Supplementary information (ESI†)

Toward Environmentally Compatible Molecular Solar Cells Processed from Halogen-Free Solvents

Mahmoud E. Farahat,[abc] Cheng-Si Tsao,[de] Yu-Ching Huang,[d] Sheng Hsiung Chang,[f] Widhya Budiawan,[abc] Chun-Guey Wu,[f] and Chih-Wei Chu[c*]

[a]Department of Engineering and System Science, National Tsing-Hua University, Hsinchu 30013, Taiwan

[b]Nanoscience and Technology Program, Taiwan International Graduate Program, Academia Sinica and National Tsing-Hua University, Taiwan

[c]Research Center for Applied Sciences, Academia Sinica, Taipei 115, Taiwan, E-mail: gchu@gate.sinica.edu.tw

[d]Institute of Nuclear Energy Research, Longtan, Taoyuan, 32546, Taiwan

[e]Department of Materials Science and Engineering, National Taiwan University, Taipei 10617, Taiwan

[f]Research Center for New Generation Photovoltaics, Jhongli, 32001, Taiwan

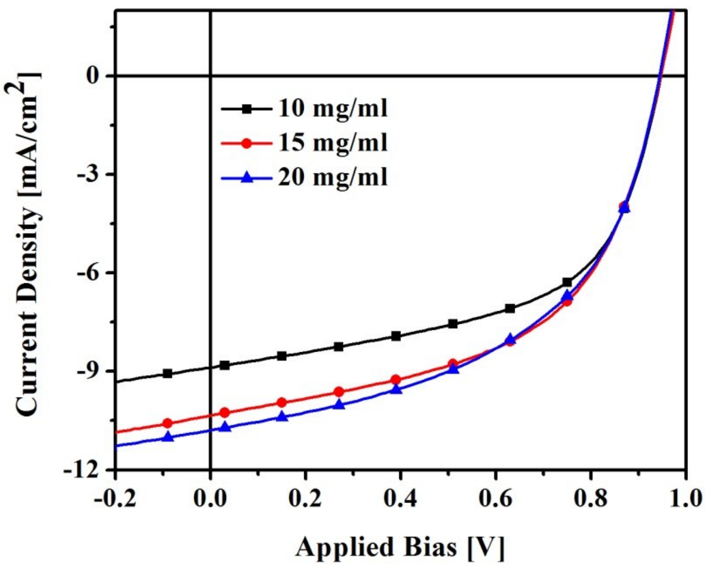
Table S1. Highest reported photovoltaic characteristics obtained using various halogen-free solvents ***for polymer blend systems***

Solvent system	Blend system	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]	Reference
***o*-Xylene + 2% NMP**	PBDT-TS1:$PC_{71}BM$	17.46	0.79	68.63	9.47	[1]
***o*-Xylene + 1% AA**	PffBT4T-2OD/$PC_{71}BM$	18.0	0.74	68.00	9.50	[2]
Tol + 1% NMP	P3HT/ICBA	10.3	0.85	75.00	6.60	[3]
NMP + 5% DIO	PBDTTT-TEG/$PC_{71}BM$	13.53	0.66	58.55	5.23	[4]
***o*-Xylene/MeOH**	P2/$PC_{61}BM$	12.8	0.82	71.00	7.50	[5]
CS_2:Acetone (83:17)	PCDTBT:$PC_{71}BM$	10.72	0.91	68.20	6.62	[6]
TMB + 2.5% DMN	PIDTT-DFBT:$PC_{71}BM$	12.97	0.97	58.00	7.26	[7]
TMB + NP	PffBT4T-C_9C_{13}:$PC_{71}BM$	19.80	0.78	73.00	11.70	[8]
Anisole	PBT-T1:$PC_{61}BM$	6.25	0.91	44.00	2.52	[9]
2-methylanisole (MA)	PBDT-TS1: $PC_{71}BM$	17.39	0.97	70.40	9.67	[10]

