Supporting Information

Substituted Quinoxaline based Small-Molecule Donor Guest Enable 19% Efficiency Ternary Organic Solar Cells

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<u>1. General Experimental Details</u>

Methods and Materials: All reagents from commercial sources were used without further purification. Solvents were dried and purified using standard techniques. Reactions were carried out under nitrogen atmosphere when appropriate. All compounds were characterized by NMR spectroscopy on Bruker Avance III Ultrashield Plus instruments using a 500 MHz proton frequency at the given temperatures. The spectra were referenced to the internal standard TMS. The photophysical and electrochemical properties of the materials were measured on UV-visible-near infrared spectrograph (Agilent Cary 60 spectrometer) and electrochemistry workstation (CHI660A, Chenhua Shanghai), respectively. Atomic force microscopy (AFM) images were characterized with a Veeco Multi-Mode 8 in a tapping mode. GIWAXS measurements were carried out on beamline BL16B1 at the Shanghai Synchrotron Radiation Facility (SSRF).

2. Synthetic Procedures



Scheme S1 The synthetic routes of QxBE and QxBC.

8,8'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6 diyl)bis(2,3-diethyl-5-(5'-hexyl-[2,2'-bithiophen]-5-yl)quinoxaline) (QxBE): А mixture of (2) (0.207 g, 0.4 mmol), (3) (0.181 g, 0.2 mmol) and Pd(PPh₃)₄ (0.023 g, 0.02 mmol) in a flask was subjected to three vacuum/nitrogen cycles, and degassed toluene (5.0 mL) was added to the flask. The reaction mixture was stirred in an oil bath for 24 hours at 120°C. The solvent was removed and the residue was purified via column chromatography over SiO₂ using CH₂Cl₂/hexanes (2/1) as the eluent. The product fraction was pooled, concentrated, purified by recrystallization, yielding QxBE as a dark red solid (176 mg, 61%). ¹H NMR (500 MHz, CDCl₃) δ 8.58 (s, 2H), 8.13 (d, J = 8.1 Hz, 2H), 8.04 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 3.6 Hz, 2H), 7.45 (d, J = 3.4 Hz, 2H), 7.15 (d, J = 3.7 Hz, 2H), 7.10 (d, J = 3.4 Hz, 2H), 6.97 (d, J = 3.4 Hz, 2H), 6.73 (d, J = 3.4 Hz, 2H), 3.16 – 3.09 (m, 8H), 2.95 (d, J = 6.8 Hz, 4H), 2.84 (t, J = 7.6 Hz, 4H), 1.74 (dt, J = 15.3, 5.0 Hz, 6H), 1.63 (t, J = 7.3 Hz, 6H), 1.54 – 1.50 (m, 10H), 1.43 - 1.34 (m, 20H), 1.04–0.89 (m, 22H). ¹³C NMR (126 MHz, CDCl₃) δ 156.36, 156.07, 155.79, 145.49, 145.35, 141.00, 140.49, 140.38, 138.05, 137.61, 137.00, 136.81, 135.48, 131.47, 130.38, 128.02, 127.08, 126.78, 125.36, 124.90, 124.56, 123.37, 123.10, 122.47, 77.32, 41.54, 37.64, 34.42, 32.63, 31.70, 31.53, 31.04, 30.34, 30.28, 29.80, 29.07, 28.92, 28.36, 25.75, 23.22, 22.70, 20.74, 20.06, 14.34, 14.21, 12.10, 11.86, 11.03, 10.70, 10.40. HRMS (+APCI, m/z): calcd. for C₈₆H₉₈N₄S₈ [M+H]⁺: 1442.56; found 1442.0068.



Figure S1 ¹H NMR spectrum of QxBE in CDCl₃.



Figure S2 ¹³C NMR spectrum of QxBE in CDCl₃.



Figure S3 High-resolution mass spectrometry (HRMS) of QxBE.

