

SUPPLEMENTARY INFORMATION

Solution-processed small-molecule solar cells: breaking the 10% power conversion efficiency

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1. Materials: All reactions and manipulations were carried out under argon atmosphere with the use of standard Schlenk techniques. All starting materials and conjugated polyelectrolyte (CPE1, CPE2 and

CPE3) were purchased from commercial suppliers and used without further purification. 5''-bromo-3,3''-dioctyl-[2,2':5',2''-terthiophene]-5-carbaldehyde (1), 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (2) and Potassium 4-oxo-2-thioxothiazolidin-3-ide (5) were synthesized according to the literature.¹⁻³

2. Measurements: The ¹H and ¹³C NMR spectra were recorded on a Bruker ARX400 Spectrometer. The Matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) were performed on an Applied Biosystems Voyager-DE-STR MALDI-TOF. The thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) analyses were carried out in flowing argon gas with a 10 °C min⁻¹ heating rate. UV-Vis spectra were obtained with a Varian Cary 50 ultraviolet-visible spectrometer. X-Ray diffraction (XRD) experiments were performed on a Panalytical X'Pert Pro X-ray Powder Diffractometer with Cu-Kα radiation (k = 1.5406 Å). Atomic force microscope (AFM) was performed using Bruker Dimension 5000 Scanning Probe Microscope (SPM) in "tapping" mode. The TEM images were taken using Titan S/TEM (FEI). The electrochemical cyclic voltammetry (CV) were carried out at room temperature conducted with Pt disk, Pt wire, and Silver wire as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol L⁻¹ tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution, and the scan rate was 100 mV s⁻¹. The half potential of Ferrocene in this condition is 0.4 V.

To measure the hole and electron mobilities, hole-only and electron-only devices were fabricated using a diode configuration of ITO/PEDOT:PSS/active layer/Au and ITO/Al/active layer/Ca/Al, respectively, by taking current-voltage current in the range of 0-6 V and fitting the results to a space charge limited form, charge limited form, where the SCLC is described by

$$J = 9\varepsilon_0\varepsilon_r\mu_h V^2/8L^3$$

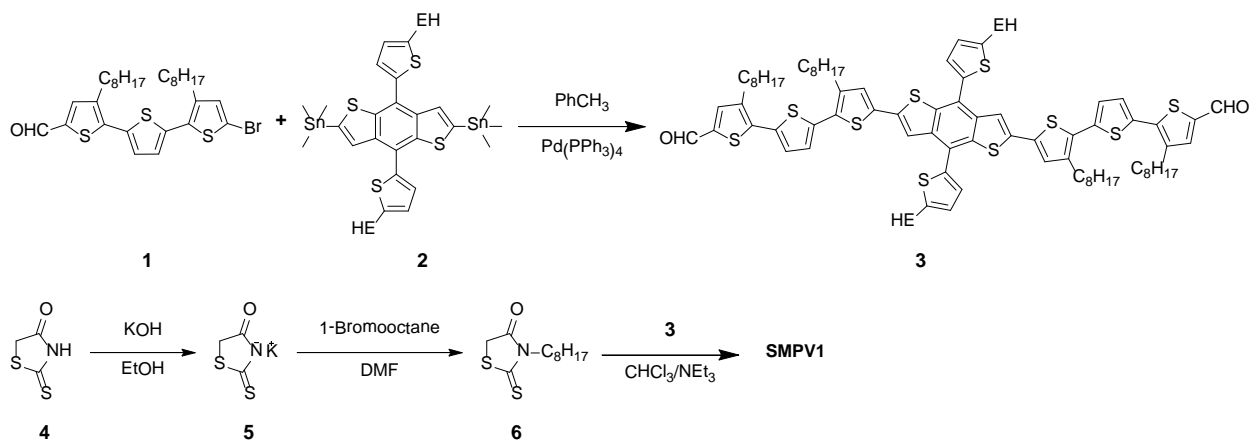
where J is the current density, L is the film thickness of active layer, μ_h is the hole mobility, ε_r is the relative dielectric constant of the transport medium, ε_0 is the permittivity of free space (8.85×10^{-12} F m⁻¹),

V is the internal voltage in the device and $V = V_{appl} - V_r - V_{bi}$, where V_{appl} is the applied voltage to the device, V_r is the voltage drop due to contact resistance and series resistance across the electrodes, and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes.

The current density-voltage (J - V) characteristics of photovoltaic devices were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under AM 1.5 G illumination at 100 mW cm^{-2} under a Newport Thermal Oriel 91192 1000W solar simulator. The light intensity was determined by a Si photodiode as a reference cell. External quantum efficiencies (EQEs) values of the encapsulated devices were obtained with an Enli Tech (in Taiwan) EQE measurement system.