Table S2. Highest reported photovoltaic characteristics obtained using various halogen-free solvents ***for small-molecule blend systems***

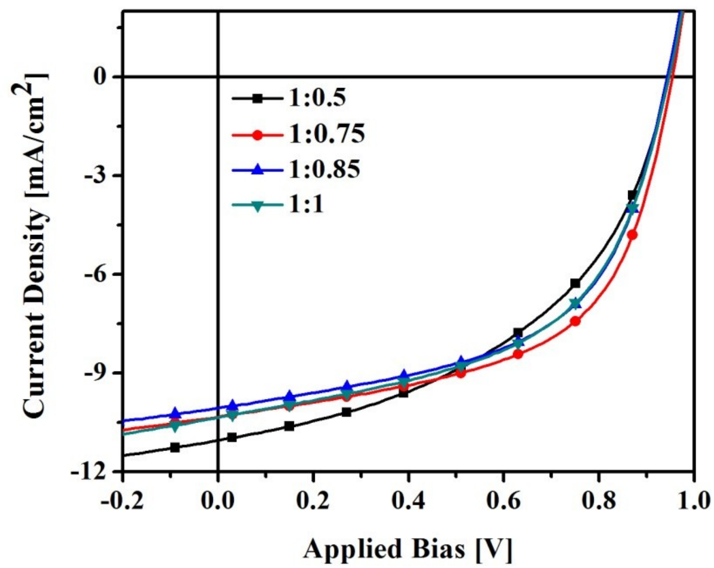
Solvent system	Blend system	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]	Reference
Benzaldehyde:mesitylene 80:20	N(Ph-2T-DCN-Et)/$PC_{71}BM$	8.37	0.96	46.68	3.75	[11]
2-MeTHF	X2:$PC_{61}BC_8$	12.30	0.72	55.00	5.10	[12]
THF+CN	SM:$PC_{71}BM$	11.23	0.91	48.00	4.96	[13]
Tol	**SMPV1:$PC_{71}BM$**	**12.55**	**0.89**	**63.03**	**7.04**	**This study**

Fig. S1 and **Table S3** present the effect of different SMPV1 concentrations on the *J*–*V* photovoltaic characteristics of SMPV1:$PC_{71}BM$ at a blend ratio of 1:1. The device performances displayed here are best obtained after optimization of thicknesses.



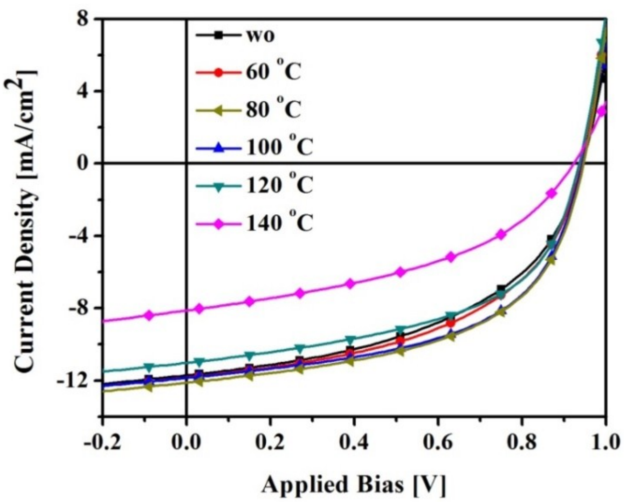
SMPV1 Conc. [mg mL^{-1}]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
10	8.89	0.95	55.89	4.72
15	10.35	0.95	53.19	5.23
20	10.80	0.94	50.63	5.14

Fig. S2 and **Table S4** present the effect of different $PC_{71}BM$ ratios on the *J–V* photovoltaic characteristics of SMPV1:$PC_{71}BM$ blends prepared at the optimized SMPV1 concentration (15 mg mL^{-1}). The device performances presented here are best obtained after optimization of thicknesses.



