Supporting Information

Highly Efficient Polymer Solar Cells Using a Non-Conjugated Small-molecule Zwitterion with Enhancement of the Electron Transfer and Collection

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Experimental Section

***Device fabrication*:** The Indium-doped tin oxide glass sheet (1.2 mm thick, ≤15 Ω/square, transmittance > 90%) was purchased from Nippon Sheet Glass Company, Ltd, and cleaned by sonication in detergent, deionized water, acetone, and isopropyl alcohol and dried in a nitrogen stream, followed by an UV-ozone treatment of 20 min. A 40-nm-thick PEDOT: PSS anode buffer layer was spin-casted on the ITO substrate and was heated on a hot plate at 140 °C for 20 min. The PTB7, $PC_{71}BM$ and DIO were purchased from 1-Material, American Dye Source, Inc. and Acros, respectively, and used as received. The PTB7 were blended with $PC_{71}BM$ and dissolved in chlorobenzene (CB) with the addition of a small amount of DIO (CB: DIO = 97:3, v/v). The blended ratios of polymer: $PC_{71}BM$ was 1:1.5 by weight, the solution was stirred overnight at 70 °C. Then the active layer was spin-coated at 2000 rpm for 120 s with a thickness of 90-110nm. Subsequently, the OEABS was fully dissolved in methanol (97%) + acetic acid (3%) mixed solution and was spin-coated on the photoactive layer at a various of thicknesses. At last, 120 nm of Al were deposited through a shadow mask (defined active area of 0.1257 cm^2) onto the photoactive layer by thermo-evaporation in a vacuum chamber with base pressure of 2×10^{-6} mbar. All device fabrication processes are carried out in a N_2-filled glove box.

***J-V characterization and EQE measurement*:** The current-voltage (*J-V*) characteristics of the unencapsulated PSCs were measured in a N_2-filled glove box using a Keithley 2440 source-measure unit and an AM 1.5 G solar simulator (Newport-Oriel® Sol3A 450W). The illumination intensity of 100 mW cm^{-2} irradiation was calibrated using a standard mono-crystal Si reference cell (PV measurements Inc.) to ensure the accurate light source intensity. The external quantum efficiency (EQE) was conducted using the measurement system (Newport-Oriel® IQE 200TM). Same data acquisition system was used for the external quantum efficiency measurement. Under full computer control, light from a 150 W xenon lamp (Oriel, U.S.A.) was focused through a mono-chromator onto the PSC under testing. The wavelength of the light from the mono-chromator was increased progressively in the visible region to generate the EQE (λ) as defined by EQE (λ) = 12400 ($J_{sc}/\lambda\varphi$), where λ is the wavelength, J_{sc} is short-circuit photocurrent density (mA cm^{-2}), and φ is the incident radiative flux (mW cm^{-2}). EQE of the unencapsulated PSCs were measured in air.

Electron mobility: Electron mobility was measured using the space charge limited current model (SCLC). Electron-only devices were fabricated with a structure of ITO/Al/polymer/OEABS (or Ca) /Al. The mobility was determined by fitting the dark current to the model of a single carrier SCLC, which is described by the following equation: $J = (9/8)\ \varepsilon_0\varepsilon_r\mu\ ((V^2) / (d^3))$, where J is the current, μ is the zero-field mobility, ε_0 is the permittivity of free space, ε_r is the relative permittivity of the material, d is the thickness of the active layer, and V is the effective voltage. The effective voltage can be obtained by subtracting the built-in voltage (V_{bi}) and the voltage drop (V_s) from the substrate's series resistance from the applied voltage (V_{appl}), $V=V_{appl} - V_{bi} - V_s$. The electron mobility can be calculated from the slope of the $J^{1/2} \sim V$ curves.

Synthesis: All reagents, unless otherwise specified, were obtained from Alfa Aesar or Sigma-Aldrich and used without further purification. Some of the solvents used were further purified before use (THF from sodium/benzopheone, methanol from CaH_2. ^1H and ^{13}C NMR spectra were measured using a Bruker AV-300. Chemical shifts were expressed in parts per million (ppm), and splitting patterns are designated as: s (singlet), d (doublet), m (multiplet) and br (broad). Coupling constants J are reported in Hertz (Hz). Elemental analyses were performed on a Vario EL elemental analysis instrument (Elementar Co.).

