Blade-coated organic solar cells from non-halogenated solvent offer 17% efficiency

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SUPPORTING INFORMATION

Experimental

Materials

Poly[(thiophene)-alt-(6,7-difluoro-2-(3-hexylundecyloxy) quinoxaline] (PHT4) were provided by coauthors. Detailed synthesis and characterization of PHT4 will be reported separately. Its molecular weight is 24.8 kDa. IT-4Cl and $PC_{71}BM$ were purchased from Derthon Optoelectronic Materials Science Technology Co., Ltd. ZnO (Avantama N-10) was bought from Avantama AG. PFN-Br was bought from Organtec Inc. PM6, Y6, and PNDIT-F3N were available in eFlexPV Ltd. The mixing ratio of PHT4 and IT-4Cl is 1 : 1 (w/w), and the total concentration is 15 mg/ml in *o*-xylene. The mixing ratio of PM6 : Y6 : $PC_{71}BM$ is 1 : 0.96 : 0.24 (w/w/w), and the total concentration is 8.5 mg/ml in *o*-xylene. The solutions were stirred at 60 °C for 2 h before active layer deposition. PFN-Br film was fabricated using the same method as Ref. [1].

Device fabrication

All devices were fabricated on ITO glass substrates. The glass substrates were ultrasonically cleaned successively with isopropanol, acetone, alkaline lotion, deionized water (three times), and isopropyl alcohol.

For PHT4:IT-4Cl device, a ZnO film (~35 nm) was firstly spin-coated on ITO. Then, a PFN-Br film (~5 nm) was spin-coated on ZnO. The PHT4:IT-4Cl film was blade-coated on top of PFN-Br at 60 °C. The gap between blade and substrate was ~80 μm, while the coating speed was 10 mm/s. Then, the films were dried in a vacuum at room temperature. The vacuum pressure is 10^{-1} Pa, and the vacuum treatment time is 2 min. Later, the PHT4:IT-4Cl film was removed from the vacuum and annealed at 120 °C for 5 min. Next, a MoO_3 (~10 nm)

and a silver (Ag, ~100 nm) were sequentially deposited on active layers by thermal evaporation. Finally, the devices were encapsulated with glass slides. The device sizes are 4 mm^2 and 1 cm^2.

For PM6:Y6:$PC_{71}BM$ device, a PEDOT:PSS (~30 nm) was firstly spin-coated on ITO. Then, the PM6:Y6:$PC_{71}BM$ film was blade-coated on top of PEDOT:PSS at 40 °C. The corresponding gap is 80 μm, and the coating speed is 8 mm/s. Next, the film was also dried in a vacuum at room temperature. The vacuum pressure is 10^{-1} Pa, and the treatment time is 5 min. Later, a PNDIT-F3N (~5 nm) was spin-coated on the active layer, following by a thermal evaporated Ag (~100 nm) layer.

Device measurements

The current density−voltage (*J*−*V*) characteristics are measured using a Keithley 2400 source meter. Standard solar radiation (AM 1.5G) is from a Class AAA solar simulator (Sun 2000, Abet). The external quantum efficiency (EQE) spectra were measured by using a QE-R test system from Enli Technology Company. Transient photovoltage (TPV), transient photocurrent (TPC), impedance spectroscopy (IS), and photo-induced charge extraction linear increasing voltage (Photo-CELIV) measurements are all performed using Paios system (FLUX-iM AG). The film thickness is measured with a surface profiler (XP-2). The film topography is investigated using atomic force microscopy (AFM, Bioscope Catalyst Nanoscope-V). UV−vis absorption spectra are recorded by a Shimadzu UV-2550 UV−vis spectrophotometer. A transient drying monitoring technique is utilized to track the film specular reflection. The setup was equipped with a blue LED and a CMOS camera (IDS uEye). GI-WAXS measurements are performed at beamline 7.3.3 and 11.0.1.2[2] at the Advanced Light Source, supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. The GIWAXS samples were fabricated using identical processing conditions as in devices. The 10 keV X-ray beam is incident at a grazing angle of 0.12°–0.16°, selected to maximize the samples' scattering intensity. The scattered x-rays are detected using a Dectris Pilatus 2M photon-counting detector. The authors thank Chenhui Zhu at beamline 7.3.3, and Cheng Wang at beamline 11.0.1.2 for assistance.