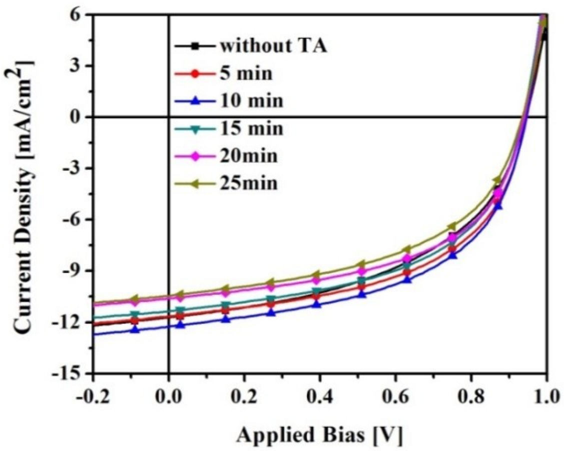
SMPV1:$PC_{61}BM$	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
1:0.5	11.00	0.95	46.99	4.91
1:0.75	10.79	0.95	52.78	5.41
1:0.85	10.06	0.95	54.83	5.24
1:1	10.35	0.95	53.19	5.23

Fig. S3 and **Table S5** display the effect of different thermal annealing temperatures on the *J*–*V* photovoltaic characteristics of devices fabricated from SMPV1:$PC_{71}BM$ blends at the optimized blend ratio (1:0.75) and optimized SMPV1 concentration (15 mg mL^{-1}). The SMPV1:$PC_{71}BM$ blend was cast from Tol containing PDMS (optimized; 0.5 mg mL^{-1}) and thermally annealed at various annealing temperatures for 10 min. The device performances presented here are best obtained after optimization of thicknesses.



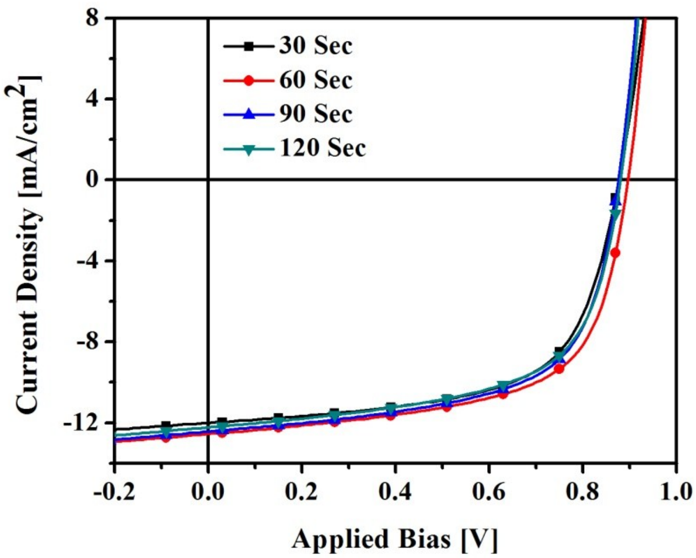
Annealing Temp [°C]	J_{sc} **[mA cm^{-2}]**	V_{oc} **[V]**	**FF [%]**	**PCE [%]**
W/o	11.35	0.94	51.00	5.44
60	11.88	0.94	50.24	5.61
80	12.13	0.95	53.80	6.20
100	11.85	0.94	55.21	6.15
120	11.02	0.94	52.61	5.45
140	8.12	0.92	43.51	3.25

Fig. S4 and **Table S6** display the effect of different thermal annealing durations on the *J*–*V* photovoltaic characteristics of devices fabricated from SMPV1:$PC_{71}BM$ blends at the optimized blend ratio (1:0.75) and SMPV1 concentration (15 mg mL^{-1}). The SMPV1:$PC_{71}BM$ blend was cast from Tol containing PDMS (optimized; 0.5 mg mL^{-1}) and thermally annealed at 80 °C for various durations. The device performances presented here are the best obtained after optimization of thicknesses.