1, 4-Butanesultone (60 mmol, 5.2 ml) was added to a solution of 2, 2'-oxybis (N, N-dimethylethan-1-amine) (20 mmol, 3.2 g) in the solvents of THF and methanol (*v/v*, 2:1). The mixture was stirred at 70 °C for 3 days under argon. The solution was filtered to give a crude white solid. The crude solid was recrystallized from methanol to afford white crystals. ^1H NMR

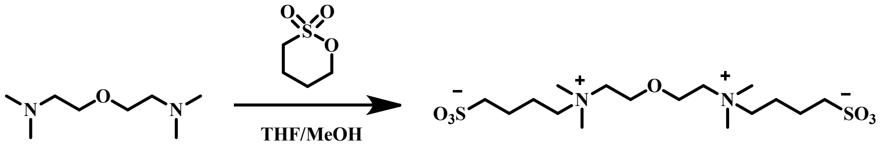
(400MHz, D_2O): 3.90 (s, 4H), 3.54 (s, 4H), 3.30-3.40 (t, J=8.4 Hz, 4H), 3.06 (s, 12H), 2.80-2.95 (t, J=7.2 Hz, 4H), 1.87 (s, 4H), 1.64-1.80 (m, 4H); ^{13}C NMR (100 MHz, D_2O): 64.6, 64.4, 63.4, 51.5, 50.0, 21.2, 21.0; MS-ESI (m/z): 432.2 (M+); Anal. calcd for $C_{16}H_{36}N_2O_7S_2$: C, 44.42; H, 8.39; N, 6.48; Found: C, 44.37; H, 8.23; N, 6.72.

Computational Details: The geometric and electronic structure of them were optimized by Density functional theory (DFT) level of theory with the three-parameter Becke-style hybrid functional (B3LYP). The HOMO and LUMO energy levels are predicated by 6-31G (d, p) basis set. All of calculations about the molecule have been performed on the huge computer origin 2000 server centre using the Gaussian 03 program package. The compositions of molecular orbits were analysed using the GaussView 3.0 program.

Measurement of HOMO levels of OEABS by Ultraviolet Photoelectron Spectroscopy:

We used the ultraviolet photoelectron spectroscopy (UPS) to investigate the surface electronic energy levels of OEABS on ITO. The HOMO level of OEABS is 6.78 eV. The HOMO level was determined by the following equation, HOMO level = hv-(E_{cutoff} - E_{onset}), where hv is incident photon energy (21.2 eV) of He I, the high binding energy cutoff (E_{cutoff}) and HOMO region (E_{onset}) are the turning points. The E_{cutoff} was determined by linear extrapolation to zero at the yield of secondary electrons, and the E_{onset} is the onset relative to the Femi level (E_f) of Au (0 eV), where the E_f is determined from the Au substrate. The LUMO level of OEABS can then be determined by adding up their optical band gaps as follows: LUMO level = HOMO level-optical band gap, where optical band gap of OEABS is 5.21 eV. The LUMO level is 1.57 eV.

Kelvin probe force microscopy (SKPM): **Figure S5** shows the Kelvin probe force microscopy (SKPM) of PTB7:$PC_{71}BM$ and PTB7:$PC_{71}BM$/OEABS.



Scheme S1 The synthetic route of the OEABS.

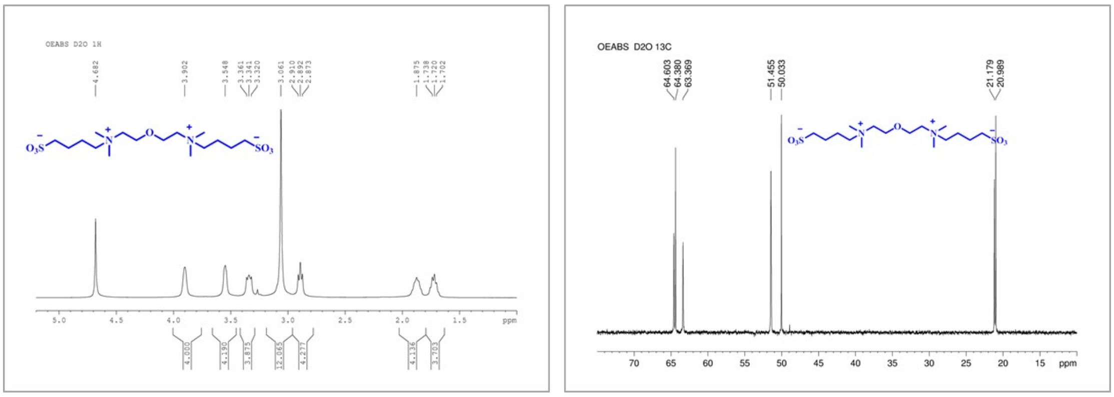


Figure S1 The ^{1}H NMR and ^{13}C NMR of compound OEABS.

