

## Electronic Supplementary Information

### Use of Two Structurally Similar Small Molecular Acceptors Enabling Ternary Organic Solar Cells with High Efficiencies and Fill Factors

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## **Solar cell fabrication and characterization**

Solar cells were fabricated in a conventional device configuration of ITO/PEDOT:PSS/active layers/ZrAcAc/Al. The ITO substrates were first scrubbed by detergent and then sonicated with deionized water, acetone and isopropanol subsequently, and dried overnight in an oven. The glass substrates were treated by UV-Ozone for 30 min before use. PEDOT:PSS (Heraeus Clevis P VP AI 4083) was spin-cast onto the ITO substrates at 4000 rpm for 30 s, and then dried at 150 °C for 15 min in air. The PM6 (Mn =40.8 KDa with PDI of 2.04):acceptors blends (1:1 weight ratio) were dissolved in chloroform (the total concentration of blend solutions were 17 mg mL<sup>-1</sup> for all blends), with the addition of 0.25% DIO as additive, and stirred overnight on a hotplate at 40°C in a nitrogen-filled glove box. The blend solution were spin-cast at 2000 rpm for 40 s on the top of PEDOT:PSS layer followed by a solvent annealing step, which was conducted by placing chloroform in the petri dish for 40s. After solvent annealing, a thermal annealing step at 100 °C for 5 min was performed to remove the residual solvent. A thin Zracac layer (1.2 mg mL<sup>-1</sup> in ethanol, 3000rpm for 30 s, about 15 nm) was coated on the active layer. was coated on the active layer, followed by the deposition of Al (100 nm) (evaporated under 5×10<sup>-5</sup> Pa through a shadow mask). The optimal active layer thickness measured by a Bruker Dektak XT stylus profilometer was about 100 nm. The current density-voltage (J-V) curves of all encapsulated devices were measured using a Keithley 2400 Source Meter in air under AM 1.5G (100 mW cm<sup>-2</sup>) using a Newport solar simulator. The light

intensity was calibrated using a standard Si diode (with KG5 filter, purchased from PV Measurement to bring spectral mismatch to unity). Optical microscope (Olympus BX51) was used to define the device area (5.9 mm<sup>2</sup>). EQEs were measured using an Enlitech QE-S EQE system equipped with a standard Si diode. Monochromatic light was generated from a Newport 300W lamp source.

### **SCLC measurements**

The electron and hole mobility were measured by using the method of space-charge limited current (SCLC) for electron-only devices with the structure of ITO/ZnO/active layer/Zracoac/Al and hole-only devices with the structure of ITO/MoO<sub>x</sub>/active layers/MoO<sub>x</sub>/Al. The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the equation:  $J = 9\epsilon_0\epsilon_r\mu V^2/8d^3$ , where  $J$  is the current density,  $d$  is the film thickness of the active layer,  $\mu$  is the charge carrier mobility,  $\epsilon_r$  is the relative dielectric constant of the transport medium, and  $\epsilon_0$  is the permittivity of free space.  $V = V_{app} - V_{bi}$ , where  $V_{app}$  is the applied voltage,  $V_{bi}$  is the offset voltage. The carrier mobility can be calculated from the slope of the  $J^{1/2} \sim V$  curves.

**Atomic force microscopy (AFM).** AFM images were obtained by using a Dimension Icon AFM (Bruker) in a tapping mode.

**GIWAXS characterization.** GIWAXS measurements were performed at beamline 7.3.3 at the Advanced Light Source (ALS). Samples were prepared on Si substrates

using identical blend solutions as used in OSC devices. The 10 keV X-ray beam was incident at a grazing angle of 0.11°–0.15°, which maximized the scattering intensity from the samples. The scattered X-rays were detected using a Dectris Pilatus 2M photon counting detector.

**Resonant soft X-ray scattering.** R-SoXS transmission measurements were performed at beamline 11.0.1.2 at the ALS. Samples for R-SoXS measurements were prepared on a PEDOT:PSS modified Si substrate under the same conditions as used for OSC device fabrication, and then transferred by floating in water to a 1.5 mm × 1.5 mm, 100-nm thick Si<sub>3</sub>N<sub>4</sub> membrane supported by a 5 mm × 5 mm, 200 mm thick Si frame (Norcada Inc.). Two dimensional scattering patterns were collected on an in-vacuum CCD camera (Princeton Instrument PI-MTE). The beam size at the sample is 100 μm × 200 μm. The composition variation (or relative domain purity) over the length scales probed can be extracted by integrating scattering profiles to yield the total scattering intensity. The purer the average domains, the higher the total scattering intensity.

**Table S1.** The photovoltaic performance parameters of the binary and ternary PSCs at different contents of ITCPTC in the acceptor under AM 1.5G irradiation at 100 mW cm<sup>-2</sup>.