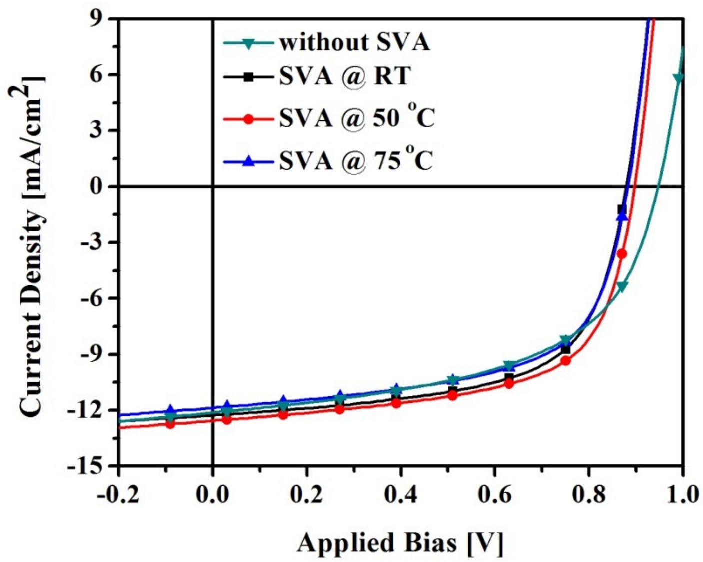
Thermal Ann. duration [min]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
W/o	11.35	0.94	51.00	5.44
5	11.65	0.95	52.95	5.86
10	12.24	0.95	52.89	6.15
15	11.35	0.94	52.30	5.58
20	10.60	0.94	53.59	5.34
25	10.45	0.93	50.73	4.93

Fig. S5 and **Table S7** display the effect of the Tol-SVA treatment duration (at 50 °C) on the *J–V* photovoltaic characteristics of devices fabricated from SMPV1:$PC_{71}BM$ blends at the optimized blend ratio (1:0.75) and SMPV1 concentration (15 mg mL^{-1}). The SMPV1:$PC_{71}BM$ blend was cast from Tol containing PDMS (optimized; 0.5 mg mL^{-1}) and thermally annealed at 80 °C for 10 min. The device performances presented here are the best obtained after optimization of thicknesses.



SVA Time [s]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	**FF** [%]	**PCE** [%]
30	12.02	0.88	62.40	6.60
60	12.55	0.89	63.03	7.04
90	12.43	0.87	62.60	6.77
120	12.22	0.88	61.65	6.63

Fig. S6 and **Table S8** display the effect of the Tol-SVA treatment temperature (for various durations) on the *J*–*V* photovoltaic characteristics of devices fabricated from SMPV1:$PC_{71}BM$ blends at the optimized blend ratio (1:0.75) and SMPV1 concentration (15 mg mL^{-1}). The SMPV1:$PC_{71}BM$ blend was cast from Tol containing PDMS (optimized; 0.5 mg mL^{-1}) and thermally annealed at 80 °C for 10 min. The device performances presented here are the best obtained after optimization of thicknesses.



Condition	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
W/o SVA	12.10	0.95	53.33	6.13
SVA @ RT	12.26	0.88	62.1	6.70
SVA @ 50 °C	12.55	0.89	63.03	7.04
SVA @ 75 °C	11.86	0.88	60.84	6.35

Table S9. Device optimization processes tested to determine the optimal device performance.