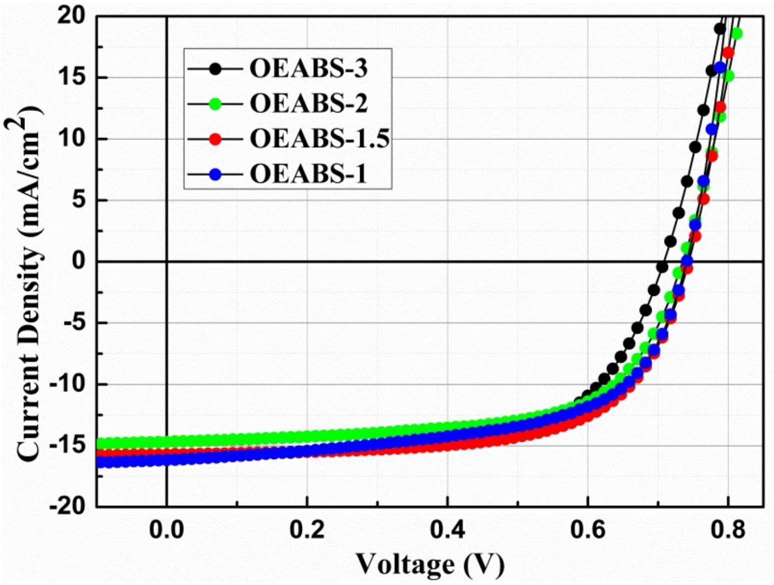
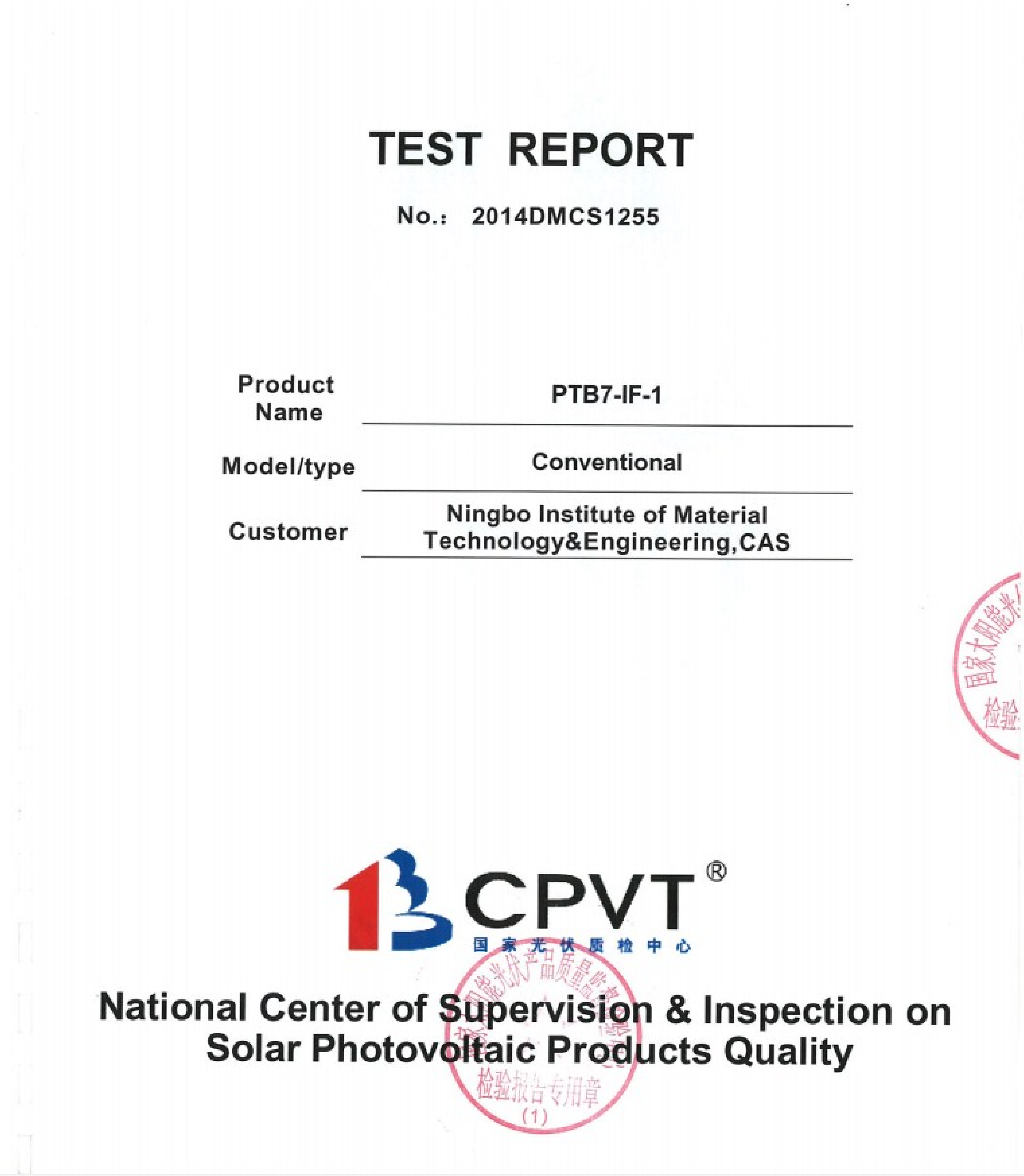


