Electronic Supplementary Information

Improving the efficiency of ternary organic solar cells by reducing energy loss[†]

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1. Experiment methods

Device fabrication. All the OSCs devices were fabricated by using a conventional structure of ITO/PEDOT:PSS/active layer/PNDIT-F3N/Ag. The ITO-coated glass substrates were washed sequentially under sonication with detergent, deionized water, alcohol, and isopropyl alcohol. Then the washed ITO glass was treated by oxygen plasma cleaning for 15 min. The PEDOT:PSS layer was deposited by spin-coating under 3500 rpm for 30 s on top of the ITO substrate and then annealed at 150 °C for 15 minutes. After the active layer blend solution were spin-coated on ITO glass, the electron-transport layer of PNDIT-F3N was spin-coated on the top of active layer from the methanol solution with a concentration of 0.5 mg/mL under 3000 rpm for 30 s. Finally, 160 nm of Ag was deposited onto the electron-transport layer under a pressure of 3×10^{-5} pa onto the PNDIT-F3N layer with a shadow mask to form a back electrode.

Except for the deposition of PEDOT:PSS layer, the other process were all carried out in the nitrogen-filles glovebox.

Fabrication details of the PM6:m-BTP-PhC6 based OSCs: the PM6:m-BTP-PhC6 ratio was kept at 1:1.2 (w/w). The optimal treatments involved are : (0.6%, v/v) chloronapthalene followed by TA at 100°C for 10 min.

Fabrication details of the PM6:Qx2 based OSCs: the PM6:Qx2 ratio was kept at 1:1.3 (w/w). The optimal treatments involved are : (0.6%, v/v) chloronapthalene associated with TA at 110°C for 10 min.

Fabrication details of the PM6:m-BTP-PhC6:Qx2 based OSCs: the PM6:acceptors ratio was kept at 1:1.4 (w/w). For different m-BTP-PhC6:Qx2 ratio, the optimal treatments involved is (0.6%, v/v) chloronapthalene associated with TA at 100°C for 10 min.

UV-vis absorption. Measured by Perkin Elmer Lambda950 spectrophot.

Contact angle measurement. Contact angles were measured with a contact angle meter (GBX DIGIDROP). The solution of each organic material was spin-coated on cleaned ITO substrates. Droplets of water and glycerol were dripped onto the different films.

Based on the Young equation, the relation between the contact angle and the surface tension of the solid surface is given:

$$\gamma_{\rm sv} = \gamma_{\rm lv} + \gamma_{\rm lv} * \cos\theta$$

(1)

(2)

where γ_{sv} , γ_{sl} , γ_{lv} are the surface tension of solid surface, liquid surface, and solid– liquid interface, respectively. θ is the inherent contact angle on the solid surface. The Flory–Huggins interaction parameter $\chi_{donor-acceptor}$ was used to evaluate the miscibility between the donor and acceptor, which could be calculated as follow:

$$\chi_{\rm donor - acceptor} = K \left(\sqrt{\chi_{\rm donor}} - \sqrt{\chi_{\rm donor}} \right)^2$$

where *K* is a positive constant, and γ_{donor} and $\gamma_{acceptor}$ are the respective surface energies of the donor and acceptor materials.

J-V and EQE Measurements. The current density-voltage (J-V) measurement of the

OSCs were measured under a illumination of AM 1.5G (100 mW cm⁻²) using Newport Thermal Oriel 91159A solar simulator, and the light intensity was calibrated with Newport Oriel PN 91150 V Si-based solar cell. J-V measurement signals were recorded by Keithley 2400 source-measure unit. Oriel Newport system (Model 66902) was used for external quantum efficiency (EQE) measurements.

Charge carrier mobility measurements. Hole and electron mobility were measured by the space-charge limited current (SCLC) method with hole-only devices and electron-only devices. The hole-only devices adopted ITO/PEDOT:PSS/active layer/MoO_x/Ag structure, while the electron-only devices adopting ITO/ZnO/active layer/PNDIT-F3N/Ag structure. The fabrication of the devices is the same as that of photovoltaic devices as described above. The hole and electron mobilities were calculated by using the space-charge-limited current (SCLC) method.