3. Device Fabrication: The photovoltaic devices, with a structure of glass/ITO/PEDOT:PSS/donor:PC₇₁BM/Ca/Al. The ITO-coated glass substrates were cleaned by ultrasonic treatment in isopropyl, detergent, deionized water, acetone, and isopropyl alcohol under ultrasonication for 20 minutes each and subsequently dried in oven for 12 hours. A thin layer of PEDOT:PSS (Baytron P VP AI 4083, filtered at $0.2 \mu\text{m}$) was spin-coated (4000 rpm, ca. 40 nm thick) onto ITO surface. After being baked at $120 \text{ }^\circ\text{C}$ for 15 min, the substrates were transferred into a nitrogen-filled glove box. Subsequently, the active layer was spin-coated from a different blend ratio (weight-to-weight, w:w) of donor (14 mg mL^{-1}) and PC₇₁BM in chloroform solution on the ITO/PEDOT:PSS substrate without further special treatments. For the active layers fabricated with PDMS additive, PDMS with desired amounts was added in the donor/PC₇₁BM blend solutions and stirred for 1 h before spin-coating. The active layer thickness was measured as ca. 120 nm using a Dektak 150 profilometer. Finally, 20 nm Ca layer and 100 nm Al layer were deposited in sequence on the active layer under high vacuum ($\sim 2 \times 10^{-6}$ Torr). The effective area of each cell was 0.10 cm^2 except the certified single junction device, which using a light mask with an area of 0.0411 cm^2 .

4. Synthesis



1. Synthesis of 5'',5''''-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,3''-dioctyl-[2,2':5',2''-terthiophene]-5-carbaldehyde) (3)

Pd(PPh₃)₄ (69 mg, 0.10 mmol) was added to a solution of Br3TCHO (**1**) (1.15 g, 1.98 mmol) and 2,6-Bis(trimethyltin)-4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene (**2**) (0.85 g, 0.94 mmol) in PhCH₃ (60 mL) under argon protection. After being stirred at 100 °C for 48 h, the reaction mixture was poured into water and extracted with dichloromethane. The organic layer was washed with water, and then dried over Na₂SO₄. After removal of solvent, the crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and hexane (2:1) as eluant to afford compound **3** (1.32 g, 85 %) as a dark red solid. Melting point: 112 °C. ¹H NMR (400 MHz, CDCl₃): δ 9.83 (s, 2H), 7.63 (s, 2H), 7.59 (s, 2H), 7.32 (d, J = 3.5 Hz, 2H), 7.24 (d, J = 3.9 Hz, 2H), 7.12 (s, 3H), 7.11 (s, 1H), 6.94 (d, J = 3.5 Hz, 2H), 2.91 (dd, J = 3.0 Hz and J = 2.9 Hz, 4H), 2.83 (t, J = 7.8 Hz, 4H), 2.76 (t, J = 7.9 Hz, 4H), 1.64-1.75 (m, 10H), 1.28-1.46 (m, 56H), 0.99 (t, J = 7.4 Hz, 6H), 0.95 (t, J = 6.9 Hz, 6H), 0.88 (t, J = 6.9 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 182.50, 146.11, 141.17, 140.95, 140.38, 140.28, 149.03, 138.74, 137.92, 137.46, 137.38, 136.78, 135.74, 134.74, 130.28, 128.39, 127.86,

126.27, 125.52, 123.42, 119.24, 118.26, 41.51, 34.37, 32.55, 31.90, 31.87, 30.49, 30.30, 29.67, 29.64, 29.51, 29.45, 29.43, 29.28, 29.25, 28.98, 25.86, 23.08, 22.68, 14.23, 14.12, 11.00. MS (MALDI-TOF): calcd for $[M]^+$, 1574.6339; found, 1574.6367.

Synthesis of potassium 4-oxo-2-thioxothiazolidin-3-ide (5)⁴

Potassium hydroxide (2.22 g, 39.59 mmol) was added to a solution of rodanine (5.07 g, 38.07 mmol) in 120 mL of ethanol. The mixture was stirred at 70 °C for 5 hours. and then cooled to room temperature. The crystalline solid was collected on a filter, washed with ethanol, and dried in air. The potassium salt of 2-thioxo-4-thiazolidinone thus obtained weighed 6.08 g. (93%). Melting point: >200 °C (with darkening). ¹³C NMR (100 MHz, CHCl₃): δ 218.97, 197.12, 48.06.

Synthesis of 3-octyl-rodanine (6)

n-Octyl bromide (6.41 g, 33.20 mmol) was slowly added to a suspension of the potassium salt of rodanine **5** (1.03 g, 6.64 mmol) and KI (3.31 g, 19.92 mmol) in acetone (35 ml) and DMF (35 ml). After being stirred at 90 °C for 36 h, the reaction mixture was poured into water (100 mL) and extracted with CH₂Cl₂. The organic layer was washed with water, and then dried over Na₂SO₄. After removal of solvent, the crude product was purified by column chromatography on silica gel using a mixture of dichloromethane and hexane (3:1) as eluent to afford 3-octyl-rodanine (1.08 g, 66 %) as a dark red liquid. ¹H NMR (400 MHz, CHCl₃): δ 3.92 (s, 2H), 3.58 (t, J = 7.5 Hz, 2H), 1.56 (m, 2H), 1.26 (m, 10H), 0.85 (t, J = 6.9 Hz, 3H). ¹³C NMR (100 MHz, CHCl₃): δ 171,74, 42.16, 33.74, 31.75, 29.11, 29.08, 27.57, 26.70, 22.62, 14.08. MS (MALDI-TOF): calcd for $[M]^+$, 245.0908; found, 245.0981.