Figure S2 Current density versus voltage (J-V) characteristics of PTB7:PC$_{71}$BM solar cells with different OEABS concentration (X mg/ml) under dark condition. (measured under 100mW/cm^2 AM 1.5G illumination)



TEST REPORT

No.： 2014DMCS1255

Product Name PTB7-IF-1

Model/type Conventional

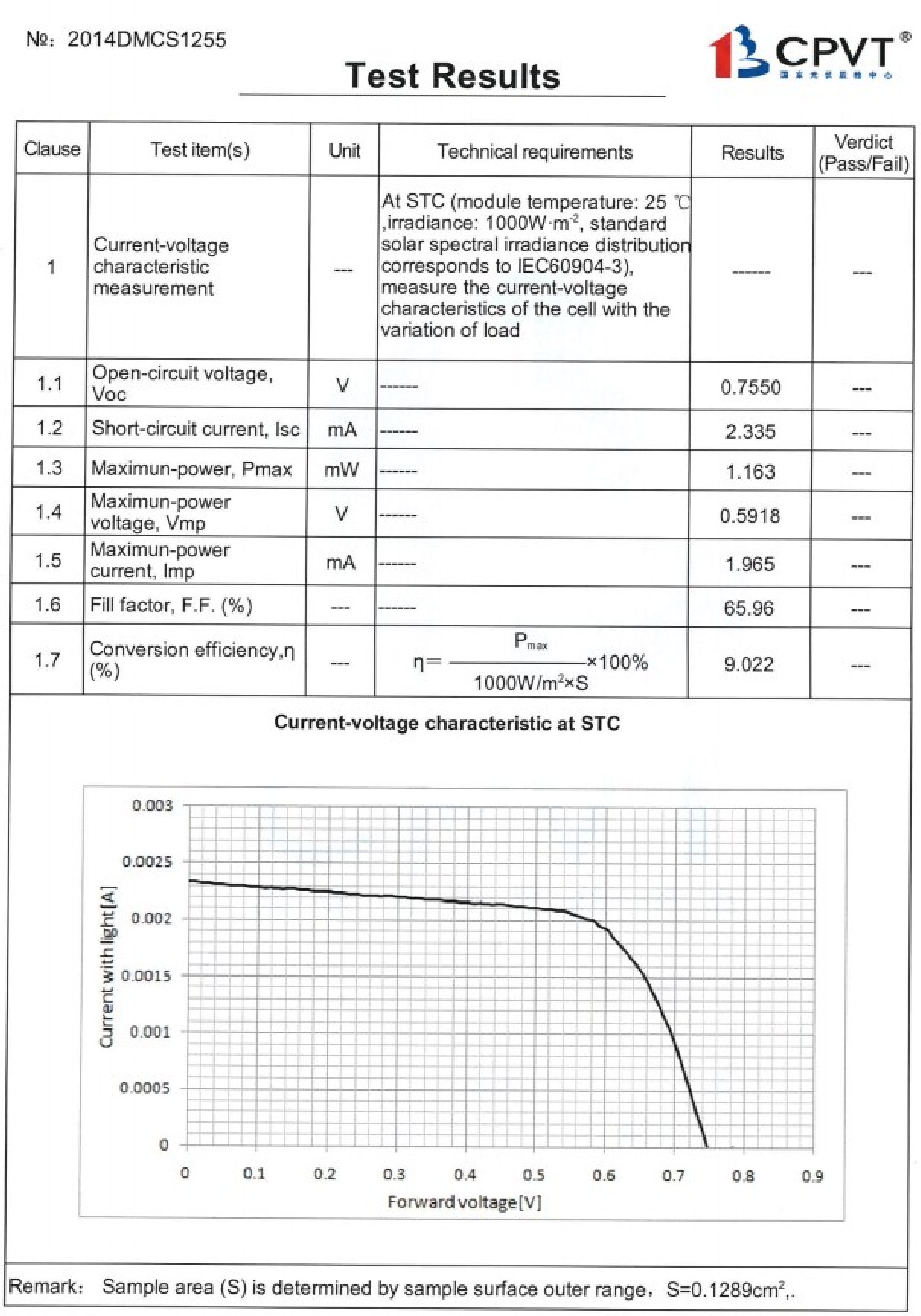
Customer Ningbo Institute of Material Technology&Engineering,CAS