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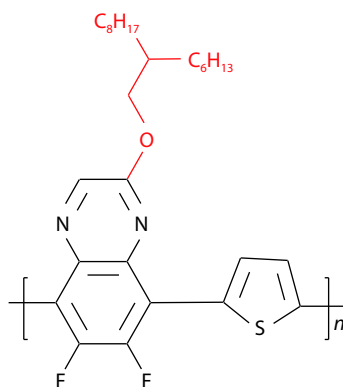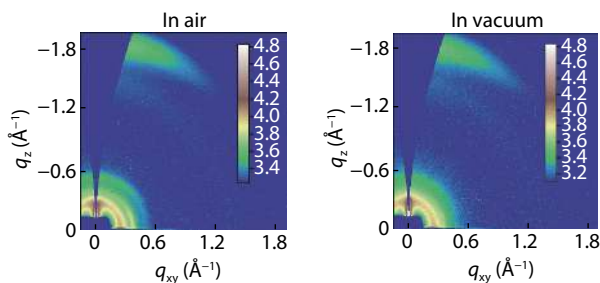
Fig. S1. Chemical structure of PTQ10.

Fig. S2. (Color online) 2D GIWAXS images for PHT4:IT-4Cl films, dried in air and vacuum, respectively.
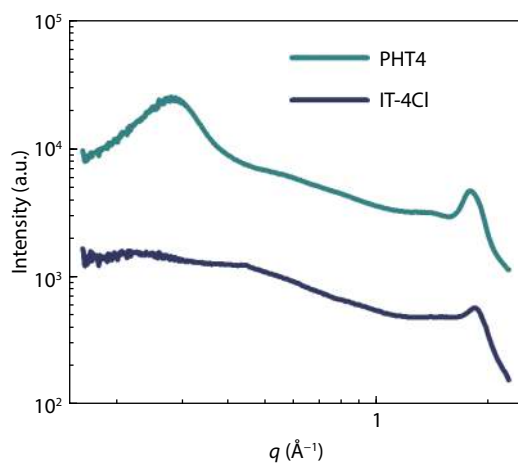

Fig. S3. The line-cut profiles of GIWAXS images for PHT4 and IT-4Cl along the out-of-plane direction.
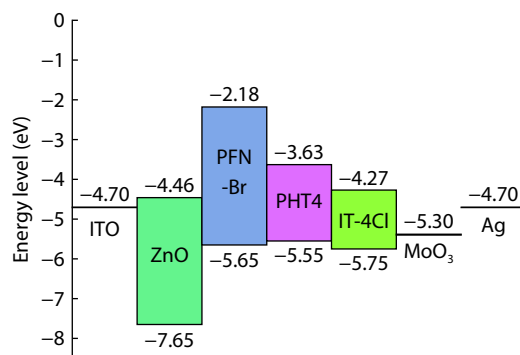

Fig. S4. (Color online) The energy level diagram for PHT4:IT-4Cl device.

When the film was dried in vacuum, the relative absorption intensity of IT-4Cl in the PHT4:IT-4Cl film increased (Fig. S7). These observations possibly due to the aggregation or packing of IT-4Cl in the blend when the drying time is changed. The relatively enhanced absorption peak of IT-4Cl results in its corresponding EQE peak increase.

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Table 1. Photovoltaic performance of the blade-coated PHT4:IT-4Cl OSCs (AM 1.5G, 1000 W/m²).

Active layer	Area (cm²)	Vacuum	V_{oc} (V)	J_{sc} (mA/cm²)	FF (%)	PCE$_{max}$ (%)	PCE$_{ave}$[a] (%)
PHT4:IT-4Cl	0.04	No	0.83	15.84	56.6	7.44	7.31
PHT4:IT-4Cl	0.04	Yes	0.84	23.60	67.8	13.44	13.20
PM6:Y6:PC$_{71}$BM	0.04	No	0.83	17.06	75.6	10.68	10.31
PM6:Y6:PC$_{71}$BM	0.04	Yes	0.85	25.53	78.3	17.01	16.73
PM6:Y6:PC$_{71}$BM	1.00	Yes	0.83	20.11	67.7	11.30	–

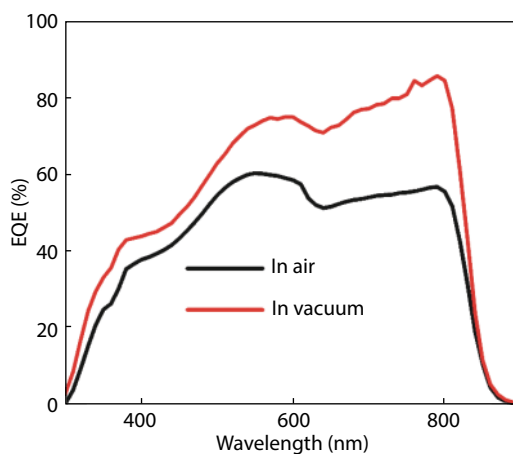[a]Average data were obtained from 10 independent devices.