Synthesis of (5E,5'E)-5,5'-((5'',5''''-(4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(3,3''-dioctyl-[2,2':5',2''-terthiophene]-5'',5-diyl))bis(methanylylidene))bis(3-octyl-2-thioxothiazolidin-4-one) (SMPV1)

3T-BDTT-3T(CHO)₂ (5) (0.44 g, 0.28 mmol) was dissolved in a solution of dry chloroform (60 mL) and five drops of triethylamine under argon. Then 3-octyl-rodanine (0.41 g, 1.68 mmol) was added and the resulting solution was heated to reflux and stirred for 48 hours. The reaction mixture was then cool to room temperature, poured into water and extracted with dichloromethane, washed with water and dried over Na₂SO₄. After removal of solvent it was chromatographed on silica gel using chloroform as eluant to afford SMPV1 as a black solid (0.49 g, 86 % yield). Melting point: 185 °C. ¹H NMR (400 MHz, CHCl₃): δ 7.70 (s, 2H), 7.55 (s, 2H), 7.32 (d, J = 3.4 Hz, 2H), 7.16 (m, 4H), 7.06 (m, 4H), 6.95 (d, J = 3.4 Hz, 2H), 4.06 (t, J = 7.6 Hz, 4H), 2.93 (d, J = 5.0 Hz, 4H), 2.75 (m, 8H), 1.76 (m, 2H), 1.68 (m, 12H), 1.41 (m, 16H), 1.28 (m, 60), 1.01 (t, J = 7.4 Hz, 6H), 0.96 (t, J = 6.7 Hz, 6H), 0.89 (t, J = 6.5 Hz, 18H). ¹³C NMR (100 MHz, CHCl₃): δ 192.19, 167.45, 145.95, 140.90, 140.83, 139.47, 138.60, 137.56, 137.29, 137.20, 136.85, 135.54, 135.10, 134.70, 130.45, 128.29, 127.87, 127.12, 126.03, 125.49, 124.74, 123.25, 120.62, 120.43, 119.10, 44.82, 41.52, 34.40, 32.58, 31.94, 31.90, 31.79, 30.43, 30.22, 29.80, 29.74, 29.62, 29.59, 29.55, 29.52, 29.48, 29.34, 29.31, 29.16, 29.14, 29.00, 26.98, 26.82, 25.87, 23.12, 22.71, 22.70, 22.65, 14.27, 14.13, 14.10, 11.03. MS (MALDI-TOF): calcd for [M]⁺, 2028.7944 ; found, 2028.7902.

5. Supporting Figures.

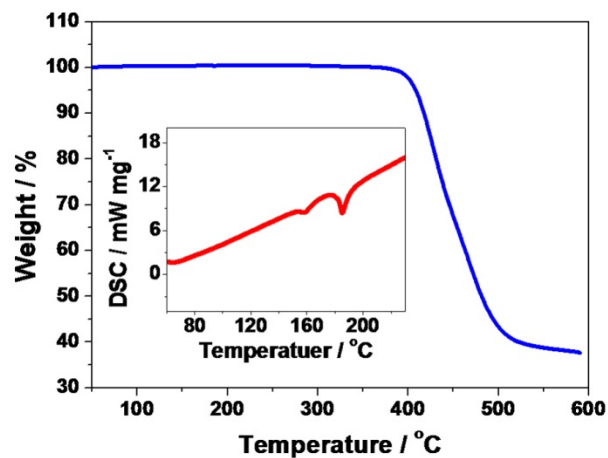


Figure S1. TGA and DSC plots of SMPV1 with a heating rate of 10 °C min⁻¹ under argon atmosphere.

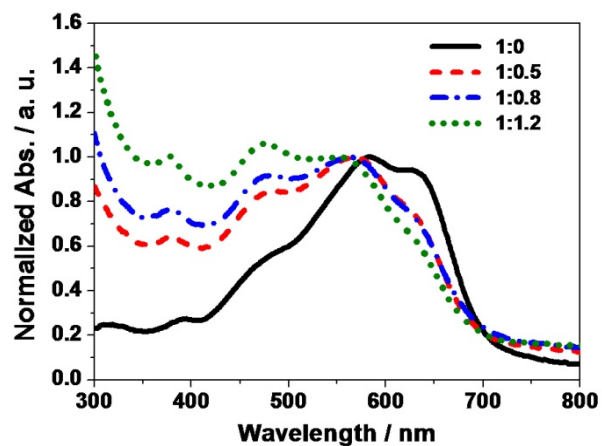


Figure S2. Normalized absorption spectra of SMPV1/PC₇₁BM in film with different blend ratio.

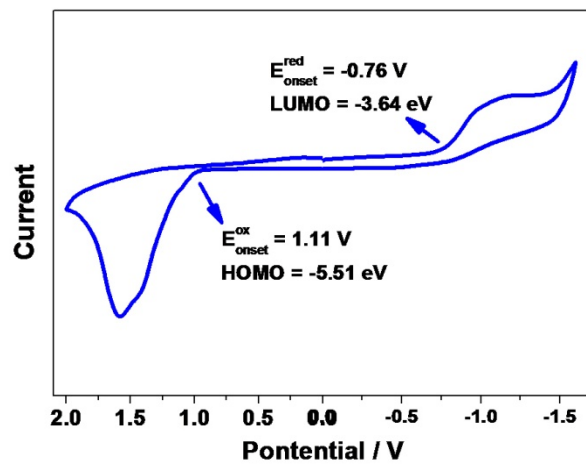


Figure S3. Cyclic voltammogram of SMPV1 cast on a platinum wire in CH_3CN with 0.1 M $(n\text{-Bu})_4\text{NPF}_6$ as supporting electrolyte and a scan speed of 100 mV s^{-1} .

