A Nonfullerene Acceptor with 1000 nm Absorption Edge Enables Ternary Organic Solar Cells with Improved Optical and Morphological Properties and Efficiencies over 15%

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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 Clevios 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 PM7:acceptors blends (1:1 weight ratio) were dissolved in chloroform (the total concentration of blend solutions were 16 mg mL^{-1} 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 3000 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 90 °C for 5 min was performed to remove the residual solvent. A thin Zracac layer was coated on the active layer. was coated on the active layer, followed by the deposition of Al (100 nm) (evaporated under 5×10^{-5} Pa through a shadow mask). The optimal active layer thickness measured by a Bruker Dektak XT stylus profilometer was about 105 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^{-2}) 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 (4.6 mm^2). 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/Zracac/Al and hole-only devices with the structure of ITO/MoO_x/active layers/MoO_x/Al. The charge carrier mobility was determined by fitting the dark current to the model of a single carrier SCLC according to the equation: $J = 9\varepsilon_0\varepsilon_r\mu V^2/8d^3$, where J is the current density, d is the film thickness of the active layer, μ is the charge carrier mobility, ε_r is the relative dielectric constant of the transport medium, and ε_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 measurement were carried out with a Xeuss 2.0 SAXS/WAXS laboratory beamline using a Cu X-ray source (8.05 keV, 1.54 Å) and a Pilatus3R 300K detector. The incidence angle is 0.2°. The samples for GIWAXS measurements are fabricated on silicon substrates using the same recipe for the devices.

GISAXS characterization. GISAXS was conducted at 19U2 SAXS beamline at Shanghai Synchrotron Radiation Facility, Shanghai, China, using the 0.15° incident angle with 10 keV primary beam.

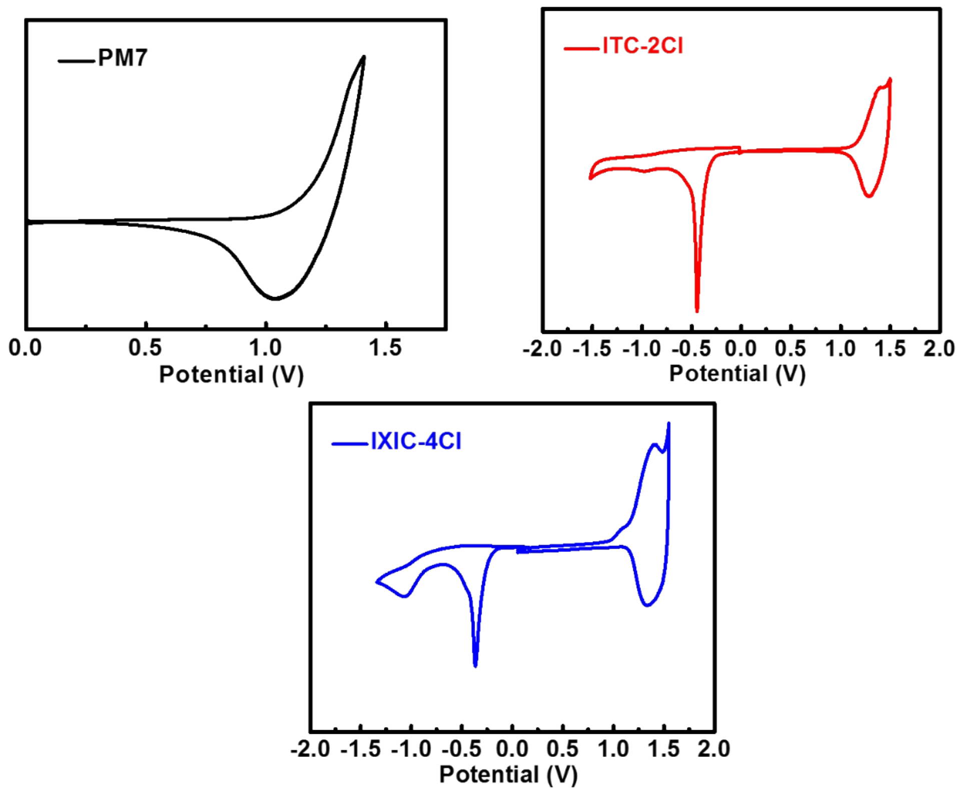

Figure S1. The CV curves of PM7, ITC-2Cl and IXIC-4Cl.

Table S1. Photovoltaic parameters of highly efficient ternary organic solar cells.