Fig. S5. EQE curves for the blade-coated PHT4:IT-4Cl OSCs, dried in air and vacuum, respectively.
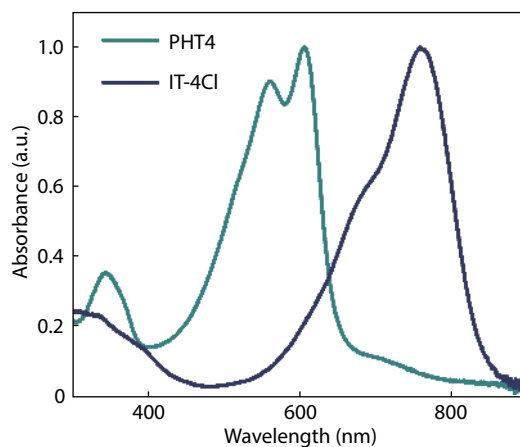

Fig. S6. Normalized absorption spectra for pristine PHT4 and IT-4Cl films.
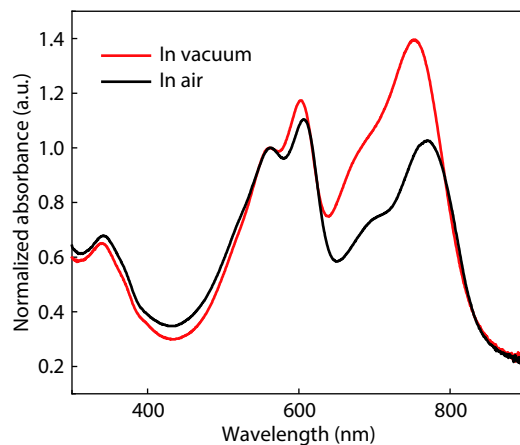

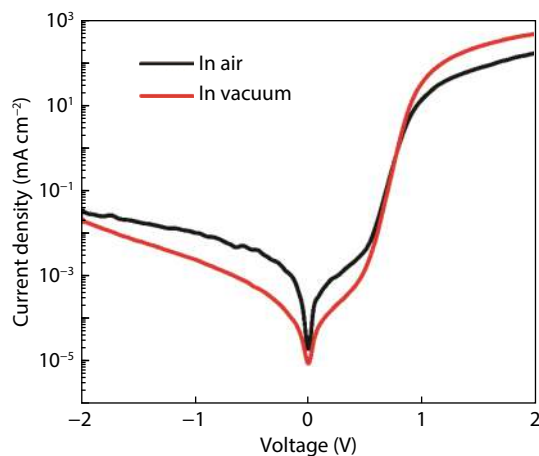Fig. S7. Normalized absorption spectra for PHT4:IT-4Cl films, dried in air and vacuum, respectively.

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Fig. S8. The dark J–V characteristics for the blade-coated PHT4:IT-4Cl OSCs, dried in air and vacuum, respectively.
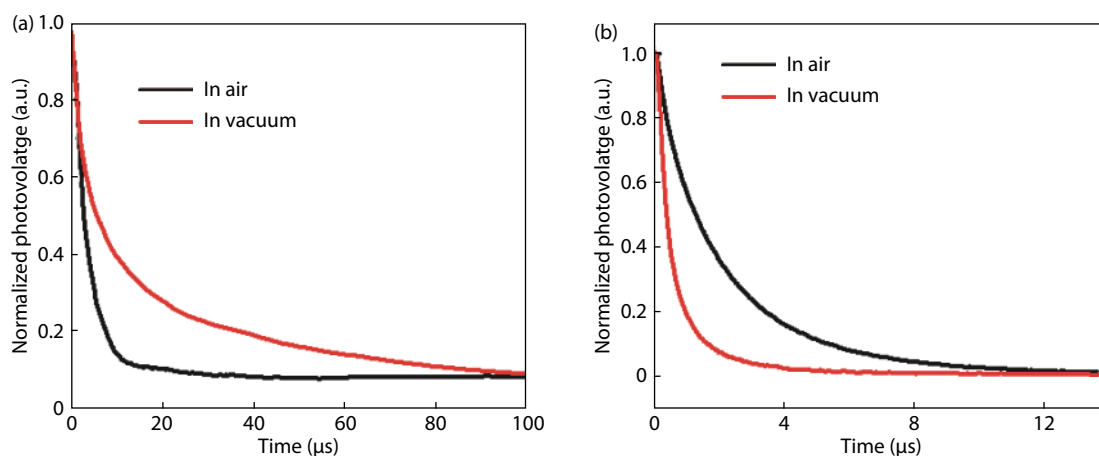