Tetraisopropyl 8,8'-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-*b*:4,5-*b*']dithiophene-2,6-diyl)bis(5-(5'-hexyl-[2,2'-bithiophen]-5-yl)quinoxaline-2,3-

dicarboxylate) (QxBC): A mixture of (1) (0.253 g, 0.4 mmol), (3) (0.181 g, 0.2 mmol) and Pd(PPh₃)₄ (0.023 g, 0.02 mmol) in a flask was subjected to three vacuum/nitrogen cycles, and degassed toluene (5.0 mL) was added to the flask. The reaction mixture was stirred in an oil bath for 24 hours at 120°C. The solvent was removed and the residue was purified via column chromatography over SiO₂ using CH₂Cl₂/hexanes (2/1) as the eluent. The product fraction was pooled, concentrated, purified by recrystallization, yielding QxBC as a dark purple solid (211 mg, 63%). ¹H NMR (500 MHz, CDCl₃) δ 8.44 (s, 2H), 8.24 (dd, J = 16.6, 8.1 Hz, 4H), 7.86 (d, J = 3.9 Hz, 2H), 7.48 (d, J = 3.4 Hz, 2H), 7.17 (d, J = 3.9 Hz, 2H), 7.10 (d, J = 3.4 Hz, 2H), 6.99 (d, J = 3.4 Hz, 2H), 6.73 (d, J = 3.4 Hz, 2H), 5.51 – 5.39 (m, 4H), 2.94 (d, J = 6.8 Hz, 4H), 2.83 (t, J = 7.6 Hz, 4H), 1.79–1.68 (m, 6H), 1.57 (d, J = 6.8 Hz, 20H), 1.54 – 1.48 (m, 4H), 1.41 (d, J = 6.3 Hz, 16H), 1.37 - 1.30 (m, 10H), 1.02 - 0.87 (m, 20H). ¹³C NMR (126 MHz, CDCl₃) & 164.15, 164.00, 145.79, 145.56, 143.67, 142.36, 141.76, 140.43, 139.08, 138.36, 137.11, 137.05, 136.90, 135.55, 134.91, 132.47, 131.15, 130.63, 128.20, 128.09, 127.51, 125.59, 124.78, 124.55, 123.67, 123.30, 122.61, 77.29, 77.04, 76.78, 70.46, 70.43, 41.32, 34.42, 32.63, 31.61, 31.46, 30.21, 28.98, 28.85, 25.73, 23.14, 22.61, 22.02, 21.73, 14.25, 14.11, 10.91. HRMS (+APCI, m/z): calcd. for C₉₄H₁₀₆N₄O₈S₈ [M+H]⁺: 1674.58; found 1674.0085.



Figure S4¹H NMR spectrum of QxBC in CDCl₃.





Figure S6 High-resolution mass spectrometry (HRMS) of QxBC.

3. Thermogravimetric analyses (TGA)

Thermogravimetric analyses (TGA) was performed with a TA TGA 50 under nitrogen atmosphere, with a set ramp rate of 10 $^{\circ}$ C/min, and using Al₂O₃ (alox) crucibles.



Figure S7 Thermogravimetric analyses (TGA) of QxBE and QxBC.

<u>4. Cyclic voltammetry (CV) and Computational analyses</u>

The electrochemical properties of the materials was measured by electrochemistry workstation (CHI660A, Chenhua Shanghai).



Figure S8 The results of cyclic voltammetry (CV) of QxBE and QxBC.



Figure S9 DFT of calculation at the B3LYP/6-31G(d,p) level of QxBE and QxBC.

SM	$\lambda_{ m abs}/{ m film}$	$\lambda_{\text{onset}}/\text{film}$	$E_{\rm opt}{}^a$	E_{HOMO}^{b}	E_{LUMO}^{c}	$E_{\rm echem}$	$ \text{HOMO} ^d$	$ LUMO ^d$	$\mathrm{HL}_{\mathrm{gap}}^{d}$
	(nm)	(nm)	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)
QxBE	564	632	1.96	-5.16	-3.20	1.96	4.97	2.60	2.37
QxBC	376	752	1.64	-5.21	-3.57	1.6 4	5.03	3.03	2.00

Table S1. Summary of optoelectronic properties of QxBE and QxBC.