CPVT®
国家光伏质检中心

National Center of Supervision & Inspection on Solar Photovoltaic Products Quality

检验报告专用章
(1)

Figure S3a Cover page of test report by CPVT on PTB7-IF-1 device.



№：2014DMCS1255

Test Results

Clause	Test item(s)	Unit	Technical requirements	Results	Verdict (Pass/Fail)
1	Current-voltage characteristic measurement	---	At STC (module temperature: 25 ℃ ,irradiance: 1000W·m^{-2}, standard solar spectral irradiance distribution corresponds to IEC60904-3), measure the current-voltage characteristics of the cell with the variation of load	------	---
1.1	Open-circuit voltage, Voc	V	------	0.7550	---
1.2	Short-circuit current, Isc	mA	------	2.335	---
1.3	Maximun-power, Pmax	mW	------	1.163	---
1.4	Maximun-power voltage, Vmp	V	------	0.5918	---
1.5	Maximun-power current, Imp	mA	------	1.965	---
1.6	Fill factor, F.F. (%)	---	------	65.96	---
1.7	Conversion efficiency,η (%)	---	$\eta = \frac{P_{max}}{1000W/m^2 \times S} \times 100\%$	9.022	---

Current-voltage characteristic at STC

Remark： Sample area (S) is determined by sample surface outer range，S=0.1289cm^2,.

Figure S3b Test results and I-V characteristics of the conventional structure of the PTB7-IF-1 device with an effective area of 12.89 mm^2, by CPVT.

