:BTP-eC9, PM6: BTP -eC9:YQX-10 and PM6:BTP-eC9:YQX-20.

Table S6. The bi-exponential fitting of the kinetics yield of PM6: BTP-eC9 , PM6: BTP-eC9:YQX-10 and PM6:BTP-eC9:YQX-20.

Active layer	$ au_1$ (ps)	$ au_2$ (ps)
PM6:BTP-eC9	0.293	13.434
PM6:BTP-eC9:YQX-10	0.251	12.466
PM6:BTP-eC9:YQX-2O	0.207	13.938

TPV and TPC



Figure S5. a) TPC profiles of binary and ternary devices. b) TPV profiles of binary and ternary devices.

S-EQE and EL measurements



Figure S6. The normalized EL and the normalized s-EQE spectra of PM6:BTP-eC9: YQX-10 and PM6:BTP-eC9:YQX-20.



Figure S7. Fitted curves of Urbach energy for binary and ternary devices.

Photovoltaics properties In-situ Photoluminescence Spectra Measurements.

In-situ Photoluminescence Spectra Measurements were performed by a laser device (MGL-III-785-300mW BH81223) with a time resolution of 0.03 s. The excitation wavelength was 660nm. For the process of in-situ measurement, during the film deposition process, the solution was spun onto the substrate, and the film was formed on the substrate. The light source emitted a beam of light, which was received by the detector after 7 passing through the sample. The absorption spectrum of the sample changed as the solvent evaporated. The spectrometer continuously recorded the absorption spectrum of the sample at different time points. By processing the recorded spectral data, the spectral changes of the sample during the film formation process can be obtained. By comparing the spectra at different time points, the spectral features and trends of the sample during the film formation process can be observed. By recording the time points of the absorption spectrum and comparing spectra at different time points, time-resolved observation of the formation process can be achieved, with the time resolution depending on the time interval of recording the spectrum and the speed of data processing. The detailed instrument Schematic diagram can refer to this paper.



Figure S8. J_{SC} depending on the variation of light intensity under one-solar condition.

The calculation processes of *Eloss*

(1) Radiative recombination above the bandgap (ΔE_{loss})

$$\Delta E_{1} = E_{g} - qV_{OC}^{SQ}$$

$$\frac{q\int_{0}^{\infty} EQE_{PV}(E)\phi_{AM1.5}(E)dE}{q\int_{0}^{\infty} EQE_{PV}(E)\phi_{AM1.5}(E)dE} + 1)$$

$$V_{OC}^{SQ} = \frac{KT}{q}\ln(J_{0}^{SQ} + 1) = \frac{KT}{q}\ln(q) + 1$$

$$q\int_{Eg}^{\infty}\phi_{BB}(E)dE + 1)$$

$$\phi_{BB}(E) = h^{3}c^{2}E^{2}e^{-\frac{E}{KT}}$$

(2) Radiative recombination below the bandgap (ΔE_2)

$$\Delta E_{2} = E_{\text{loss,rad}} = q V_{OC-q}^{SQ} V_{OC}^{rad}$$

$$\frac{q \int_{0}^{\infty} EQE_{PV}(E) \phi_{AM1.5}(E) dE}{q \int_{0}^{\infty} EQE_{PV}(E) \phi_{BB}(E) dE} + 1)$$

(3) Non-radiative recombination ΔE_3

 $\Delta E_3 = E_{\text{loss,non-rad}} = -\frac{KT}{q} \text{ InEQE}_{\text{EL}}$ Where E_g, V_{OC}^{SQ} , KT, q, ϕ_{BB}, V_{OC}^{rad} and are energy bandgap, Shockley-Queisser (SQ) open-circuit voltage limit, the Boltzmann constant, the temperature, the elementary charge, the black body spectrum and radiative recombination open-circuit voltage limit.

Morphology characterization



Figure S9. AFM height images, phase images and Statistical data extracted from Pi-FM measurements of PM6:BTP-eC9, PM6:BTP-eC9:YQX-1O and PM6:BTPeC9:YQX-2O.



Figure S10. Two-dimensional (2D) GIWAXS diffraction patterns of PM6, BTP-eC9, YQX-10 and YQX-20.



Figure S11. The IP and OOP of line-cut profiles of the PM6, BTP-eC9,YQX-1O and YQX-2O.

	q _z (010)	dπ	FWHM	CCL
	(Å-1)	(Å)	(Å-1)	(Å)
BTP-eC9	1.74	3.61	0.36	15.71
YQX-10	1.67	3.76	0.48	11.75
YQX-20	1.75	3.59	0.55	10.31
PM6:BTP-eC9	1.67	3.76	0.31	18.07
PM6:BTP-eC9:YQX-10	1.69	3.71	0.31	18.28
PM6:BTP-eC9:YQX-2O	1.70	3.69	0.30	18.75

Table S7. Crystallographic parameters of pure films for BTP-eC9,YQX-10,YQX-20PM6:BTP-eC9, PM6: BTP-eC9:YQX-10 and PM6:BTP-eC9:YQX-20 in the OOP.