PM6:ITCPTC:MeIC	V <sub>oc</sub> <sup>a)</sup> (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
1:1:0	0.960±0.005	17.149±0.187	0.744±0.006	12.236±0.171

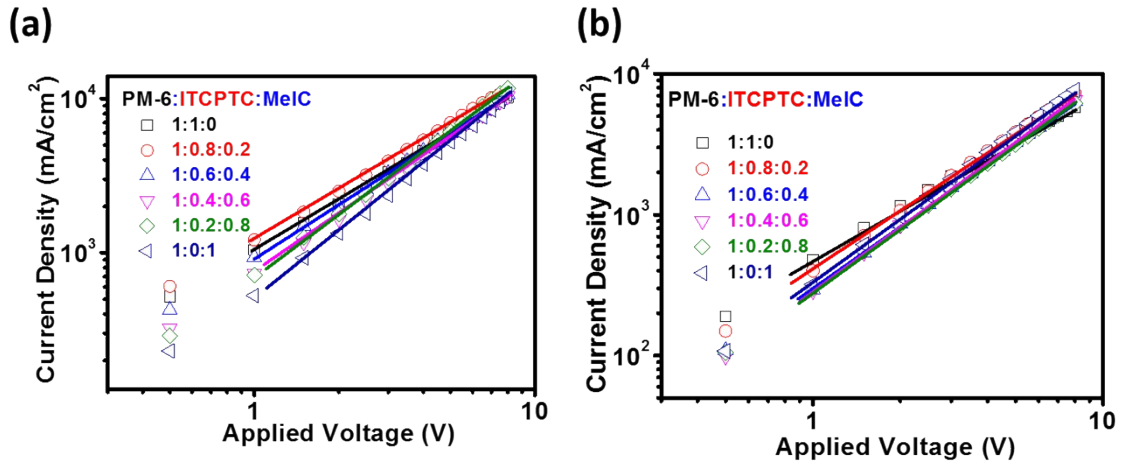
1:0.8:0.2	0.964±0.004	17.331±0.274	0.750±0.008	12.533±0.102
1:0.6:0.4	0.971±0.004	18.068±0.295	0.769±0.006	13.481±0.192
1:0.4:0.6	0.976±0.004	18.233±0.190	0.777±0.004	13.828±0.188
1:0.2:0.8	0.981±0.005	18.169±0.224	0.755±0.004	13.456±0.263
1:0:1	0.986±0.004	18.230±0.210	0.705±0.006	12.670±0.193

a) Average PCEs in brackets for 30 devices.

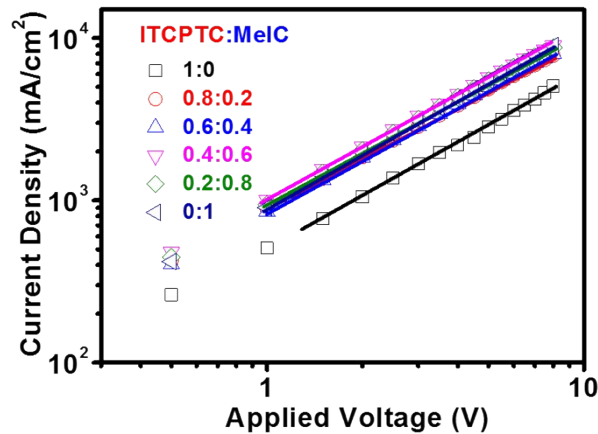
**Table S2.** Packing parameters for the pure PM6, ITCPTC and MeIC film, and the blend films based on the GIWAXS measurements.

Samples	In plane (100)			Out of plane(010)		
	Position	d-spacing	CL	Position	d-spacing	CL
	Å <sup>-1</sup>	Å	Å	Å <sup>-1</sup>	Å	Å
<b>PM6</b>	0.29	21.66	65.42	1.65	3.81	17.44
<b>ITCPTC</b>	0.34	18.47	49.84	1.70	3.69	13.96
<b>MeIC</b>	0.33	19.03	63.43	1.76	3.57	23.26

Samples	In plane (100) (donor/acceptor)			Out of plane(010)		
	Position	d-spacing	CL	Position	d-spacing	CL
	Å <sup>-1</sup>	Å	Å	Å <sup>-1</sup>	Å	Å
<b>PM6:ITCPTC</b>	0.29/0.34	21.66/18.47	120.31/148.46	1.70	3.69	17.92
<b>PM6:ITCPTC:MeIC</b>	0.29/0.31	21.66/20.26	167.02/62.18	1.70	3.69	18.47
<b>PM6:MeIC</b>	0.29/0.34	21.66/18.47	114.18/135.05	1.73	3.63	20.26



**Figure S1.** (a) PM6:ITCPTC:MeIC blend films with different ITCPTC content in hole-only devices; (b) PM6:ITCPTC:MeIC blend films with different ITCPTC content in electron-only devices.