^{*a*}Optical bandgaps estimated from the onset of the UV-Vis absorption spectra (films). ^{*b*}Estimated from cyclic voltammetry (CV) measurements; ${}^{c}E_{HOMO} \rightarrow E_{LUMO}$ gaps (E_{opt}); ^{*d*}DFT-calculated HOMO and LUMO energy levels (absolute values), and HOMO \rightarrow LUMO gaps (HL_{gap}).

<u>5. Device Fabrication</u>

The solar cells were prepared on glass substrates with tin-doped indium oxide (ITO, 15 Ω sq⁻¹) patterned on the surface (device area: 0.1 cm²). Substrates were first scrubbed with dilute Extran 300 detergent solution to remove organic residues before immersing in an ultrasonic bath of dilute Extran 300 for 15 min. Samples were rinsed in flowing deionized water for 5 min before being sonicated (Branson 5510) for 15 min

each in successive baths of acetone and isopropanol. Next, the samples were exposed to a UV-ozone plasma for 30 min. The PEDOT:PSS solution was spin coated onto a cleaned ITO, subsequently annealed at 150°C for 15 min in the air to obtain a PEDOT:PSS-covered ITO., and then transferred into a dry nitrogen glovebox (< 0.01 ppm O_2).

The chloroform solution with 0.5 vol% of 1-CN was spin-coated on PEDOT:PSS layer with 4000 rpm for 30 s to obtain a photosensitive active layer. The active layers were spin-cast from the solutions at an optimized speed of 4000 rpm in a time period of 30 s, using a programmable spin coater from Specialty Coating Systems (Model G3P-8), resulting in films of ca. 100 nm in thickness. At last, the Ag electrode were slowly evaporated onto the surface of PDINN layer under a vacuum pressure of 5 \times 10⁻⁶ Torr.

The J-V characteristics of the organic solar cells devices were measured by IVS-KA6000 Enlitech sunlight simulator equipped with an AM 1.5 filter at 100 mW cm⁻² and Keithley SMU source after correcting the light intensity with a standard calibration cell. The corresponding EQE spectrum was acquired in air by a QE-R system from Enli Technology Co. Ltd.

Table S2 Device parameters of PM6:QxBE:L8-BO (0.5%CN) with different weight ratio under thermal annealing at 90°C for 10 min.

Weight ratio	V_{OC} [V]	J_{SC} [mA cm ⁻²]	FF [%]	PCE [%]
1:0.05:1.2	0.889	26.26	78.09	18.24
1:0.1:1.2	0.895	26.38	78.89	18.63
1:0.2:1.2	0.896	26.47	77.37	18.35

Table S3 Device parameters of PM6:QxBC:L8-BO (0.5%CN) with different weight ratio under thermal annealing at 90°C for 10 min.

Weight ratio	V_{OC} [V]	J_{SC} [mA cm ⁻²]	FF [%]	PCE [%]
1:0.05:1.2	0.892	26.31	78.86	18.51
1:0.1:1.2	0.898	26.49	80.04	19.04
1:0.2:1.2	0.900	26.51	78.23	18.66

Table S4 Performance metrics for binary devices.									
Active Layer	V_{OC} [V]	J_{SC} [mA cm ⁻²]	FF [%]	PCE _{ave} ^a (PCE _{max}) [%]					
QxBE:L8-BO	0.886	15.37	38.40	5.21 (5.09±0.05)					
QxBC:L8-BO	0.895	15.61	39.04	5.45 (5.37±0.04)					

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^a Values represent averages derived from 10 distinct batches.



Figure S10 Current density-voltage (J-V) curves of SMDs:L8-BO binary devices.