Acceptor ratio	**Additive**	**TA temp. [°C]**	**TA dura. [min]**	**SVA dura. [s]**	J_{sc} **[mA cm⁻²]**	V_{oc} **[V]**	**FF [%]**	**PCE [%]**
1:0.5	None	RT	–	–	11.00	0.95	46.99	4.91
1:0.75	None	RT	–	–	11.35	0.94	51.00	5.44
1:0.85	None	RT	–	–	10.06	0.95	54.83	5.24
1:1	None	RT	–	–	10.35	0.95	53.19	5.23
1:0.75	0.5 mg mL^{-1} PDMS	60	10	–	11.88	0.94	50.24	5.61
1:0.75	0.5 mg mL^{-1} PDMS	80	10	–	12.13	0.95	53.80	6.20
1:0.75	0.5 mg mL^{-1} PDMS	100	10	–	11.85	0.94	55.21	6.15
1:0.75	0.5 mg mL^{-1} PDMS	120	10	–	11.02	0.94	52.61	5.45
1:0.75	0.5 mg mL^{-1} PDMS	140	10	–	8.12	0.92	43.51	3.25
1:0.75	0.5 mg mL^{-1} PDMS	80	5	–	11.65	0.95	52.95	5.86
1:0.75	0.5 mg mL^{-1} PDMS	80	10	–	12.13	0.95	53.80	6.20
1:0.75	0.5 mg mL^{-1} PDMS	80	15	–	11.35	0.94	52.30	5.58
1:0.75	0.5 mg mL^{-1} PDMS	80	20	–	10.60	0.94	53.59	5.34
1:0.75	0.5 mg mL^{-1} PDMS	80	25	–	10.45	0.93	50.73	4.93
1:0.75	0.5 mg mL^{-1} PDMS	80	10	30	12.02	0.88	62.40	6.60
1:0.75	0.5 mg mL^{-1} PDMS	**80**	**10**	**60**	**12.55**	**0.89**	**63.03**	**7.04**
1:0.75	0.5 mg mL^{-1} PDMS	80	10	90	12.43	0.87	62.60	6.77
1:0.75	0.5 mg mL^{-1} PDMS	80	10	120	12.22	0.88	61.65	6.63

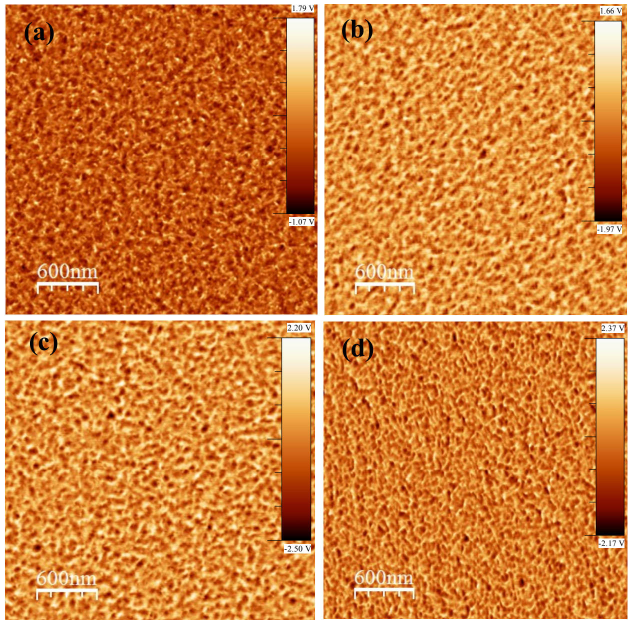


Fig. S7 AFM phase images of SMPV1:$PC_{71}BM$ active layers processed from Tol and subjected to SVA using various treatment solvents; (a) Tol-SVA, (b) THF-SVA, (c) CS_2-SVA, and (d) Hex-SVA.