Binary blend (D:A)	**PCE (%)**	***The third component***	**PCE (%)**	**Increased PCE (%)**	**Ref**
PBDB-T:IT-M	11.10	N2200	12.10	1.0	1
PBT1-C:ITIC-2Cl	11.47	MeIC2	12.55	1.08	2
PBDB-T:ITCPTC	11.0	IDT6CN-M	11.9	0.9	3
PFTB-O:ITIC-Th	10.2	SF-PDI_2	10.5	0.3	4
PTB7-Th:CO*i*8DFIC	11.47	BDTThIT-4F	13.08	1.71	5
PBDB-T:NNBDT	11.7	FDNCTF	12.8	1.1	6
J51:ITIC	8.9	PTB7-Th	9.7	0.8	7
PSEHTT:PTB7-Th	8.1	PTB7-Th	8.5	0.4	8
PBDB-T:ITIC	10.8	PDTfBO-TT	12.1	1.3	9
PBDB-T:IT-M	11.71	P1	13.52	1.81	9
PTB7-Th:IOTIC-2F	12.1	ITIC-2F	12.9	0.8	10
PTB7-Th:3TT-FIC	12.21	PCBM	13.54	1.33	11
PBDB-T:INPIC-4F	12.55	MeIC1	13.73	1.19	12
PM6:ITCPTC	13.04	MeIC	14.13	1.09	13
PBDB-T-2F:IT-4Cl	13.45	IT-2Cl	14.18	0.73	14
PM7:ITC-2Cl	**13.72**	**IXIC-4Cl**	**15.37**	**1.65**	**This work**

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Appendix: Summary of Certificate

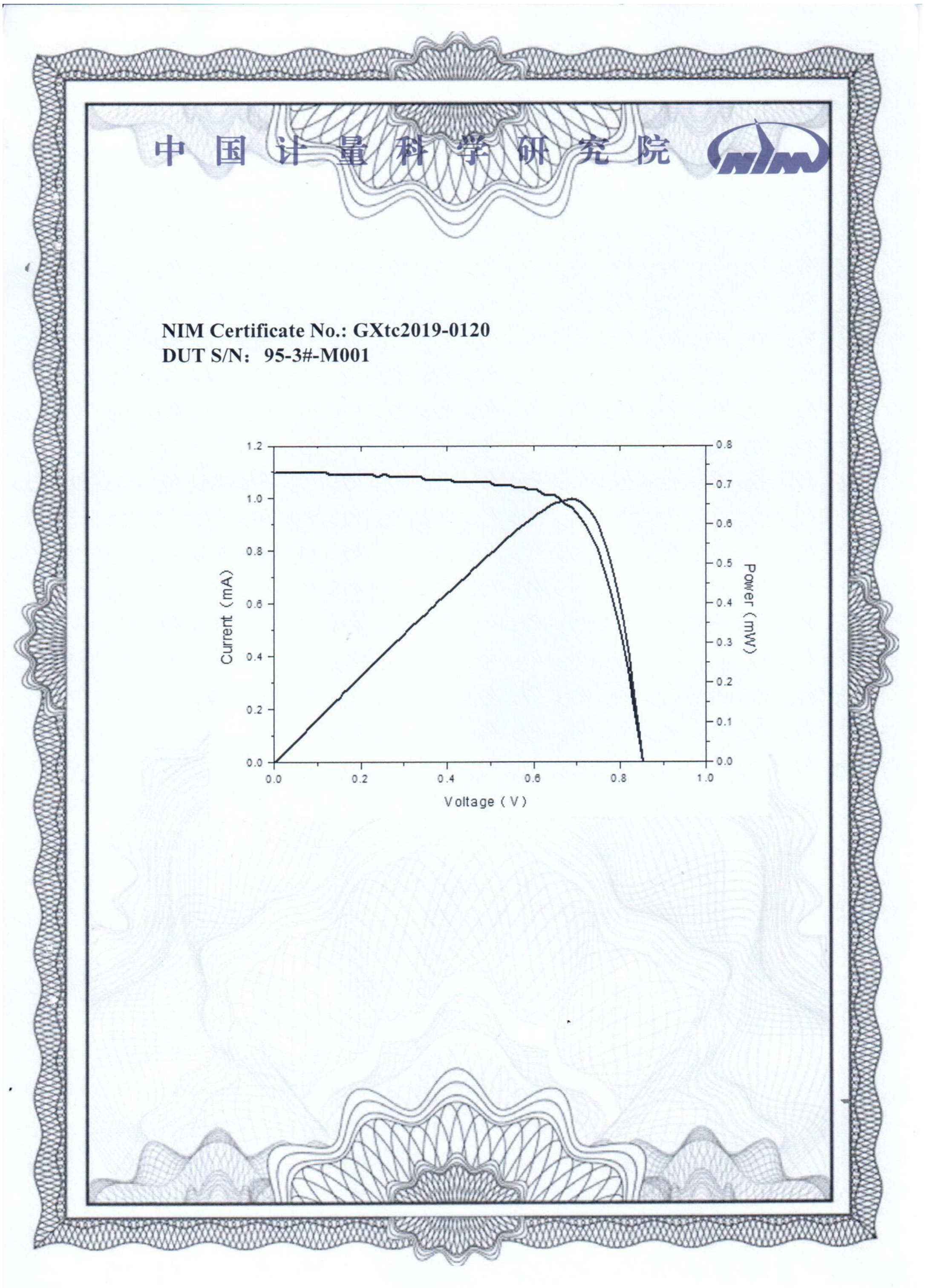
NIM Certificate No.: GXtc2019-0120
DUT S/N：95-3#-M001
Date of Test: 01/18/2019
Manufacturer：Hong Kong University of Science and Technology
Type：Organic Solar Cells
Temperature Sensor/Control System: None
Mask: An aperture area of 4.638 mm^2 (Certificate No.: CDjc2019-0416)
Environmental conditions at the time of calibration: (20.8±1) ℃, RH (22±2) %