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	No.	V_{OC} [V]	J_{SC} [mA cm ⁻²]	FF [%]	PCE [%]	Reference
-	1	0.904	26.73	78.52	18.96	1
	2	0.86	27.56	79.77	18.91	2
	3	0.906	26.91	76.1	18.55	3
	4	0.871	27.36	77.72	18.53	4
	5	0.889	26.86	77.52	18.52	5
	6	0.84	27.7	79.5	18.5	6
	7	0.860	27.97	76.9	18.50	7
	8	0.901	26.64	76.7	18.41	8
	9	0.895	26.84	76.5	18.41	9
	10	0.859	27.58	77.34	18.32	10
	11	0.868	26.43	78.8	18.07	11
	12	0.863	27.38	74.46	18.07	12
	13	0.856	27.13	77.6	18.02	13
	14	0.898	26.49	80.04	19.04	This Work

Table S5 Photovoltaic parameters of the reported 2D1A type ternary OSCs with SMD (PCE>18%) and this work.

6. Transient photovoltage (TPV) and transient photocurrent (TPC)

Transient photovoltage (TPV) and transient photocurrent (TPC) were characterized using Fluxim (PAIOS-4.0). TPV measurement was conducted under 1 sun conditions by illuminating the device with a white light-emitting diode, and the champion device was set to the open-circuit condition. For TPC measurement, the champion device was set to the short-circuit condition in dark. The output signal was collected by key sight oscilloscope. Voltages at open circuit and currents under short circuit conditions were measured over a 1 M Ω and a 50 Ω resistor, respectively.

7. SCLC Mobility

The hole and electron mobilities of the third component in optimized BHJ thin films were determined by fitting the dark current to the space-charge-limited current (SCLC) following configuration: model using the diode Glass/ITO/PEDOT:PSS/BHJ/MoO₃/Ag for hole-only diode, and Glass/ITO/ZnO/BHJ/PDINN/Ag for electron-only diode. The ITO substrates, bottom PEDOT:PSS layers and BHJ layers were prepared. A top MoO₃ layer (7.5 nm) was used as the electron-blocking layer and Silver cathode (100nm) were thermally evaporated through a shadow mask defining an active area of 0.04 cm^2 in the hole-only diodes. For electron-only device, the ZnO layer was spin coated by solution-processed method on top of ITO substrate. A PDINN layer (ca. 5nm) as the hole-blocking layer and Ag layer (100nm) as the anode were then thermally evaporated. Hole mobility and electron mobility were obtained by fitting the current density-voltage curves and calculated by the Eq. (1).

$$J(V) = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_0 \exp\left(0.89\beta \sqrt{\frac{V - V_{bi}}{L}}\right) \frac{(V - V_{bi})^2}{L^3} (1)$$

Where J is current density, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material (assumed to 3), μ_0 is hole mobility or electron mobility, V is applied voltage, V_{bi} is the buit-in voltage (0 V), and L is the thickness of BHJ (ca. 100 nm).



Figure S11 Dark current density-voltage characteristics at room temperature of optimized binary and ternary blend films for (a) hole-only diodes and (b) electron-only diodes. Note: The experimental data is fitted using the single-carrier SCLC model (solid lines). The solid lines are fits to the experimental data according to Equation.

Active lover	Carrier mobility [
	$\mu_{ m h}$	$\mu_{ m e}$	$\mu_{ m h}/\mu_{ m e}$
PM6:L8-BO	9.29	7.46	1.25
PM6:QxBE:L8-BO	11.10	9.53	1.16
PM6:QxBC:L8-BO	11.50	10.60	1.08

Table S6 The carrier mobility of binary and ternary devices.

8. Contact Angles (CA)

Table S7 Summary of contact angles and interaction parameters for PM6, QxBE, QxBC and L8-BO.