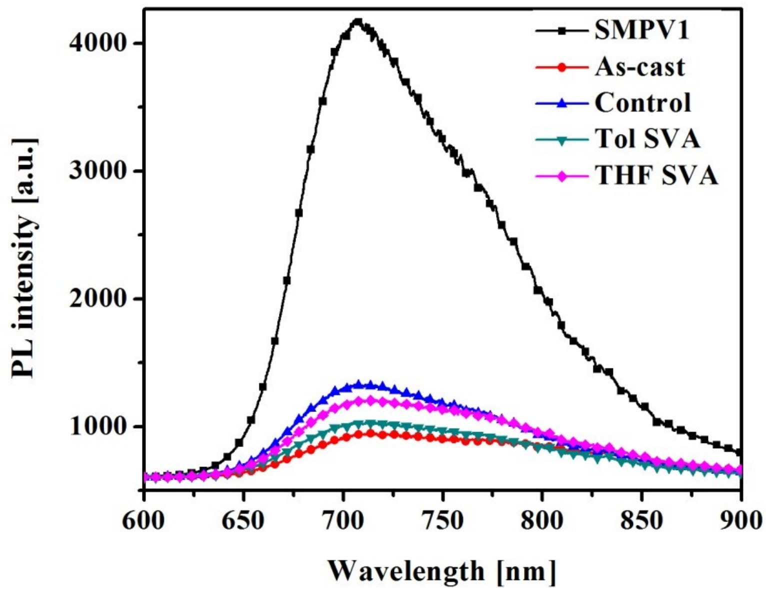


Fig. S8. PL spectra of SMPV1:$PC_{71}BM$ active layers processed from Tol and subjected to SVA using different treatment solvents.

(a) (b)

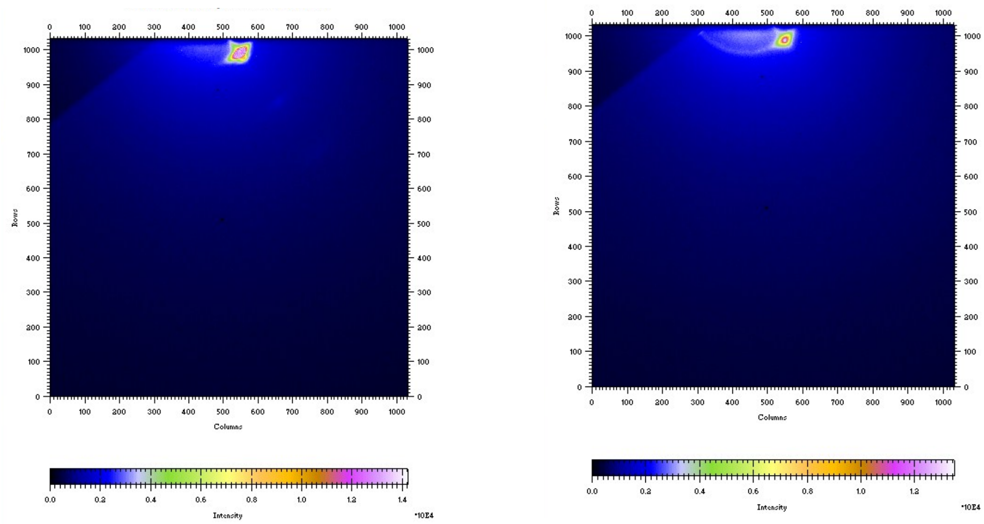
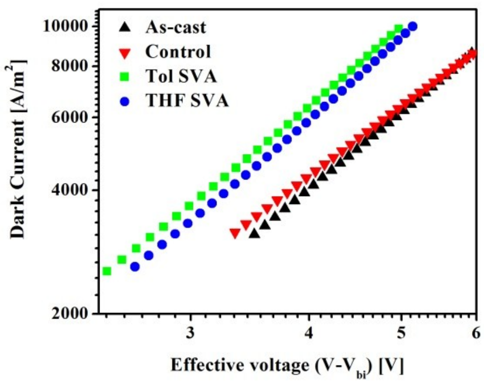


Fig. S9. 2D GIWAXS patterns of a (a) pristine SMPV1 film and (b) SMPV1:PC71BM blend film revealing diffraction spots of the (100) lamellar plane dominate in the out-of-plane direction.

(a)



(b)

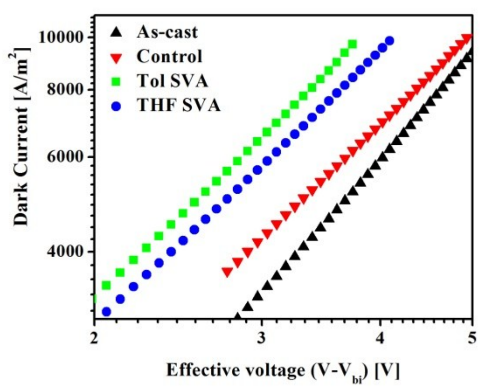


Fig. S10. Charge carrier mobilities of SMPV1:$PC_{71}BM$ devices fabricated with SVA under various conditions. (a) Electron- and (b) hole-only devices.