Table S8. Crystallographic parameters of pure films for BTP-eC9,YQX-10,YQX-20

	q _z (100)	dп	FWHM	CCL
	(Å-1)	(Å)	(Å-1)	(Å)
BTP-eC9	0.39	15.94	0.13	43.50
YQX-10	0.33	18.76	0.15	38.21
YQX-20	0.36	17.57	0.09	62.55
PM6:BTP-eC9	0.31	20.20	0.14	40.39
PM6:BTP-eC9:YQX-10	0.31	20.27	0.13	44.53
PM6:BTP-eC9:YQX-2O	0.30	20.94	0.12	47.12

PM6:BTP-eC9, PM6: BTP-eC9:YQX-1O and PM6:BTP-eC9:YQX-2O in the IP.

Table S9. Morphology parameters fitted by the GISAXS profiles (ξ is the intermixing domain size; R_g is the crystal domain size).

	ξ(nm)	2R _g (nm)
PM6:BTP-eC9	30.04	25.62
PM6:BTP-eC9:YQX-1O	35.14	17.92
PM6:BTP-eC9:YQX-2O	46.27	29.23

The device stability measure



Figure S12. Normalized PCE of inverted devices of encapsulated ternary device and binary device with constant illumination.

Table S10. Device efficiencies for ternary devices by monitoring the solution phase to solid-state film transition of multi-acceptor-based bulk heterojunctions (BHJs) using in situ optical spectroscopy.

Host system	Guest	Binary	Ternary	Dofononao
Host system	component	performance	performance	Kelefence
PM6:BTP-eC9	Y6-10	17.86	18.81	[1]
PM6:BTP-eC9	PC71BM	17.86	18.66	[1]
PM6:BTP-eC9	Y6-10:PC71BM	17.86	19.35	[1]
PM6:BTP-eC9	Qx-5Cl	18.78	19.83	[2]
PM6:BTP-eC9	Qx-8Cl	18.78	18.81	[2]
PBQx-TF:eC9-2Cl	ATIC-C11	17.72	19.28	[3]
PBQx-TF:eC9-2Cl	ATIC-BO	17.72	18.52	[3]
D18:BTP-eC9-4F	DM-F	18.37	19.49	[4]
D18:L8-BO	DM-F	19.26	20.09	[4]
PM6:BO-4Cl	BO-5Cl	17.43	18.56	[5]
PM6:BTP-eC9	SMA	19.32	20.22	[6]

¹H NMR and MALDI-TOF-MS of the key intermediates and acceptors.



Figure S13. ¹H NMR spectrum of compound 3 in CDCl₃.



Figure S14. LC-Q-TOF mass spectrum of compound 3.



Figure S15. ¹H NMR spectrum of compound 5 in CDCl₃.



Figure S16. LC-Q-TOF mass spectrum of compound 5.



Figure S17. ¹H NMR spectrum of compound 6 in CDCl₃.



Figure S18. LC-Q-TOF mass spectrum of compound 6.



Figure S19. ¹H NMR spectrum of compound 8 in CDCl₃



Figure S20. LC-Q-TOF mass spectrum of compound 8.



Figure S21. ¹H NMR spectrum of compound 9 in CDCl₃



Figure S22. ¹H NMR spectrum of YQX-10 in CDCl₃



Figure S23. LC-Q-TOF mass spectrum of YQX-10.



Figure S24. ¹H NMR spectrum of compound 13 in $CDCl_3$



Figure S25. ¹H NMR spectrum of compound 14 in CDCl₃.



Figure S26. ¹H NMR spectrum of YQX-20 in CDCl₃



Figure S27. LC-Q-TOF mass spectrum of YQX-2O.

Uncategorized References

[1] W. Zhang, Y. Yue, R. Yang, Y. Zhang, W. Du, G. Lu, J. Zhang, H. Zhou, X. Zhang and Y. Zhang, Energy Environ. Sci., 2024, **17**, 2182-2192.

[2] L. Xie, Z. Chen, D. Yang, X. Yu, X. Tong, J. Ge, W. Song, S. Yang, J. Zhu and P. Ding, Energy Environ. Sci., 2024, **17**, 7838-7849.

[3] Y. Lang, H. Lai, Y. Fu, R. Ma, P. W. Fong, H. Li, K. Liu, X. Yang, X. Lu and T. Yang, Adv. Mater., 2025, **37**, 2413270.

[4] H. Lu, D. Li, W. Liu, G. Ran, H. Wu, N. Wei, Z. Tang, Y. Liu, W. Zhang and Z. Bo, Angew. Chem. Int. Ed.2024, 63, e202407007.

[5] C. He, Z. Chen, T. Wang, Z. Shen, Y. Li, J. Zhou, J. Yu, H. Fang, Y. Li and S. Li, Nat. Commun., 2022, **13**, 2598.

[6] Z. Chen, J. Ge, W. Song, X. Tong, H. Liu, X. Yu, J. Li, J. Shi, L. Xie and C. Han, Adv. Mater., 2024, **36**, 2406690.