GIWAXS and GISAXS measurements

To prepare samples for GIWAXS and GISAXS measurements, all films were cast on silicon wafers and received the same processing procedure as used in devices. GIWAXS was conducted at the I07 beamline of Diamond Light Source, UK. A custom sample cell with a Kapton exit window was constructed to surround the sample with helium in order to minimize air scatter. To export linecuts in the out-of-plane, the 1D profiles are exported at the specular beam position within the region of $q_{xy} = 0 \pm 0.03$ Å^{-1}. To export linecuts in the in-plane direction, the 1D profiles are exported at the specular beam position within the region $q_z = 0.03 \pm 0.03$ Å^{-1}. GISAXS measurements were performed at the beamline BL16B1 of the Shanghai Synchrotron Radiation Facility in China. The 1D profiles are exported at the specular beam position within the region $q_z = 0.03 \pm 0.002$ Å^{-1}.

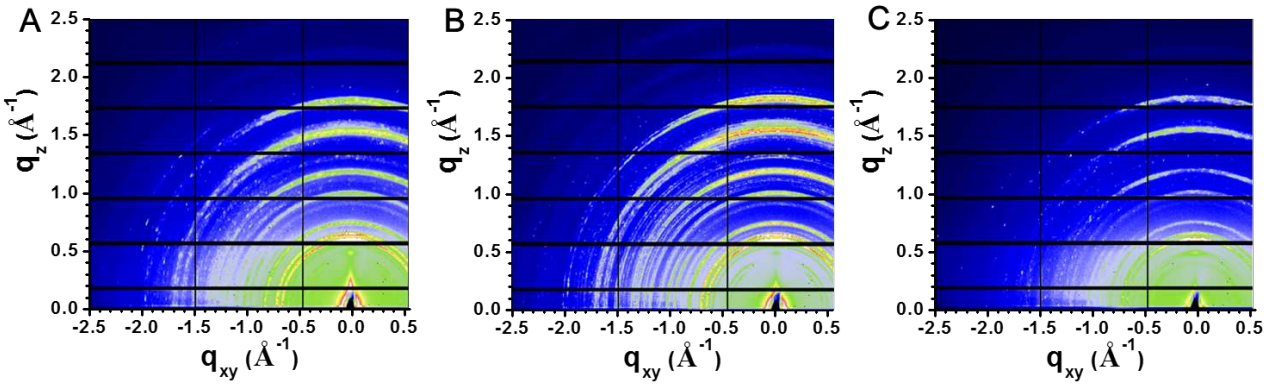

Figure S1 2D GIWAXS images of pure CO*i*8DFIC films (A) cast at RT, (B) cast at RT with SA and (C) cast on 100 ºC HS.

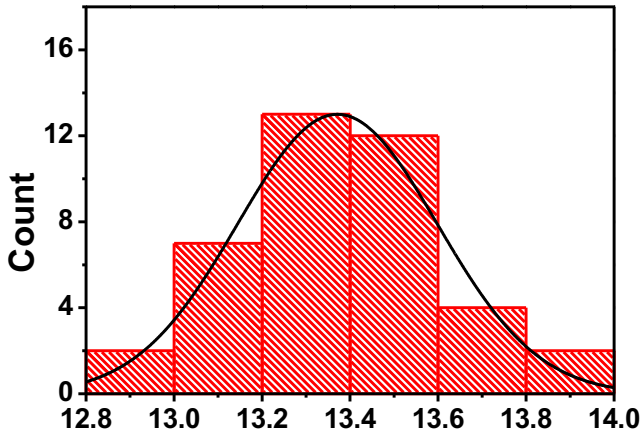

Figure S2 The efficiency distribution of device cast on 100 ºC HS. Statistics was obtained from 40 devices.

