# **Electronic Supplementary Information**

# Improving voltage and quantum efficiency in bladed-coated ITO-free organic solar cells processed with a non-halogenated solvent

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## **Experimental section**

#### Materials

The donor material PM6 (9'-(2,12-di-tert-butyl-5,9-dioxa-13b-boranaphtho [3,2,1anthracen-7-yl)-9,9"diphenyl-9H,9'H,9"Hde] 3,3':6',3"-tercarbazole) was synthesized according to the literature (Adv. Mater. 2015, 27, 4655). Mn of PM6 determined from Gel Permeation Chromatography (GPC) is 139.1 kDa, Mw is 274.9 kDa, and PDI is 1.98. The acceptor materials Y6 ((2,2'-((2Z,2'Z)-((12,13-bis(2ethylhexyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4 e]thieno[2,"3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2b]indole-2,10-diyl)bis(methanylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1Hindene-2,1-divlidene))dimalononitrile)), (2,2'-((2Z,2'Z)-((12,13-bis(2-Y6DT decyltetradecyl)-3,9-diundecyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4e]thieno[2",3":4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-b]indole-2,10-diyl)bis(methaneylylidene))bis(5,6-difluoro-3-oxo-2,3-dihydro-1H-indene-2,1diylidene))dimalononitrile), and L8BO ((2,2'-((2Z,2'Z)-((12,13-bis(2-ethylhexyl)-3,9dibutyloctyl-12,13-dihydro-[1,2,5]thiadiazolo[3,4e]thieno[2,"3'':4',5']thieno[2',3':4,5]pyrrolo[3,2-g]thieno[2',3':4,5]thieno[3,2-

b]indole-2,10-diyl)bis(methanylylidene))bis(5,6-dif luoro-3-oxo-2,3-dihydro-1Hindene-2,1-diylidene))dimalononitrile)) were purchased from Nanjing Zhiyan Technology Co. , Ltd. The organic solvent OXY, CF and CN were purchased from Sigma-Aldrich.

#### **Device** fabrication

The OSCs were fabricated using the device architecture of glass/Ti/Al/Ti/active layer/MoO<sub>3</sub>/Au/Ag. The glass substrates were cleaned with detergent and then treated with a TL-1 solution, a mixture of water, ammonia, and hydrogen peroxide with a volume ratio 5:1:1, heated on a hotplate at 90 °C for 40 minutes. Subsequently, a multilayer of Ti (2 nm)/Al (80 nm)/Ti (2 nm) electrode was thermally evaporated onto the cleaned glass substrate in a vacuum chamber (<  $10^{-6}$  mbar). Then, the active layer was deposited on the Ti/Al/Ti electrode by spin coating at 3000 rpm for 30 s, or blade coating with a gap of 20 µm and a speed of 50 mm/s, in a nitrogen-filled glove box. The concentration of the active layer OXY solutions of PM6:Y6, PM6:Y6DT and PM6:L8BO was 18 mg/mL, and the concentration of the CF with 0.5 vol% CN solutions of PM6:Y6 was 20 mg/mL. After that, the MoO<sub>3</sub> (10 nm)/Au (1 nm)/Ag (5

nm) top electrode was thermally deposited onto the active layer in a vacuum chamber (<  $10^{-6}$  mbar). The active area of the solar cells was 0.04 cm<sup>2</sup>.

#### **Characterizations**

*J-V* measurements were conducted utilizing a solar simulator with an intensity of 100 mW cm<sup>-2</sup> (Newport Oriel VeraSol<sup>-2TM</sup> Class AAA) as the illumination and a Keithley 2450 digital source meter. The  $V_{OC}$  vs. light intensity curves were obtained by tuning the intensity of the solar simulator employing a set of optical filters.

**EQE and Highly sensitive EQE measurements** were determined by utilizing monochromatic light obtained from a halogen lamp (LSH-75, Newport) and a monochromator (CS260-RG-3-MC-A, Newport). To eliminate the overtone wavelengths from the monochromator, a series of long-pass optical filters were used. The monochromatic light was chopped with a frequency of 173 Hz by the optical chopper (3502 Optical Chopper, Newport). To record the current signal from the OSCs, a phase-locked amplifier (SR830, Stanford Instrument) and a front-end current amplifier (SR570, Stanford Instrument) were used. A Si detector (Hamamatsu s1337-1010BR) was used to calibrate the lamp intensity. The illuminated area was 0.5 mm<sup>2</sup>.