Table S10. Charge carrier mobilities of SMPV1:$PC_{71}BM$ devices fabricated with SVA under various conditions.

Condition	μ_e [cm^2 V^{-1} s^{-1}]	μ_h [cm^2 V^{-1} s^{-1}]	μ_e /μ_h
As-cast	4.37×10^{-5}	1.12×10^{-5}	3.90
Control	7.82×10^{-5}	3.57×10^{-5}	2.19
Tol-SVA	3.67×10^{-4}	2.75×10^{-4}	1.33
THF-SVA	2.25×10^{-4}	1.37×10^{-4}	1.64

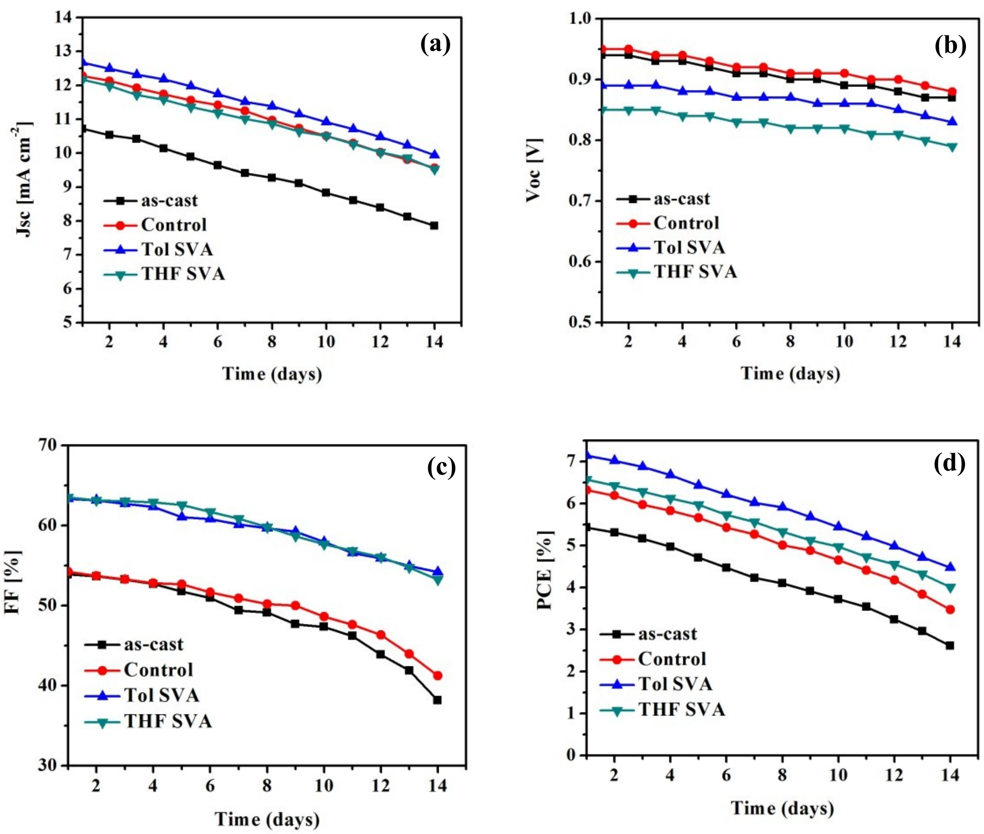


Fig. S11. Presents stability of SMPV1:$PC_{71}BM$ devices prepared at under various treatment conditions after 14 days storage in in N_2-filled glove box. (a) Short-circuit current density (J_{sc}), (b) Voltage (V), (c) Fill factor (FF) and (d) Power conversion efficiency (PCE)

Supporting References

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