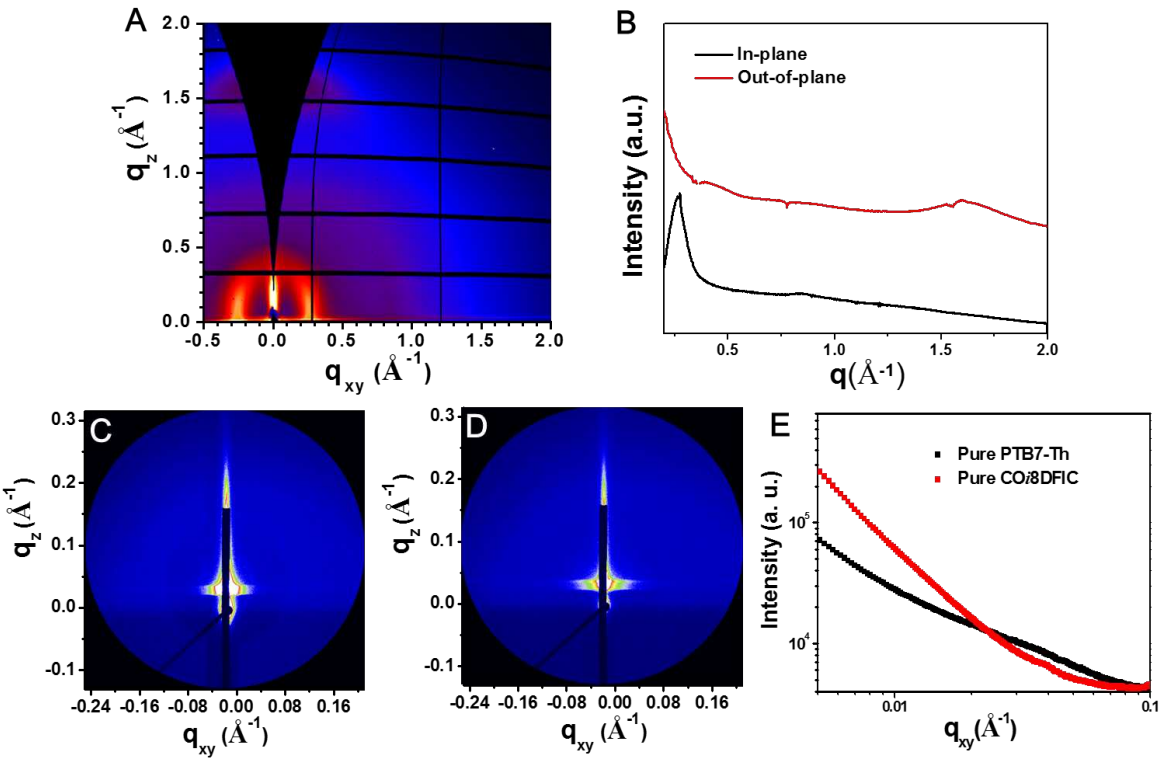

Figure S3 (A) 2D GIWAXS image of pure PTB7-Th film and its (B) out-of-plane and in-plane profiles. 2D GISAXS images of pure (C) PTB7-Th (D) and CO*i*8DFIC films. (E) GISAXS profiles of pure PTB7-Th and CO*i*8DFIC films along the q_{xy} axis.

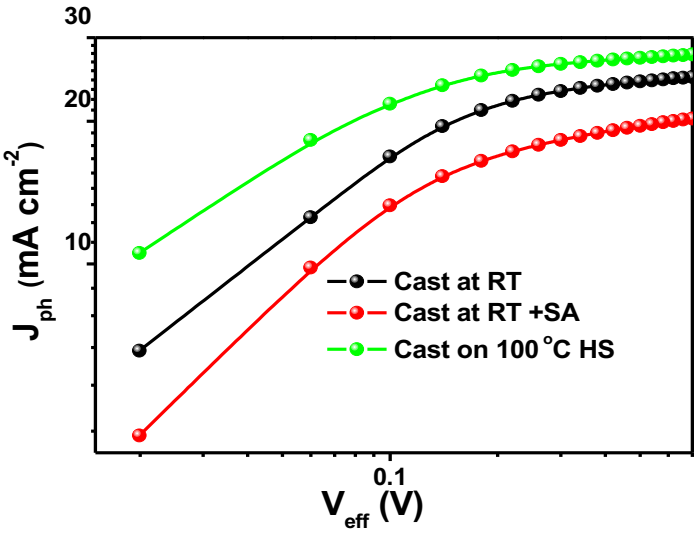

Figure S4 Photocurrent density versus effective voltage curves of PTB7-Th:CO*i*8DFIC films prepared using different methods.

Space-charge limited current (SCLC) measurements

The hole and electron mobilities of devices were extracted using the space charge limited current (SCLC) method. The device structures for hole-only and electron-only devices are ITO/PEDOT:PSS/PTB7-Th:CO*i*8DFIC/MoO_3/Ag and ITO/TiO_2/PTB7-Th:CO*i*8DFIC/Ca/Ag,

respectively. Mobilities were obtained by fitting the current-voltage curves in the range from 2.5 to 6 V of the space charge limited range, where the SCLC is described following the equation below:

$$J = \frac{9\varepsilon_r\varepsilon_0\mu_0(V - V_{bi})^2}{8L^3}$$

Here ε_0 is the permittivity of free space ($8.85\text{x}10^{-12}$ F m^{-1}), ε_r is the relative permittivity of the material (3), μ_0 is the hole or electron mobility, V is the applied voltage, V_{bi} is the built-in voltage, L is the thickness of the organic layer (To avoid current leakage induced by CO*i*8DFIC large crystals in the active layer, the thicknesses of the active layer was controlled round 200 nm.)