Fig. S9. (a) TPV and (b) TPC measurements on the blade-coated PHT4:IT-4Cl OSCs, dried in air and vacuum, respectively.
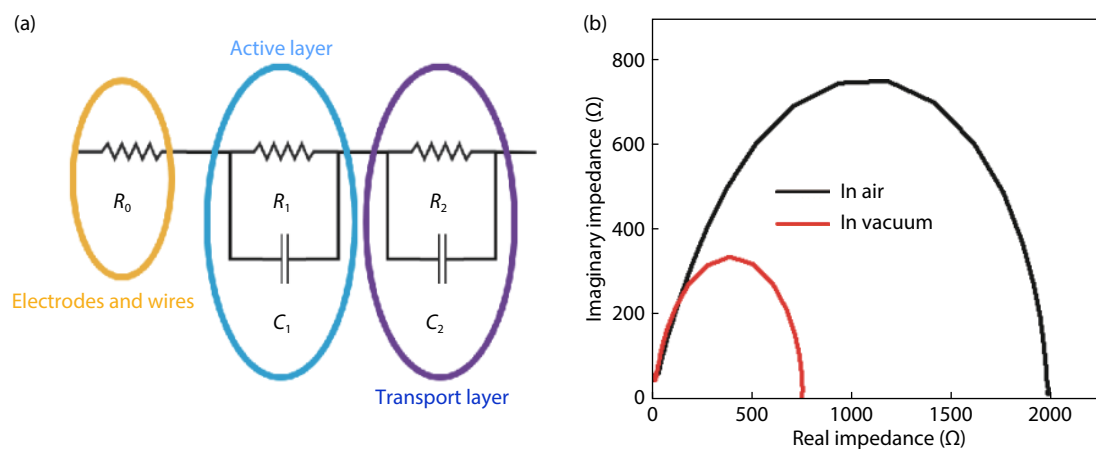

Fig. S10. (a) The equivalent circuit model used to fit the impedance data. (b) Complex impedance Cole-Cole plots for the blade-coated PHT4:IT-4Cl OSCs, dried in air and vacuum, respectively.

Table 2.   The fitting values of impedance for the blade-coated PHT4:IT-4Cl OSCs, dried in air and vacuum, respectively.

Drying process	R_0 (Ω)	R_1 (Ω)	R_2 (Ω)	C_1 (F)	C_2 (F)	τ_{avg} (μs)
In air	15.89	275.1	1561.0	1.7×10^{-8}	3.1×10^{-8}	4.68
In vacuum	17.05	180.3	654.1	4.1×10^{-8}	2.7×10^{-8}	7.39

The equivalent circuit model is shown in Fig. S10(a)[1], where R_0 represents the equivalent resistance of electrodes, C_1 and R_1 in parallel connection come from the active layer, C_2 and R_2 in parallel connection come from the transport lay-
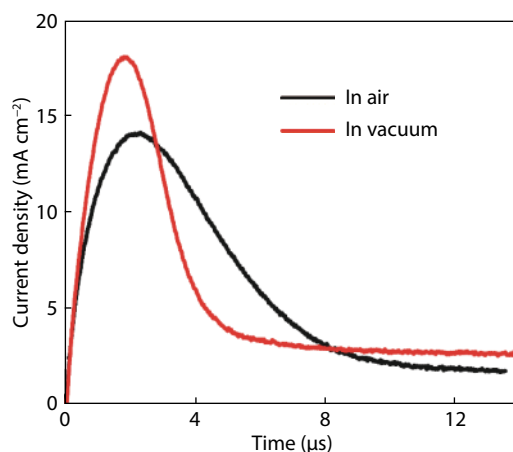
Fig. S11. Photo-CELIV curves for the blade-coated PHT4:IT-4Cl OSCs, dried in air and vacuum, respectively.