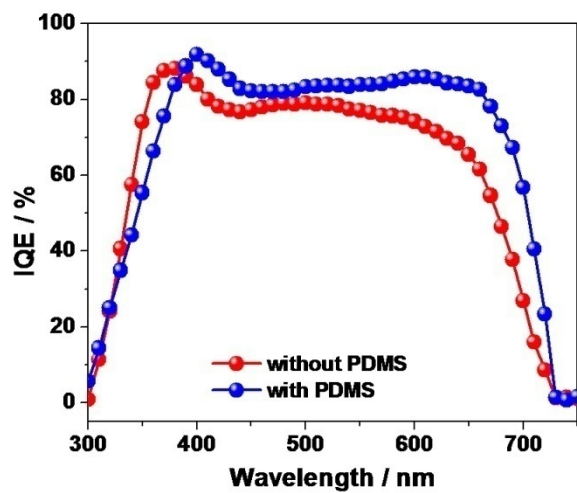


Figure S4. IQE of single junction devices based on SMPV1/ PC_{71}BM (1:0.8) with and without PDMS additive

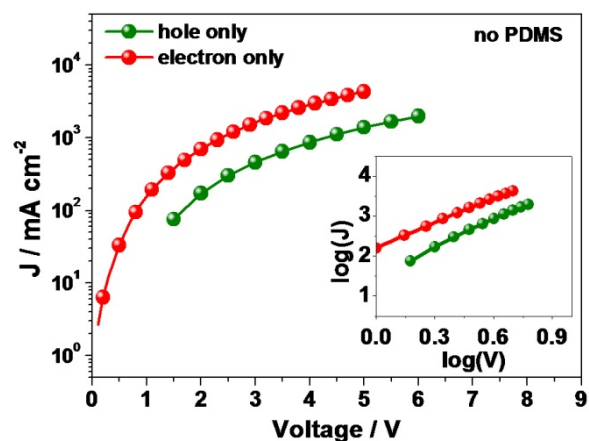


Figure S5. Semilogarithmic plots of the J-V curve of the hole-only and electron-only diodes base on SMPV1/PC71BM (1:0.8, w:w) without PDMS additive. Inset is the $\log(J)$ - $\log(V)$ curve of the related hole only and electron only device.

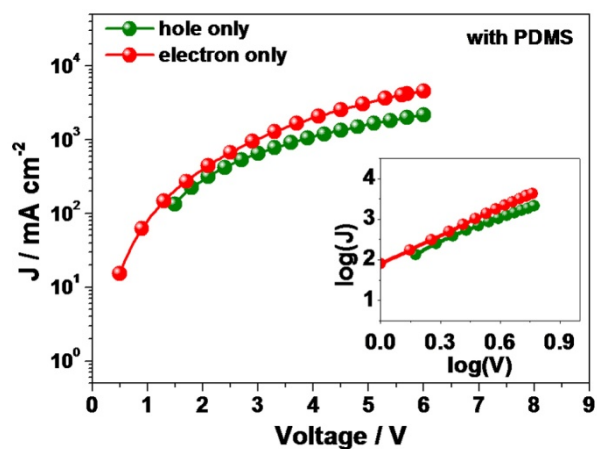


Figure S6. Semilogarithmic plots of the J-V curve of the hole-only and electron-only diodes base on SMPV1/PC71BM (1:0.8, w:w) with PDMS (0.5 mg ml^{-1}) as additive. Inset is the $\log(J)$ - $\log(V)$ curve of the related hole only and electron only device.

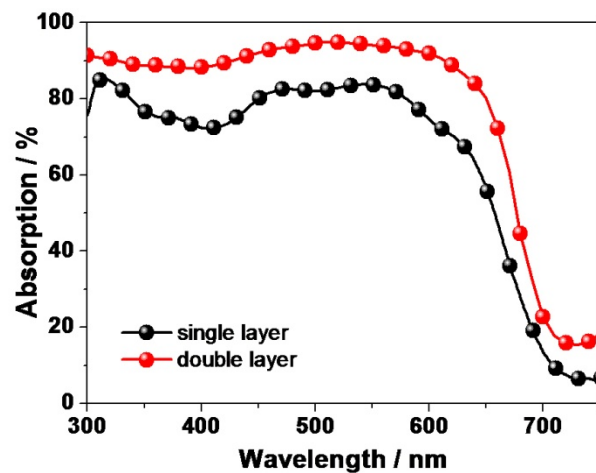


Figure S7. Absorption of single junction and tandem solar cells.

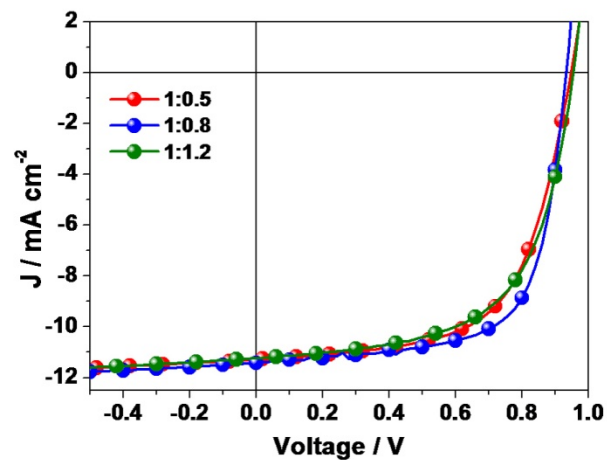


Figure S8. J-V curves of SMPV1/PC₇₁BM with different weight ratio.