The calibration has been conducted by the PV Metrology Lab of NIM (National Institute of Metrology, China). Measurement of irradiance intensity and all other measurements are traceable to the International System of Units (SI). The performance parameters reported in this certificate apply only at the time of the test for the sample.

I_{sc} [mA]	1.100	V_{oc} [V]	0.854	P_{max} [mW]	0.664
I_{max} [mA]	0.962	V_{max} [V]	0.690	Efficiency [%]	14.32
FF [%]	70.70	Area [mm^2]	4.638		

Methods:
I-V: IEC60904-1: Measurement of photovoltaic current-voltage characteristics
JJF 1622-2017: Calibration Specification of Solar Cells：Photoelectric Properties
Standard Test Conditions (STC):
Spectrum: AM 1.5G (ASTM G173-03/IEC 60904-3 ed.2); 1000 W/m^2 at 25.0 ℃.
Secondary Reference Cell:
Device S/N: 81#
Device Material: Mono-Si
Solar Simulator:
Classification: AAA (Double-light source: Xeon and Halogen)
Total irradiance: 1000 W/m^2 based on I_{sc} of the above Secondary Reference Cell.

Issue Date	01/18/2019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NIM Certificate No.: GXtc2019-0120

DUT S/N：95-3#-M001

Figure S2. Certificate report of a packaged conventional device based on PM7:ITC-2Cl:IXIC-4Cl in National Institute of Metrology, China.