Table 3. Charge carrier mobility, lifetime (τ), and extraction time (τ_{ex}) extracted from TPV, TPC, and Photo-CELIV data, by using the Characterization Suite Software installed in PAIOS system.

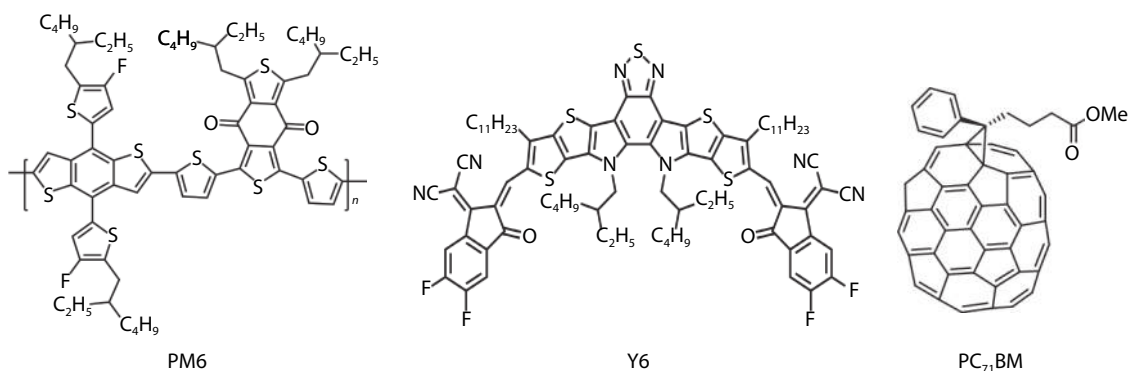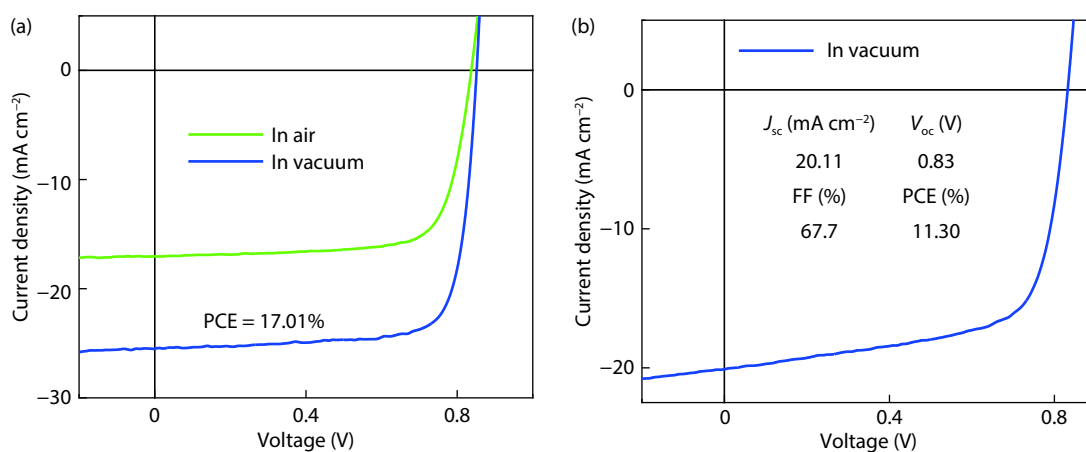| Vacuum	Mobility ($cm^2/(V \cdot s)$)	τ (μs)	τ_{ex} (μs)
NO	7.9×10^{-5}	3.8	2.8
Yes	2.8×10^{-4}	12.7	0.6

Fig. S12. Chemical structures of PM6, Y6, and $PC_{71}BM$.