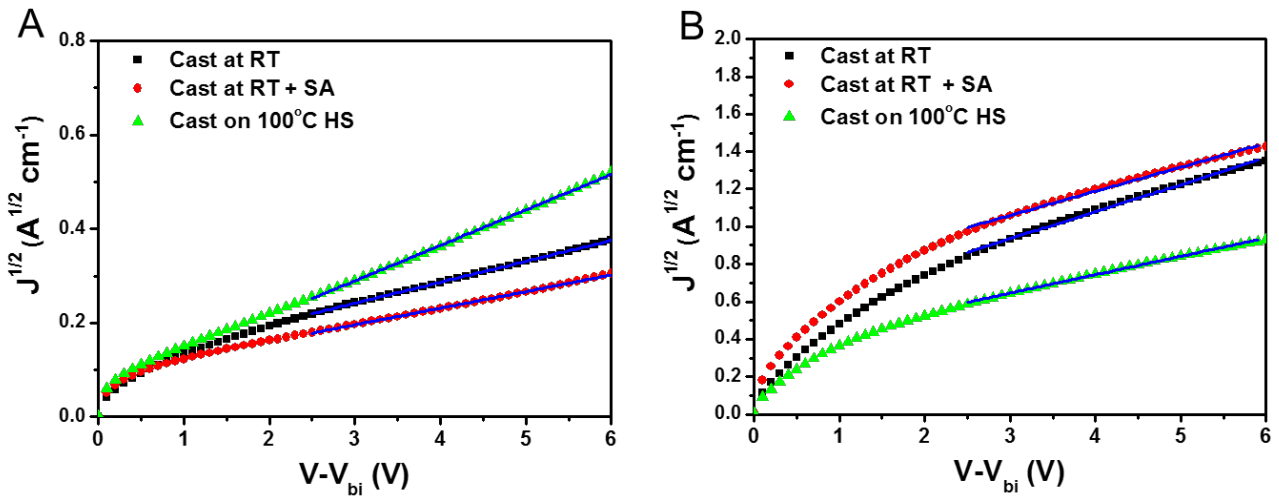

Figure S5 Root square plots of (A) electron current densities versus bias voltage of the ITO/TiO_2 /Active layer/Ca/Ag electron-only devices and (B) hole current densities versus bias voltage of the ITO/PEDOT:PSS/Active layer/MoO_3/Ag hole-only devices.

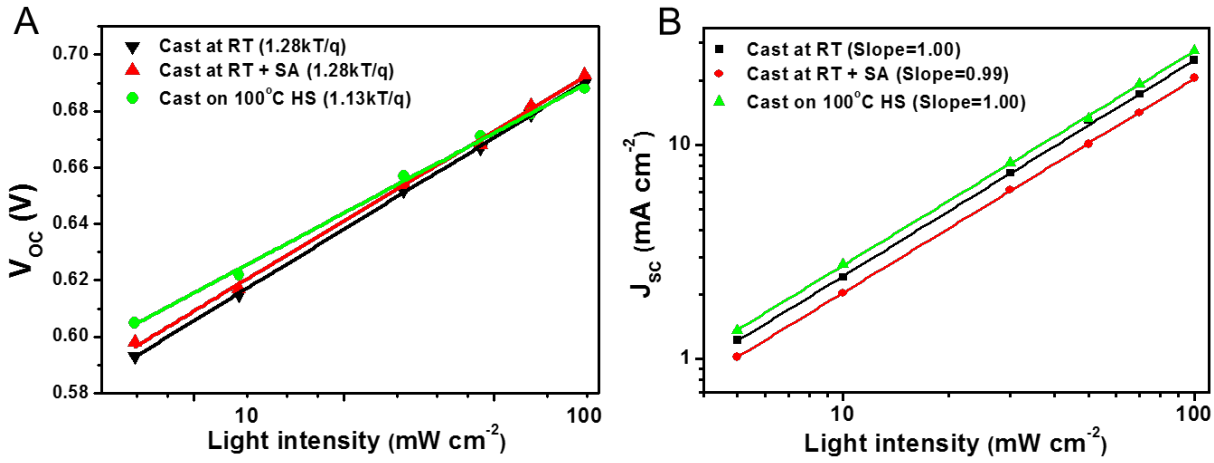

Figure S6 (A) V_{oc} versus light intensity and (B) J_{sc} versus light intensity of PTB7-Th:CO*i*8DFIC OPVs prepared with different methods. The slope gradients are indicated in brackets.