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3} \exp\left[0.89\gamma \sqrt{\frac{V}{d}}\right]$$

Where J is the current density, L is the thickness of the active layer, μ is the mobility, ε_0 is the free space permittivity, V (= V_{app} - V_{bi}) is the internal voltage, where V_{app} is the applied voltage, and V_{bi} is the built-in voltage.

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

TPV and TPC were measured by applying a 488 nm solid state laser (Coherent OBIS CORE 488LS) with a pulse width of=30 ns. The current traces were recorded by a mixed domain oscilloscope (ekeronix MDO3032) through converting the registered voltage drop across a 2 Ω resistor load connected in series to the solar cell. The absorbance spectra were obtained by using a UV-vis spectrometer (PE Lambda 650/850/950 UV-vis spectrophotometer).

Energy loss measurements. Highly sensitive EQE was measured by using integrated system (PECT-600, Enlitech), where the photocurrent was amplified and modulated by a lock-in instrument. EQE_{EL} measurements were performed by applying external voltage/current sources through the devices (ELCT-3010, Enlitech). EQE_{EL} measurements were performed for all devices according to the optimal device preparation conditions. EQE_{EL} values were obtained by the ratio of emitted photons and

injected electrons. The calculation formula is described as follow,

$$\eta_{\text{ELEQE}} = \frac{P\lambda/hc}{I/e}$$
(4)

Where P is the emitted power, λ is the emitted wavelength, h is the Plank's constant, c is the light speed, e is the electric charge.

Morphology and crystallization characterization. The atomic force microscopy (AFM) characterization was performed by Bruker Multimode 8 in ScanAsyst Mode in air. Grazing incidence wide-angle X-ray scattering

(GIWAXS) were performed by XEUSS waxs/saxs system, Xenocs, France. The X-ray wavelength is 1.5418 Å. The incident angle is 0.18°. 2D scattering patterns were collected by Pilatus 300K. The samples were prepared on Si/PEDOT:PSS substrates. The coherence length (CCL) was calculated from Scherrer equation:

$$CCL = \frac{2\pi K}{\Delta q}$$
(5)

Where Δq , is the full-width at half maximum of the peak and K is a shape factor (K=0.93 was used here)

2. Supplementary Tables

Active Layer combinations	Qx2 Content [%]	Voc (V)	Jsc (mA/cm^2)	Jsc ^b (mA/cm^2)	Fill Factor (%)	Efficiency ^a (%)
PM6:m-BTP-	0	0.850	25.69	24.04	78.43	17.12
PhC6	0	(0.848 ± 0.004)	(25.48 ± 0.23)	24.94	(78.37 ± 0.40)	(16.92 ± 0.12)
	10	0.860	26.08	25.27	77.98	17.49
	10	(0.852 ± 0.004)	(25.98 ± 0.18)	23.37	(78.23±0.46)	(17.31±0.12)
PM6:m-BTP- PhC6:Qx2	20	0.867	25.85	25.15	78.15	17.52
		(0.864±0.002)	(25.96±0.12)	25.15	(77.96±0.39)	(17.48±0.03)
	30	0.875	25.91	25.22	79.12	17.97
		(0.869±0.004)	(25.96±0.26)	25.52	(78.76±0.72)	(17.77±0.10)
	40	0.877	26.00	24.07	77.61	17.70
		(0.872 ± 0.005)	(25.82±0.18)	24.97	(77.59±0.23)	(17.46±0.15)
	50	0.881	25.72	24.05	77.19	17.50
		(0.880±0.003)	(25.64±0.11)	24.95	(77.00±0.45)	(17.37±0.11)
PM6:Qx2	100	0.935	24.28	22.00	75.37	17.11
		(0.937±0.003)	(24.34±0.25)	23.09	(74.29±0.79)	(16.95±0.10)

Table S1. Photovoltaic parameters of optimized binary and ternary OSCs under AM 1.5G irradiation (100 mW cm⁻²).

a) Average PCE values with standard deviation were obtained from at least 10 individual devices.

b) The values are the calculated current densities using EQE curves.