Fig. S13. (a) *J–V* characteristics of the blade-coated PM6:Y6:PC_{71}BM OSCs, dried in air and vacuum, respectively. (b) *J–V* characteristics of above device with 1 cm^2 area.

er. The measured impedance (Z) with the fitting curve is presented in a Cole-Cole plot (Fig. S10(b)). The experimental and theoretical results have a good agreement using this model. The parameters are summarized in Table S2. R_0, R_1, and R_2 were significantly decreased for the active layer when the vacu-um-assisted drying was introduced, leading to better charge carrier transport and extraction in the device. The average carrier lifetime (τ_{avg}) based on this equivalent circuit can be calculated from the following equation: $\tau_{avg} = C_1 R_1$. The long τ_{avg} means the low charge recombination.
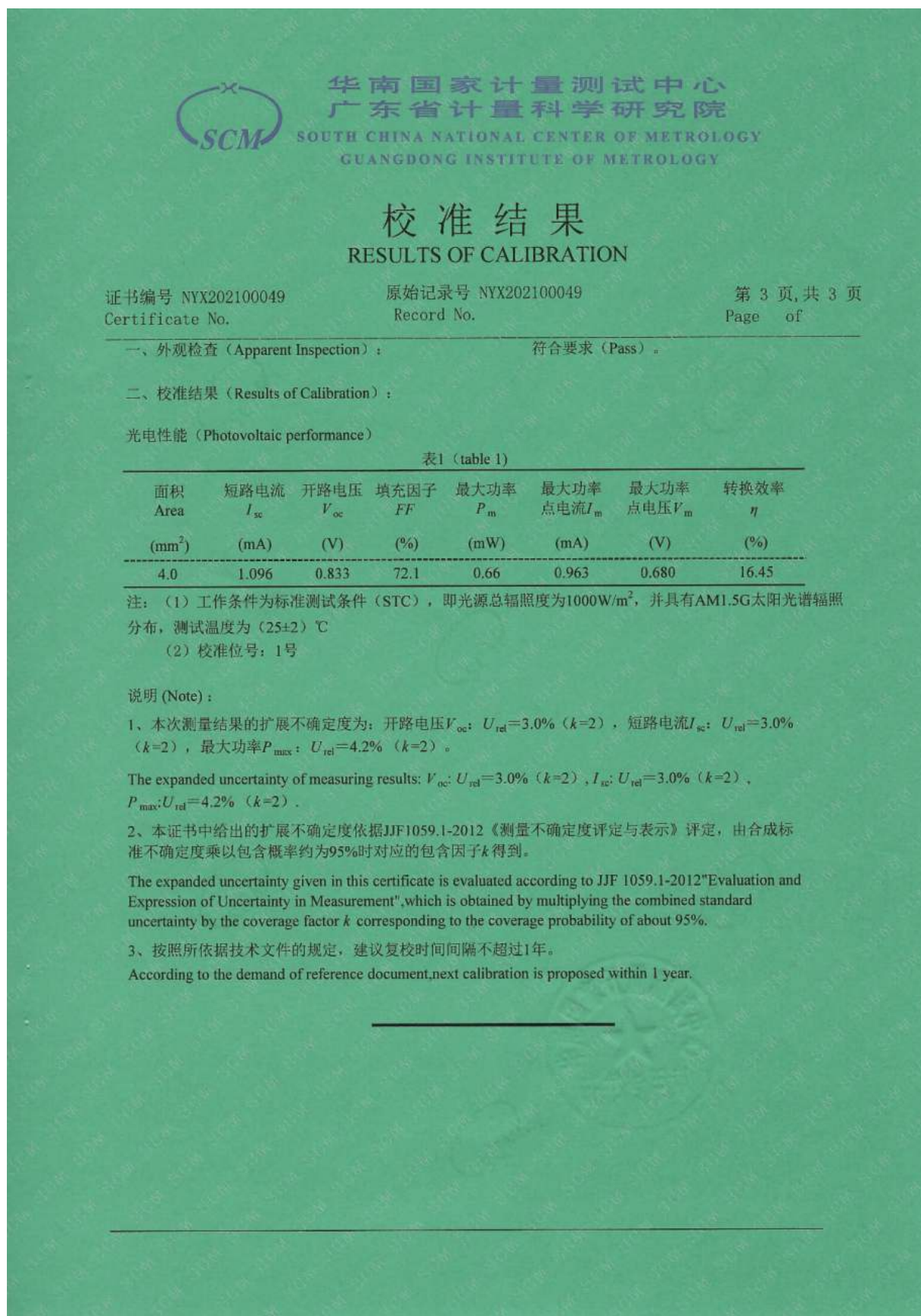
Fig. S14. (Color online) The PCE certificate from South China National Center of Metrology.

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