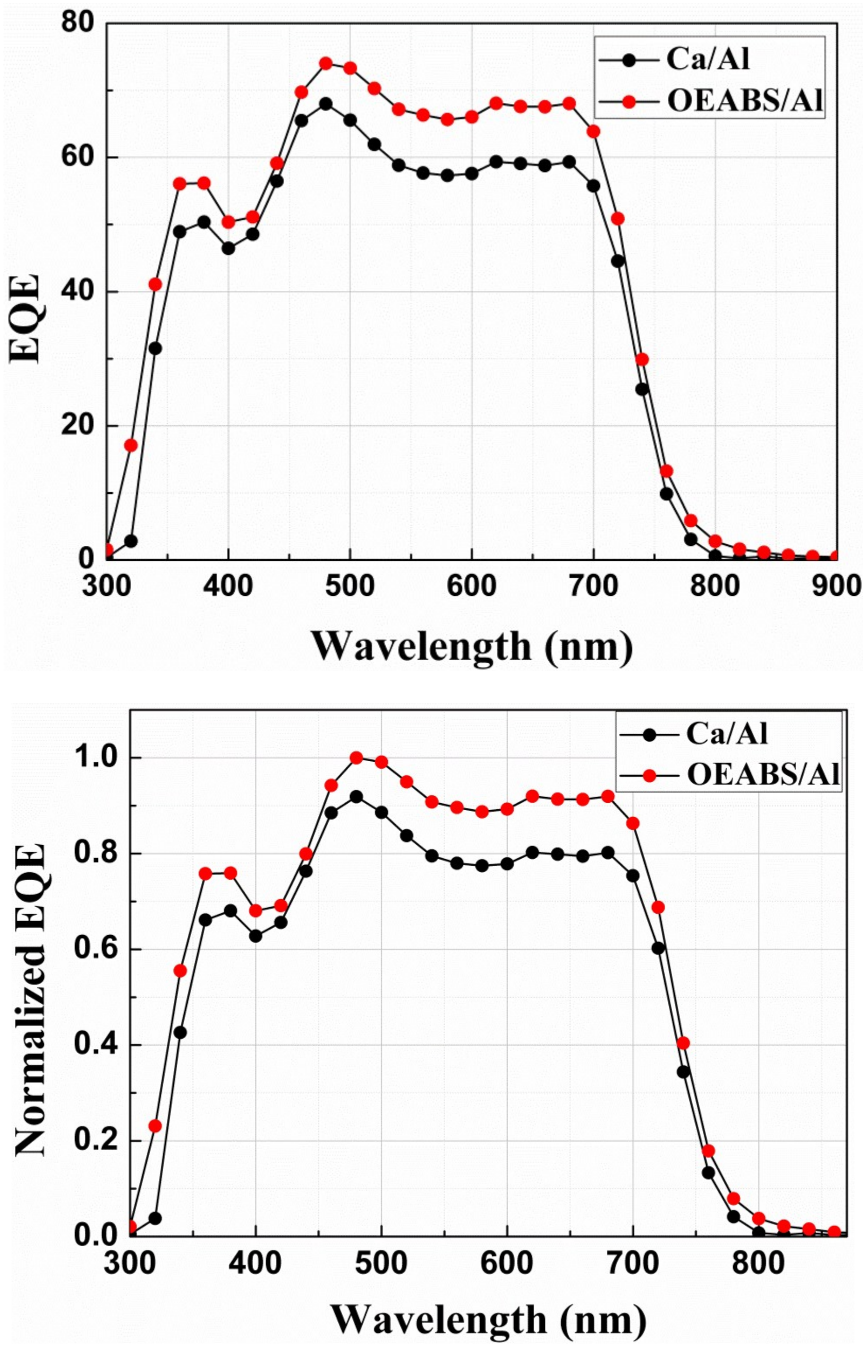


Figure S4 EQE spectra for Ca interlayer (blue symbols, 20 nm) and OEABS (red symbols, 7 nm) devices.

Table S1 The SCLC electron mobility of PTB7: $PC_{71}BM$ (100nm)/OEABS or Ca (X nm) double layer films. Device configuration: ITO/Al/PTB7: $PC_{71}BM$ (100nm)/OEABS or Ca (X nm)/Al.

PTB7: $PC_{71}BM$ (100nm)[a]/OEABS or Ca (X nm)

Thickness (x nm)	Electron mobility (cm^2 V^{-1} S^{-1})[b]
LiF (1)	1.57×10^{-6}
Ca(20)	5.88×10^{-6}
OEABS (17)	5.67×10^{-6}
OEABS (13)	4.13×10^{-5}
OEABS (10)	2.46×10^{-4}
OEABS (7)	3.62×10^{-4}
OEABS (5)	4.38×10^{-4}

[a] The thickness of PTB7: $PC_{71}BM$ film is 100 nm. [b] The average electron mobility of the PTB7: $PC_{71}BM$ (100 nm) [a]/OEABS (X nm), Ca (20 nm) and LiF (1nm) double layer film.