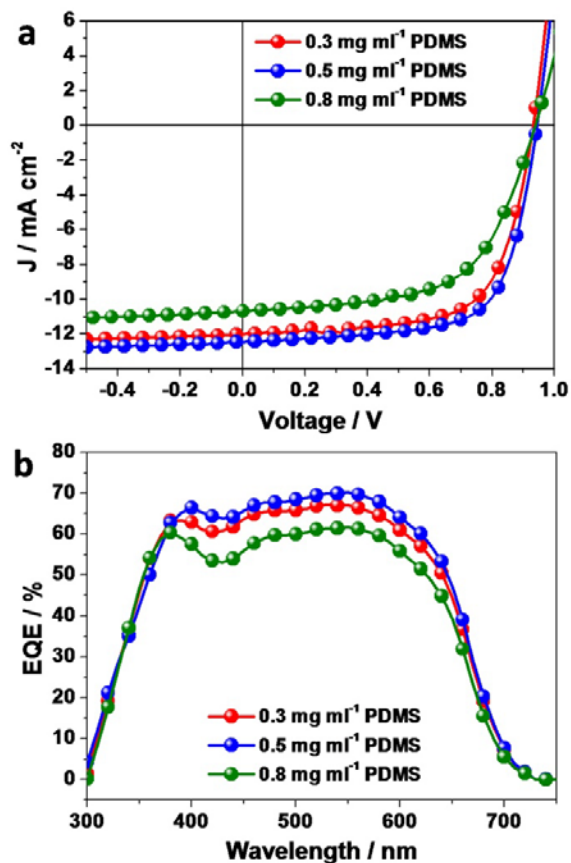


Figure S9. (a) J-V curves of SMPV1/PC₇₁BM (1:0.8, w:w) using PDMS as additive. (b) EQE of related devices.

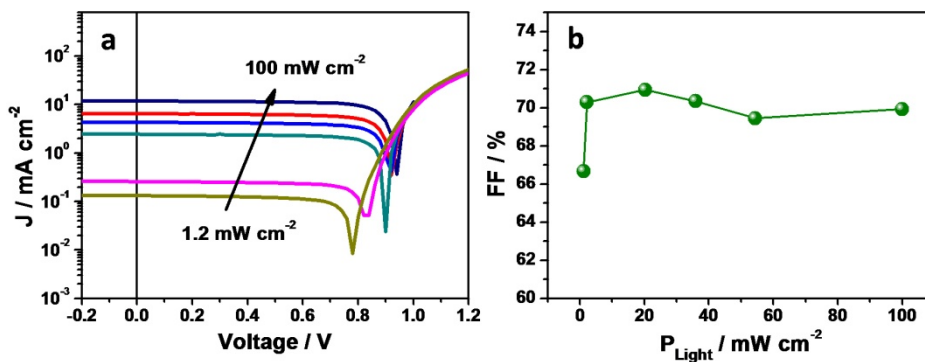


Figure S10. OSCs performance parameters of SMPV1/PC₇₁BM (1:0.8, w:w) using PDMS (0.5 mg ml^{-1}) as additive based device under low light intensity (from 1.2 to 100 mW cm^{-2} , 0.012–1 Sun). (a) J-V curves of the device under different light intensity; (b) FF as a function of light intensity.

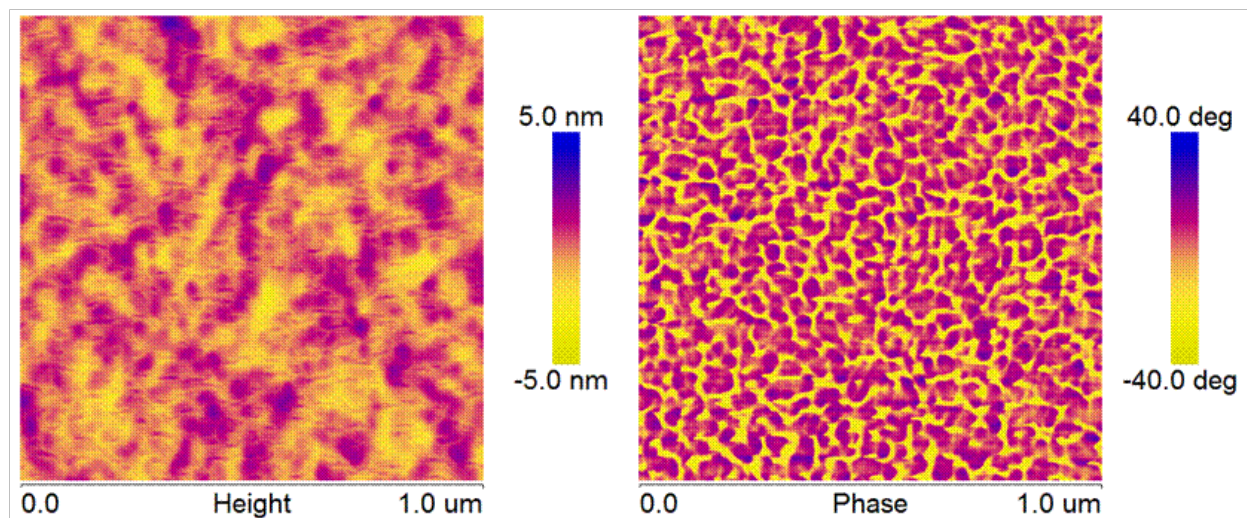


Figure S11. Tapping-mode AFM height (left) and phase (right) images ($1 \times 1 \mu\text{m}$) of blend film (w:w: 1:0.8) using PDMS (0.3 mg ml^{-1}) as additive.