Matarial	Water contact	EG contact	γ^d	γ^p	Surface tension	Х _{РМ6:X}	<i>X</i> _{L8} – B0:Σ
wiateriai	angle [°]	angle [°]	[mN m ⁻¹]	[mN m ⁻¹]	[mN m ⁻¹]	[K]	[K]
PM6	103.4	76.5	24.43	0.47	24.90		_
QxBE	97.0	72.3	20.40	0.37	20.77	0.19	0.24
QxBC	88.2	68.3	15.61	7.15	22.76	0.05	0.08
L8-BO	93.8	68.4	22.84	2.67	25.51		

 γ^d and γ^p represent the dispersion component and polar component of surface free energy,

respectively, γ is the surface free energy, $\gamma = \gamma^d + \gamma^p$.

9. The molecular electrostatic potential (ESP)



Figure S12 The ESP of PM6, QxBE, QxBC and L8-BO.

10. Photoluminescence (PL) spectra



Figure S13 PL spectra of pristine PM6, two distinct SMDs, and their blend films.



<u>11. Transmission electron microscopy (TEM)</u>

Figure S14 TEM images of the binary and ternary blend films.

12. Grazing Incidence Wide-angle X-ray Scattering (GIWAXS)

GIWAXS and GISAXS was carried out on beamline BL16B1 at the Shanghai Synchrotron Radiation Facility (SSRF). The beam line has two detectors (PILATUS 900K for GIWAXS, with a pixel size of 172 μ m × 172 μ m) installed in-line downstream of the sample to collect successively X-ray scattering data simultaneously. The distance from the sample to the detector set to 160 mm and 2000 mm. An incident photon energy of 10 keV was applied, with a corresponding wavelength of 0.124 nm. An incident angle α of 0.15° (near the critical angle) was applied in the GIWAXS experiment, thus providing a global and strong (averaged) scattering signal for the sample.¹⁴ The GIWAXS data are collected with an exposure time of 30 s. One dimensional experimental data were obtained with the SGTools software package programmed by Zhao et al.¹⁵

Data analysis. The structural information of blend films such as the period of arrangement and lamellar stacking spacing is obtained via the Bragg equation, as well as the crystal coherence length (CCL) can be obtained from the Scherrer formula, and

the specific expressions of the Bragg equation and Scherrer formula are as follows:¹⁶

$$a = \frac{1}{2\sin(\theta)} = \frac{1}{q} \#(2)$$
$$CCL = \frac{K\lambda}{FWHM \cdot \cos(\theta)} \#(3)$$

where *d* is the lamellar stacking spacing, and *CCL* is the crystal domain along the specified direction called crystal coherence length, which is generally considered to be equivalent to the grain size. λ is the value of X-ray wavelength; *K* is a dimensionless shape factor, generally taken as K = 0.89; FWHM is the half-peak width of the scattering peak; θ is the scattering angle.¹⁷

	(010) diffraction peak				(100) diffraction peak			
	Q D FWHM CCL			Q	D	FWHM	CCL	
	$[nm^{-1}]$	[nm]	$[nm^{-1}]$	[nm]	$[nm^{-1}]$	[nm]	$[nm^{-1}]$	[nm]
PM6:L8-BO	17.44	0.36	3.81	1.65	2.91	2.16	1.09	5.76
PM6:QxBE:L8-BO	17.45	0.36	3.73	1.68	3.00	2.09	1.03	6.10
PM6:QxBC:L8-BO	17.53	0.36	3.05	2.06	3.04	2.07	0.86	7.30

 Table S8 Detailed GIWAXS parameters of the binary and optimized ternary films.