**EL and PL measurements** were performed by using a fluorescence spectrometer (KYMERA-328I-B2, Andor Technology) equipped with visible and near-infrared wavelength ranges to collect the emitted wavelengths from the samples. Two cameras included in the fluorescence spectrometer: the Si EMCCD camera (DU970P-BVF, Andor Technology) was used to record the emission intensity between the 400 to 1000 nm wavelength range, while the InGaAs camera (DU491A-1.7, Andor Technology) were used to collect the emission intensity of other wavelength ranges. For the EL measurement of the OSC, a Keithley 2400 source meter was employed to inject a current into the device. For the PL spectra measurement, a super continuous white laser (SuperK EXU-6, NKT photonics) and a narrow-band filter (LLTF Contrast SR-VIS-HP8, LLTF Contrast SR-SWIR-HP8, NKT photonics) were used as the excited light source, the excitation wavelength was 550 nm.

 $EQE_{EL}$  were obtained by using a home-built setup. The Keithley 2400 digital source meter was used to inject current into the OSC. The light emitted by the device was collected using a standard Si detector. Additionally, the current signal from the Si

detector was recorded through the Keithley 6482 picoammeter.

**TPV measurements** were performed using a green light-emitting-diode (LED) powered by the Keithley 2450 SourceMeter to provide the bias illumination. To provide the pulsed illumination, another green LED connected with an arbitrary function generator (AFG3022C, Tektronix) was employed. The OSC was placed in front of the LEDs and the voltage decay signal of the device was collected utilizing an oscilloscope (MDO4104C, Tektronix).

**SCLC measurements** were performed following the protocols developed in reference (org. electron. 2014, 15, 1263-1272). To evaluate the hole mobilities, hole-only devices with structure of ITO/PEDOT:PSS 4083/active layer/MoO<sub>3</sub>/Ag were fabricated. To determine the electron mobilities, electron-only devices with structure of ITO/ZnO/active layer/PFN-Br/Ag were made.

**AFM measurement.** AFM images were obtained utilizing the atomic force microscope of MFP-3D-BIO<sup>TM</sup> (Asylum Research), in a Tapping-Mode.

**Films thicknesses measurement.** The thicknesses of the films in this work, were measured using the profilometer (KLA-Tencor P-7 Stylus Profiler).

**UV-NIR-VIS spectra** in this work films were recorded employing a UV-Vis spectrometer (Lambda 950, PerkinElmer).

**TMM simulations.** The optical constants (n, k) of the materials used for the TMM simulations were determined by spectroscopic ellipsometry (J. A. Woolam M-2000). The thicknesses of the electrode films, interface films and active layer film used for the simulation are as follows: Glass/Ag (5 nm)/Au (1nm)/MoO3 (10 nm)/Active layer (100 nm)/Ti (2 nm)/Al (80 nm)/Ti (2 nm).

**GIWAXS measurements** were performed at beamline BL16B1 at Shanghai Synchrotron Radiation Facility. A 10 KeV X-ray beam was incident at a grazing angle of 0.15°. The scattered X-rays were recorded using a Dectris Pilatus 1-M photon counting detector. The samples were prepared on Si substrates.

**GPC measurements** were carried out at 45 °C on the ACQUITY APC instrument using THF as eluent equipped with two ACQUITY APC XT columns, a double flow type refractive index (RI) detector, and a TUV detector. The flow-rate was 0.5 mL min<sup>-1</sup>. Data acquisition was performed using the Empower software, and molecular weights and molecular weight distributions were calibrated with polystyrene standards.

TEM measurements were done using Talos F200X G2 (Thermo Scientific).



## **Supplementary Figures and Tables**

**Figure S1. (a)** Reflectance spectra of the Ag and Ti/Al/Ti electrodes used in this work. **(b)** Reflectance and transmittance spectra of the ITO and MoO<sub>3</sub>/Au/Ag electrodes used in this work. **(c)** Normalized absorption coefficient spectra of the PM6:Y6 active layers processed by spin-coating CF solution, spin-coating OXY solution, and blade-coating OXY solution. **(d)** Normalized absorption coefficient spectra of the PM6:Y6DT and PM6:L8BO active layers processed by blade-coating OXY solution.



**Figure S2.** IQE spectra calculated by dividing the measured EQE spectra by the TMM simulated EQE spectra, for the PM6:Y6 OSCs processed with different solvents and coating methods.