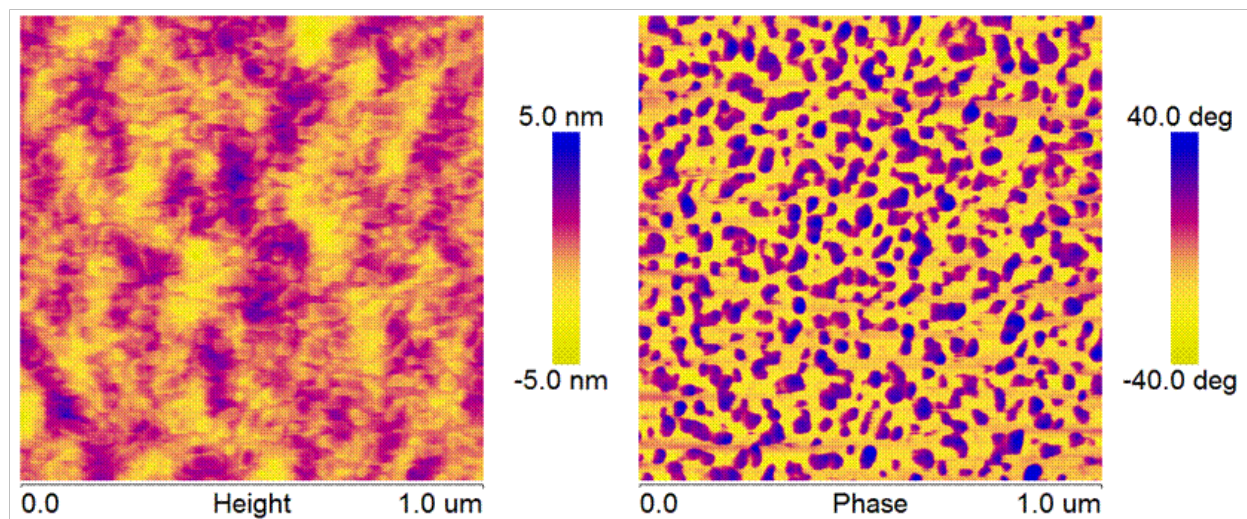


Figure S12. Tapping-mode AFM height (left) and phase (right) images ($1 \times 1 \mu\text{m}$) of blend film (w:w: 1:0.8) using PDMS (0.8 mg ml^{-1}) as additive.

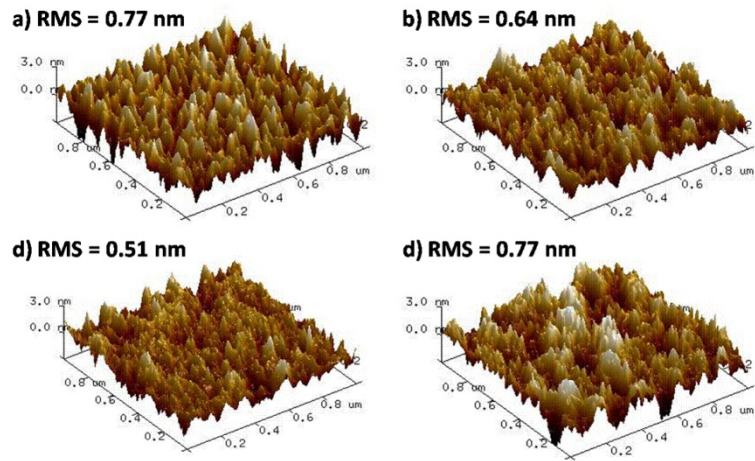




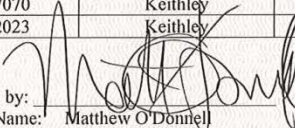
Figure S13. Tapping-mode AFM 3D topographic images ($1 \times 1 \mu\text{m}$) of blend films of SMPV1/PC₇₁BM (1;0.8,w:w) with different PDMS concentration, (a) no PDMS, (b) 0.3 mg ml^{-1} PDMS, (c) 0.5 mg ml^{-1} PDMS and (d) 0.8 mg ml^{-1} PDMS.

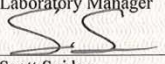
	 Calibration Cert. # 2893.01	Technology and Application Center PV Lab Newport Calibration Cert. # 0808
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Calibration Conducted For:
Professor Yang Group
 Room 2121C, Engineering V Building
 Department of Materials Science and Engineering, UCLA
 405 Hilgard Ave.
 Los Angeles, CA 90095

Calibration Conducted By:
Newport Corporation
TAC – PV Lab
 1791 Deere Ave.
 Irvine, CA 92606

Equipment ID	Manufacturer	Model	Due Date
20010088	Newport Oriel ®	QE-PV-SI	May 2013
101	Newport Oriel ®	Sol3A	Mar 2014
PVM 284 KG5	PV Measurements	PVM 284	Jun 2013
74004-260	Newport Oriel ®	Spectroradiometer	Apr 2014
27061031044M	Sciencscope	XT-D8126-XY	Aug 2013
12110	Newport Corp	818-UV-L	Aug 2013
1300696	Keithley	2700	Nov 2013
1274410	Keithley	2440	Mar 2014
1117070	Keithley	2440	Jan 2014
0842023	Keithley	2400	Jun 2013

Approved by:  Date: 5-1-2013
 Name: Matthew O'Donnell
 Title: Laboratory Manager

Verified by:  Date: 5-1-2013
 Name: Scott Snider
 Title: Test Engineer

Cal Cert V1.6	Issue Date: May 01, 2013	Page 1 of 2
Reviewed and Approved by: Matthew O'Donnell		

Figure S14a . Cover page of test report by Newport Corporation based on SMPV1.