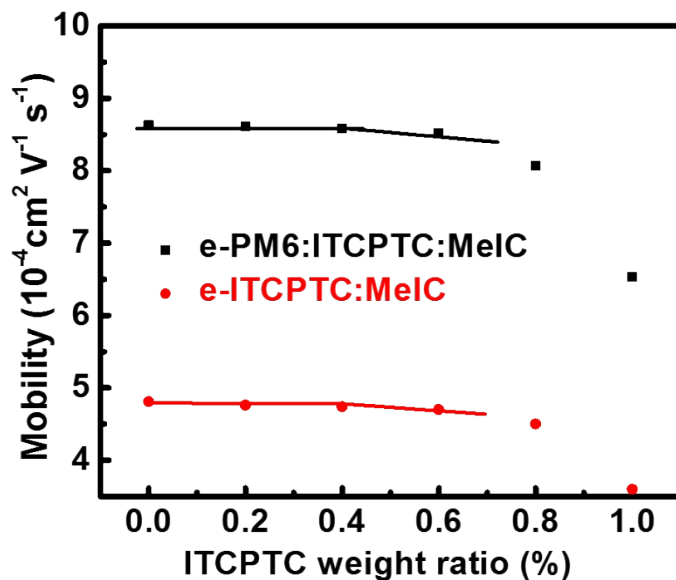
**Figure S2.** ITCPTC:MeIC blend films with different ITCPTC content in electron-only devices.

**Table S3.** The hole and electron mobility of PM6:ITCPTC:MeIC blend films with different ITCPTC content.

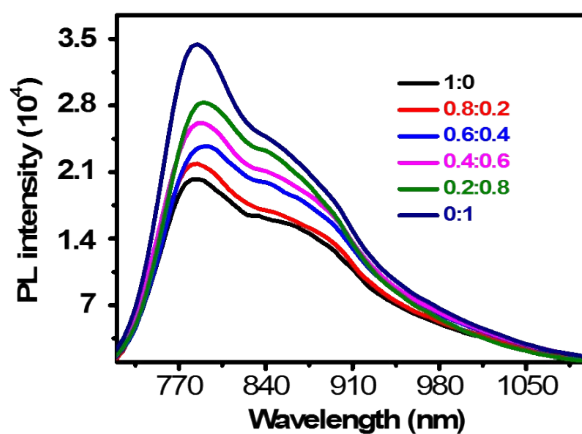
ITCPTC contents	$\mu_h$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )	$\mu_e$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ )	$\mu_h/\mu_e$
100%	$5.50 \times 10^{-4}$	$3.6 \times 10^{-4}$	1.53
80%	$6.77 \times 10^{-4}$	$4.50 \times 10^{-4}$	1.50
60%	$6.79 \times 10^{-4}$	$4.70 \times 10^{-4}$	1.45
40%	$6.81 \times 10^{-4}$	$4.74 \times 10^{-4}$	1.43
20%	$7.09 \times 10^{-4}$	$4.76 \times 10^{-4}$	1.49
0%	$8.44 \times 10^{-4}$	$4.81 \times 10^{-4}$	1.75

**Table S4.** The electron mobility of ITCPTC:MeIC blends with different ITCPTC contents.

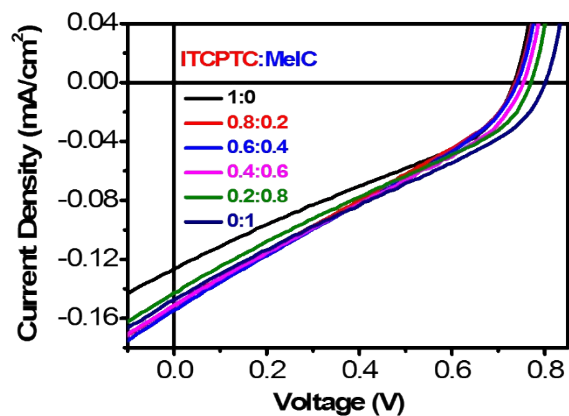
ITCPTC contents	0%	20%	40%	60%	80%	100%
$\mu_e$ ( $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ )	8.53	8.61	8.58	8.52	8.07	6.53



**Figure S3.** Electron mobilities of ternary blend films and ITCPTC:MeIC blend films with different ITCPTC contents.



**Figure S4.** PL spectra of ITCPTC:MeIC blend films with different ITCPTC contents (excited at 690 nm).



**Figure S5.** The current density-voltage (J-V) characteristics of organic solar cells based on ITCPTC, MeIC, and ITCPTC:MeIC blend films with different ITCPTC contents under simulated AM 1.5G irradiation ( $100 \text{ mW cm}^{-2}$ ).