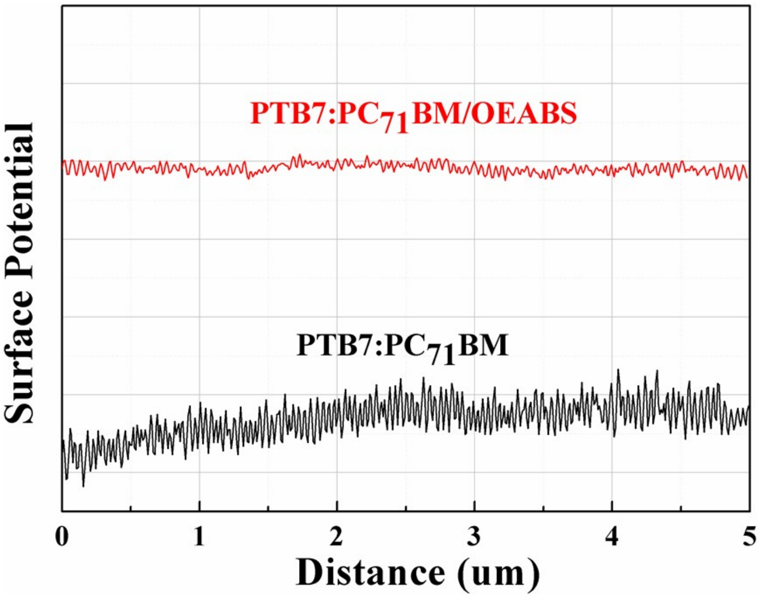


Figure S5 The surface potential of PTB7:PC$_{71}$BM and PTB7:PC$_{71}$BM/OEABS.

Table S2 Photovoltaic Parameters of PTB7:$PC_{71}BM$ solar cells with different OEABS (x nm) thickness. (defined active area of 0.04 cm^2)

Device	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	PCE(average%)
OEABS (17nm)	0.74	15.69	65	7.57	7.46
OEABS (13nm)	0.73	16.27	65	7.79	7.71
OEABS (10nm)	0.74	16.94	70	8.85	8.65
OEABS (7nm)	0.76	17.74	71	9.52	9.40
OEABS (5nm)	0.75	17.77	68	9.13	9.07

Table S3 Photovoltaic Parameters of PTB7:$PC_{71}BM$ solar cells with different OEABS (x nm) thickness. (defined active area of 0.1257 cm^2)

Device	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)	PCE(average%)
OEABS (17nm)	0.74	17.49	61	7.97	7.80
OEABS (13nm)	0.75	17.71	63	8.42	8.40
OEABS (10nm)	0.75	17.83	68	9.15	9.13
OEABS (7nm)	0.75	17.80	71	9.51	9.45
OEABS (5nm)	0.76	17.79	69	9.25	9.20

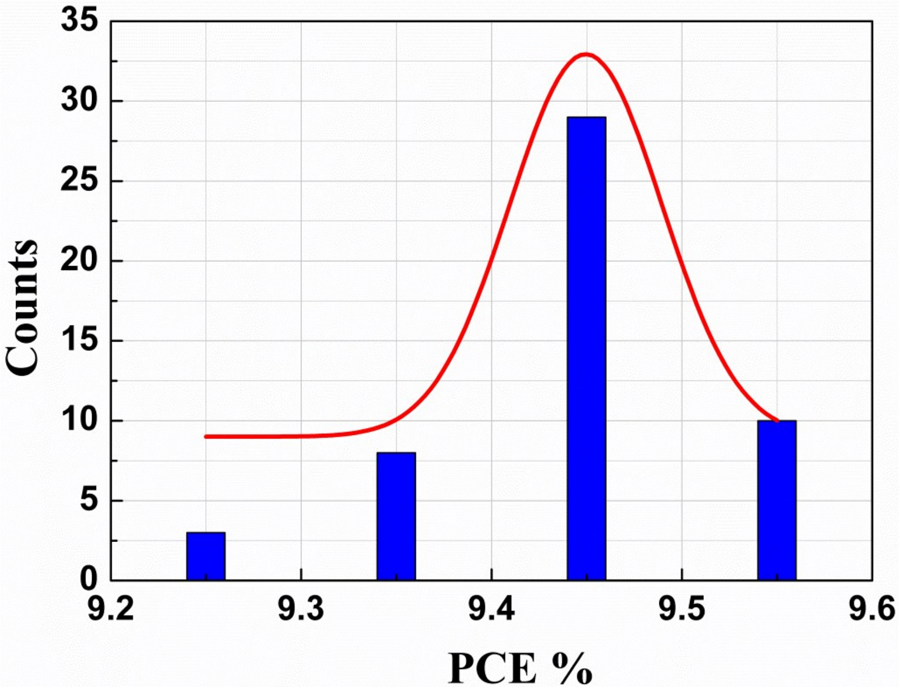


Figure S6 Histogram of cell efficiencies for 50 devices.