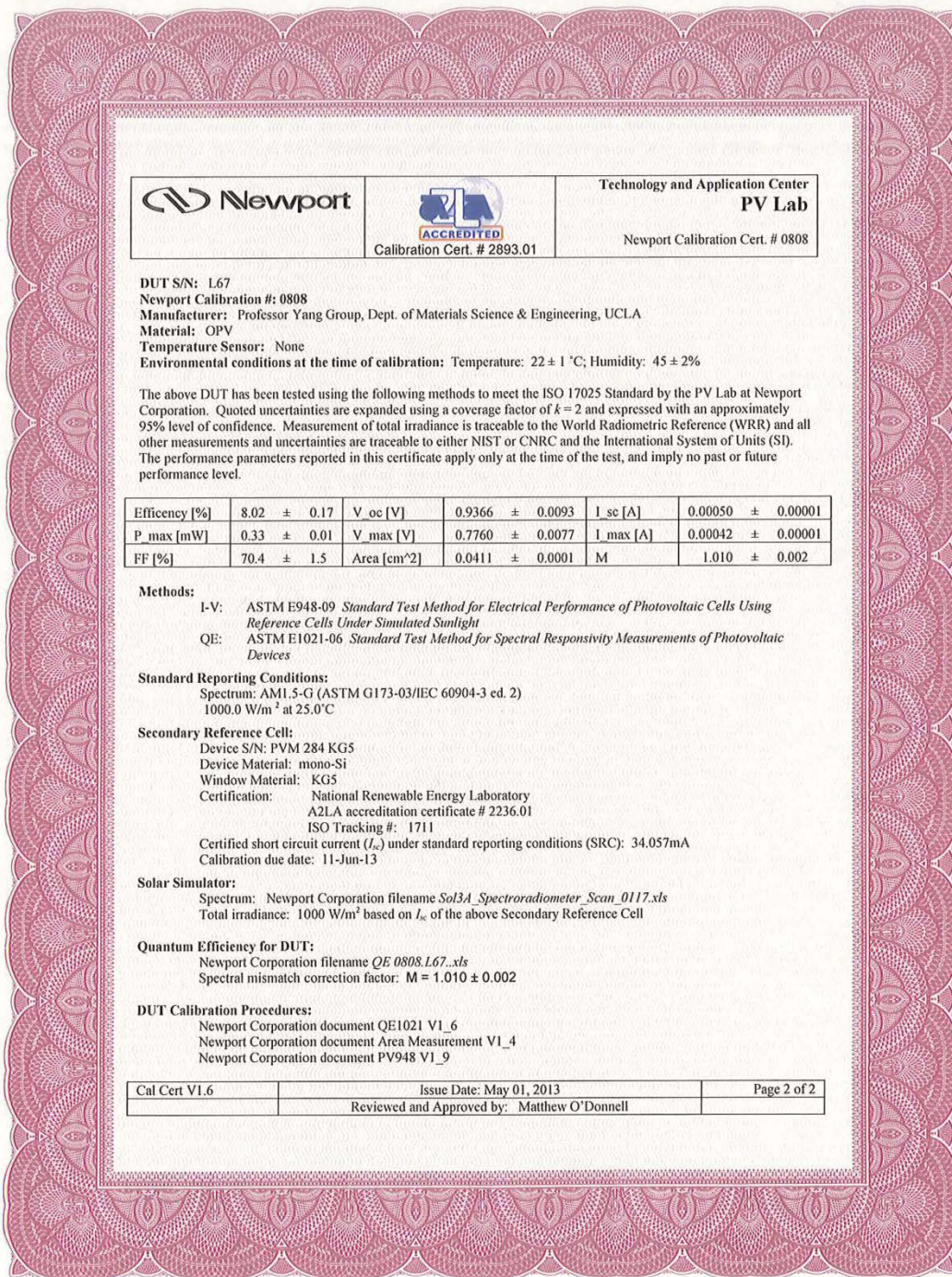
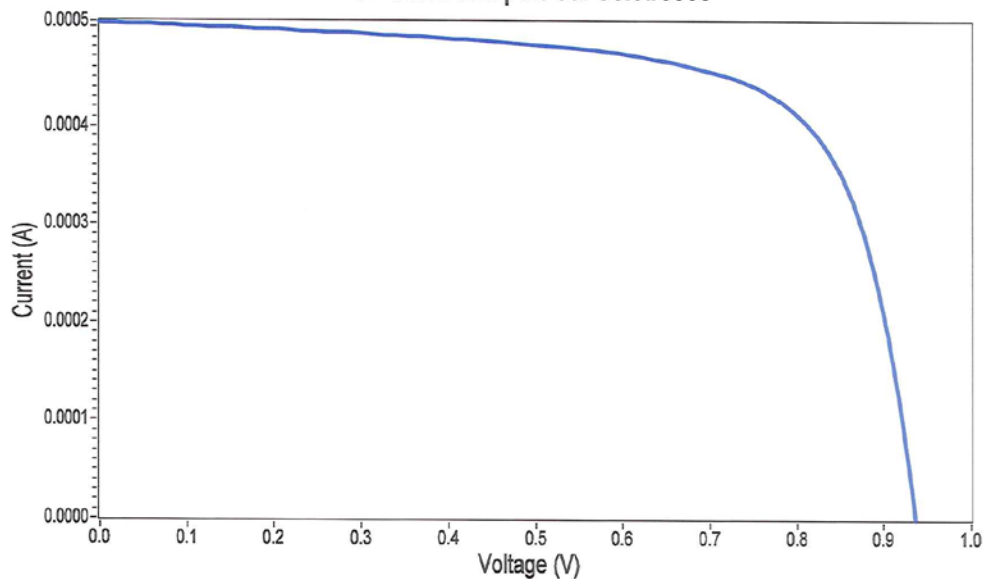