Table S2. Photovoltaic parameters of PM6:m-BTP-PhC6 and PM6:Qx2 based binary OSCs with a donor: acceptor ratio of 1:1.4 under AM 1.5G irradiation (100 mW cm⁻²).

	Voc	$J_{ m SC}$	Fill Factor	Efficiency	
Active Layer	(V)	(mA/cm^2)	(%)	(%) ^{a)}	
DM(DTD DLC(-1.1.4	0.850	25.50	78.38	16.99	
PM6:m-B1P-PhC6=1:1.4	(0.854±0.004)	(25.08±0.42)	(78.66±1.05)	(16.85±0.12)	
PM6:Qx2=1:1.4	0.937	23.78	75.55	16.84	
	(0.936±0.04)	(23.96±0.31)	(74.42±1.03)	(16.69±0.13)	

a) Average PCE values with standard deviation were obtained from at least 10 individual devices.

Table S3. Charge mobilities of the binary and ternary SCLC devices.

Qx2 content[wt%]	$u_{h}(cm^{2}V^{-1}s^{-1})$	$u_{e}(cm^{2}V^{-1}s^{-1})$	u/u h e
0	2.044E-04	1.5526E-04	1.3165
10	2.506E-04	1.9178E-04	1.3069
20	3.114E-04	2.4270E-04	1.2831
30	3.976E-04	3.4253E-04	1.1609
40	3.415E-04	2.8239E-04	1.2092
50	3.229E-04	2.5605E-04	1.2610
100	1.678E-04	1.0470E-04	1.6027

Table S4. Energy loss of the binary OSCs and the TOSCs with different Qx2 contents.

Qx2 content [wt%]	E _g (eV)	qV _{oc} (eV)	EQE _{EL}	qV _{oc} ^{SQ} (eV)	qV _{oc} ^{rad} (eV)	E _{loss} (eV)	ΔE_{1}	ΔE_2	ΔE_{3}
0	1.419	0.859	1.00E-4	1.156	1.094	0.560	0.263	0.062	0.238
10	1.418	0.863	1.42E-4	1.156	1.092	0.555	0.262	0.064	0.229
20	1.420	0.870	1.60E-4	1.157	1.097	0.550	0.263	0.060	0.226
30	1.420	0.881	1.94E-4	1.157	1.100	0.539	0.262	0.057	0.221
40	1.420	0.888	2.26E-4	1.157	1.100	0.532	0.262	0.057	0.217
50	1.421	0.892	2.96E-4	1.159	1.105	0.529	0.262	0.054	0.210
100	1.427	0.934	5.95E-4	1.164	1.124	0.493	0.263	0.040	0.192

 Table S5. The parameters of surface energy.

Film	θ _{Water} (°)	θ Glycerol (°)	γ (mN m ⁻¹)	γ^p (mN m ⁻¹)	γ^d (mN m ⁻¹)
PM6	102.38	85.36	14.11	3.52	10.59
m-BTP-PhC6	90.55	72.66	20.10	7.38	12.72
Qx2	97.65	79.40	16.86	4.49	12.37
m-BTP-PhC6:Qx2	94.78	75.89	18.56	5.22	13.34

3. Supplementary Figures



Figure S1. a) Current–voltage (J-V) characteristics of the optimized binary and ternary devices with different amounts of Qx2 under simulated AM 1.5 G illumination at 100 m W cm⁻²; b) corresponding EQE curves.



Figure S2. a) $J_{ph}-V_{eff}$ curves of optimized binary and ternary OSCs. b, c) Light intensity dependence of J_{SC} and V_{OC} of devices.



Figure S3. Semilogarithmic plots of normalized EL spectra and FTPS-EQE spectra as a function of energy for device based on a) PM6:m-BTP-PhC6, b) PM6:m-BTP-PhC6 :Qx2 c) PM6:Qx2 blends.