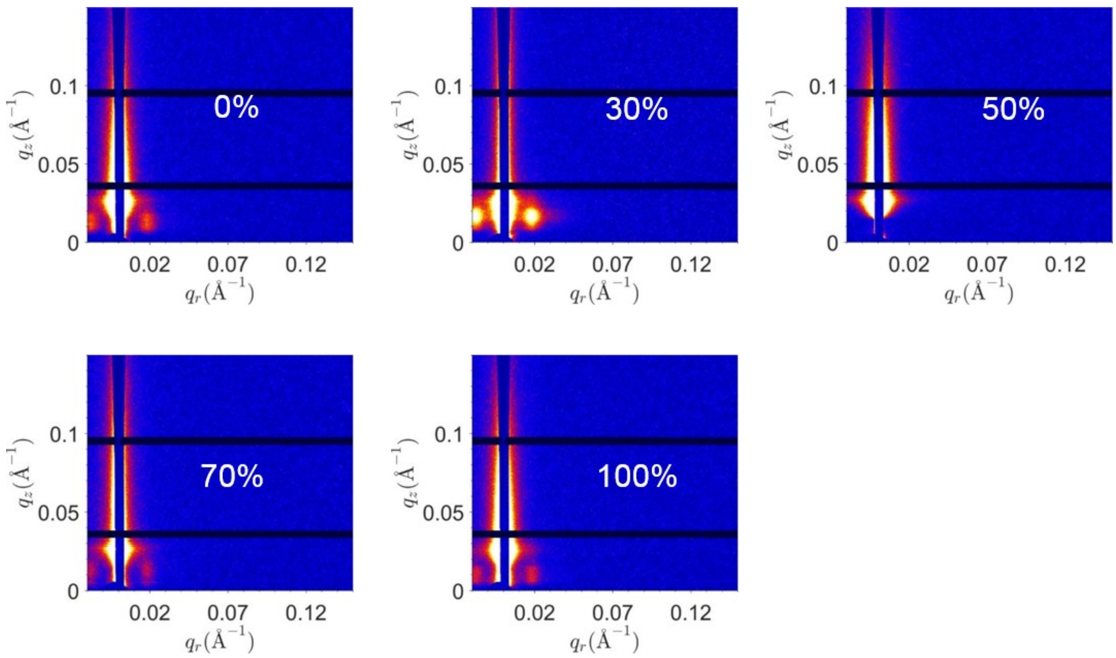

Figure S3. 2D GISAXS patterns of the ternary blend films with different IXIC-4Cl contents.

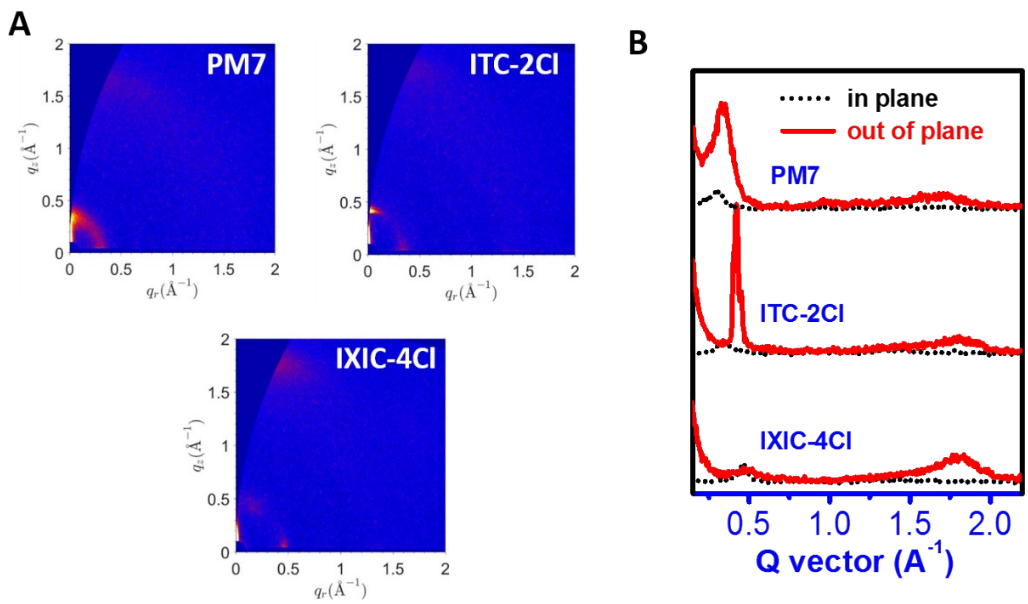

Figure S4. (a) GIWAXS patterns of PM7, ITC-2Cl and IXIC-4Cl neat film; b) The out-of-plane (red line) and in-plane (black line) line-cut profiles of GIWAXS patterns.

Table S2. The parameters of exciton dissociation efficiency and charge collection efficiency.

PM7:ITC-2Cl:IXIC-4Cl	J_{sat} (mA cm^{-2})	J_{ph}^{a} (mA cm^{-2})	J_{ph}^{b} (mA cm^{-2})	η_{diss} (%)	η_{coll} (%)
1:1:0	20.94	20.27	17.79	96.8	84.9
1:0.5:0.5	24.58	23.99	21.40	97.6	87.1
1:0:1	23.44	21.60	18.61	92.2	79.4

a: Under short circuit condition; b: Under the maximal power output condition

Table S3. The hole and electron mobility of PM7:ITC-2Cl:IXIC-4Cl blend films with different IXIC-4Cl content.

IXIC-4Cl contents	μ_h (cm^2 V^{-1} s^{-1})	μ_e (cm^2 V^{-1} s^{-1})	μ_h/μ_e
0%	6.50×10^{-4}	3.90×10^{-4}	1.67
30%	6.89×10^{-4}	4.50×10^{-4}	1.53
50%	7.08×10^{-4}	4.80×10^{-4}	1.48
70%	7.51×10^{-4}	4.35×10^{-4}	1.73
100%	8.39×10^{-4}	4.36×10^{-4}	1.92

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