Figure S14b. Test results of the SMPV1 based single junction device from Newport Corporation.

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Figure S14c. *J-V* characteristics the SMPV1 based single junction device from Newport Corporation.

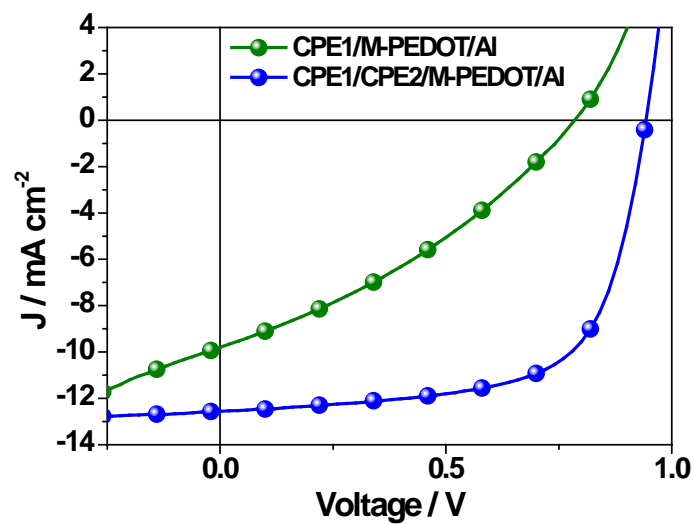


Figure S15. J-V curves of ITO/PEDOT:PSS/SMPV1:PC₇₁BM (1:0.8, w:w)/CPE1/M-PEDOT/Al and ITO/PEDOT:PSS/SMPV1:PC₇₁BM (1:0.8, w:w)/CPE1/CPE2/M-PEDOT/Al. All the active layer using PDMS (0.5 mg ml⁻¹) as additive.⁴

6. Supporting Tables.

Table S1. *d*-Spacing values of Compounds SMPV1.

	PDMS (mg ml^{-1})	$2\theta(^{\circ})$	d_{100} (\AA)
SMPV1	0	4.18	21.1
SMPV1/PC ₇₁ BM	0	4.22	20.9
SMPV1/PC ₇₁ BM	0.5	4.16	21.2

Table S2. Solar cell parameters of SMPV1/PC71BM based devices with different weight ratio.

	Blend ratio (w:w)	Voc (V)	Jsc (mA cm^{-2})	PCE (%)	FF (%)
SMPV1/PC71BM	1:0.5	0.95	11.28	6.6	62
SMPV1/PC71BM	1:0.8	0.93	11.43	7.2	68
SMPV1/PC71BM	1:1.2	0.95	11.24	6.5	61

Table S3. Solar cell parameters of SMPV1/PC₇₁BM (1:0.8) based devices using PDMS as additive.

	Blend ratio (w:w)	PDMS mg ml^{-1}	Voc (V)	Jsc (mA cm^{-2})	PCE (%)	FF (%)
SMPV1/PC ₇₁ BM	1:0.8	0.3	0.94	12.0	7.6	67
SMPV1/PC ₇₁ BM	1:0.8	0.5	0.94	12.5	8.1	69
SMPV1/PC ₇₁ BM	1:0.8	0.8	0.94	10.7	6.0	60

Table S4. Solar cell parameters of T4/PC₇₁BM (1:0.8) based devices using PDMS (0.5 mg ml^{-1}) as additive and CPE as interlayer.

	Voc (V)	Jsc (mA cm^{-2})	PCE (%)	FF (%)
CPE1/M-PEDOT	0.78	9.80	2.58	33.7
CPE1/CPE2/M-PEDOT	0.94	12.55	7.81	66.2

Reference

- 1 Zhou, J. Y. *et al.* A Planar Small Molecule with Dithienosilole Core for High Efficiency Solution-Processed Organic Photovoltaic Cells. *Chem Mater* **23**, 4666-4668, doi:Doi 10.1021/Cm202588h (2011).

- 2 Huo, L. J. *et al.* Replacing Alkoxy Groups with Alkylthienyl Groups: A Feasible Approach To Improve the Properties of Photovoltaic Polymers. *Angew Chem Int Edit* **50**, 9697-9702 (2011).
- 3 Xie, Y. L. *et al.* Discovery of a novel submicromolar inhibitor of the lymphoid specific tyrosine phosphatase. *Bioorg. Med. Chem. Lett.* **18**, 2840-2844 (2008).
- 4 Zhou, Y. H. *et al.* A Universal Method to Produce Low-Work Function Electrodes for Organic Electronics. *Science* **336**, 327-332 (2012).