**Figure S3.** *J-V* curves of the PM6:Y6 electron-only devices constructed by (**a**) spin-coating CF solution, (**b**) spin-coating OXY solution, and (**c**) blade-coating OXY solution, corrected for the series resistance, for the determination of electron mobilities. *J-V* curves of the PM6:Y6 hole-only devices constructed by (**d**) spin-coating CF solution, (**e**) spin-coating OXY solution, and (**f**) blade-coating OXY solution, corrected for the series resistance, for the determination of hole mobilities. Statistical results are based on data from 4 individual devices.



**Figure S4.** Normalized reduced absorption and PL spectra of the PM6:Y6 active layers processed by (a) spin-coating CF solution, (b) spin-coating OXY solution, and (c) blade-coating OXY solution. The  $E_g$  values are determined from the crossing points of the absorption and PL spectra (*Sustainable Energy Fuels* **2018**, 2, 538).



**Figure S5.** TPV decay curves of the ITO-free PM6:Y6 OSCs processed by (**a**) spin-coating CF solution, (**b**) spin-coating OXY solution and (**c**) blade-coating OXY solution. (**d**) TPV decay lifetime as a function of bias photovoltage for the PM6:Y6 OSCs.



**Figure S6.** *J-V* curves of the PM6:Y6 electron-only devices constructed by (a) spin-coating CF solution, (b) spin-coating OXY solution, and (c) blade-coating OXY solution, for the determination of the density of electron traps. Statistical results are based on data from 4 individual devices.



**Figure S7.** *J-V* curves and the photovoltaic performance parameters of the PM6:Y6 OSCs, processed with a solvent additive (0.25% CN), or annealed at 100 °C for 5 min, compared to the as-cast device.



OSCs blade-coated from OXY in a glove box							
Active Layer	J <sub>SC</sub> (mA cm <sup>-2</sup> )	V <sub>OC</sub> (V)	FF (%)	PCE (%)			
PM6:Y6	18.4	0.74	67.5	9.2			
PM6:Y6DT	22.9	0.83	71.1	13.5			
PM6:L8BO	22.0	0.82	70.4	12.7			

OSCs blade-coated from OXY in air							
Active	$J_{ m SC}$	Voc	FF	PCE			
Layer	(mA cm <sup>-2</sup> )	(V)	(%)	(%)			
PM6:Y6	18.1	0.74	62.0	8.3			
PM6:Y6DT	22.4	0.83	69.5	12.9			
PM6:L8BO	21.8	0.82	65.4	11.7			

**Figure S8.** *J-V* curves and photovoltaic performance parameters of the OSCs based on PM6:Y6, PM6:Y6DT, and PM6:L8BO, blade-coated from OXY solution, constructed in air and in a glove box.



Figure S9. (a) A photograph of an ITO-free OSC, processed by blade-coating OXY solution with a large area of  $2.0 \text{ cm}^2$ . (b) A schematic picture of the architecture of the large-area device. (c) *J-V* curves, and (d) EQE spectra of the large-area devices based on PM6:Y6, PM6:Y6DT, and PM6:L8BO, processed by blade-coating OXY solution in glovebox. The photovoltaic performance parameters of the large-area devices are listed below in Table S1.

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Active Layer	$J_{\rm SC}$ (mA cm <sup>-2</sup> )	V <sub>OC</sub> (V)	FF (%)	PCE (%)
PM6:Y6	18.4	0.73	61.5	8.3
PM6:Y6DT	21.8	0.83	70.6	12.8
PM6:L8BO	20.4	0.82	65.7	11.0

**Table S1.** Representative photovoltaic performance parameters of the large-area OSCs (2 cm<sup>2</sup>), processed by blade-coating OXY solution in glovebox.



Figure S10. Normalized reduced absorption and PL spectra of the active layers based on (a) PM6:Y6DT and (b) PM6:L8BO, processed by blade-coating OXY solution. The  $E_g$  values are determined from the crossing points of the absorption and PL spectra.



**Figure S11.** *J-V* curves of the electron-only devices based on (a) PM6:Y6, (b) PM6:Y6DT, and (c) PM6:L8BO, constructed by blade-coating OXY solutions. Statistical results are based on data from 4 individual devices.



**Figure S12. (a)** Spectral irradiance distribution of AM1.5. **(b-i)** The optical constants (n, k) for the different layers in the OSC based on PM6:Y6-CF (spin-coated), with a device architecture of glass/Ti/Al/Ti/active layer/MoO<sub>3</sub>/Au/Ag.