13. Film-depth-dependent light absorption spectroscopy (FLAS)

A self-developed soft plasma source generated by glow-discharging of low-pressure oxygen was used to incrementally etch the film without degage to the underneath films, which were in-situ monitored by a spectrometer. FLAS is extracted from the evolution of the light absorption spectra during soft plasma etching. The film-depth-dependent exciton generation is obtained upon the modified optical transmission matrix method, taking film-depth-dependent light absorption spectra and optical interference into simulation. The detail of the optical modeling is available in the literature published by Lu et al.¹⁸

13. Reference

- 1 C. Zhang, J. Li, W. Deng, J. Dai, J. Yu, G. Lu, H. Hu and K. Wang, *Adv. Funct. Mater.*, 2023, **33**, 2301108.
- X. Liao, M. Liu, H. Pei, P. Zhu, X. Xia, Z. Chen, Y. Zhang, Z. Wu, Y. Cui, G. Xu, M. Gao, L. Ye, R. Ma, T. Liu, X. Lu, H. Zhu and Y. Chen, *Angew. Chemie Int. Ed.*, 2024, 63, 2318595.
- 3 C. Liu, Z. Wu, N. Qiu, C. Li and Y. Lu, *ACS Appl. Mater. Interfaces*, 2023, **15**, 9764–9772.
- Z. Chen, W. Song, K. Yu, J. Ge, J. Zhang, L. Xie, R. Peng and Z. Ge, *Joule*, 2021, 5, 2395–2407.
- 5 Y. Yan, Y. Zhang, Y. Liu, Y. Shi, D. Qiu, D. Deng, J. Zhang, B. Wang, M. A. Adil, K. Amin, W. A. Memon, M. Wang, H. Zhou, X. Zhang and Z. Wei, *Adv. Energy Mater.*, 2022, **12**, 2200129.
- 6 D. Li, L. Wang, C. Guo, Y. Liu, B. Zhou, Y. Fu, J. Zhou, D. Liu, W. Li and T. Wang, *ACS Mater. Lett.*, 2023, **5**, 2065–2073.
- W. Zou, C. Han, X. Zhang, J. Qiao, J. Yu, H. Xu, H. Gao, Y. Sun, Y. Kan, X. Hao,
 G. Lu, Y. Yang and K. Gao, *Adv. Energy Mater.*, 2023, 13, 2300784.
- 8 Z. Li, C. Liu, J. Liu, C. Long, Y. Chen, X. Huang, L. Wei and N. Qiu, *New J. Chem.*, 2023, **47**, 17406–17412.
- 9 C. Zhang, J. Li, L. Ji, H. Hu, G. Li and K. Wang, *J. Mater. Chem. A*, 2022, **10**, 22812–22818.
- Y. Cheng, B. Huang, X. Huang, L. Zhang, S. Kim, Q. Xie, C. Liu, T. Heumüller, Z. Liu, Y. Zhang, F. Wu, C. Yang, C. J. Brabec, Y. Chen and L. Chen, *Angew. Chemie Int. Ed.*, 2022, 61, 2200329.
- W. Feng, S. Wu, H. Chen, L. Meng, F. Huang, H. Liang, J. Zhang, Z. Wei, X. Wan, C. Li, Z. Yao and Y. Chen, *Adv. Energy Mater.*, 2022, 12, 2104060.
- 12 M. Guan, W. Tao, L. Xu, Y. Qin, J. Zhang, S. Tan, M. Huang and B. Zhao, *J. Mater. Chem. A*, 2022, **10**, 9746–9752.
- 13 X. Chen, D. Wang, Z. Wang, Y. Li, H. Zhu, X. Lu, W. Chen, H. Qiu and Q. Zhang, *Chem. Eng. J.*, 2021, 424, 130397.
- 14 X. Sun, K. Liu, N. Zhao, F. Bian, C. Yang and Y. Huang, J. Phys. Chem. B, 2022, 126, 1625–1632.
- N. Zhao, C. Yang, F. Bian, D. Guo and X. Ouyang, *J. Appl. Crystallogr.*, 2022, 55, 195–203.
- 16 A. Mahmood and J. Wang, *Sol. RRL*, 2020, **4**, 2000337.
- 17 D.-M. Smilgies, J. Appl. Crystallogr., 2009, 42, 1030–1034.
- 18 L. Bu, M. Hu, W. Lu, Z. Wang and G. Lu, *Adv. Mater.*, 2018, **30**, 1704695.