Supplementary Information (ESI†)

Efficient Molecular Solar Cells Processed from Green Solvent Mixtures†

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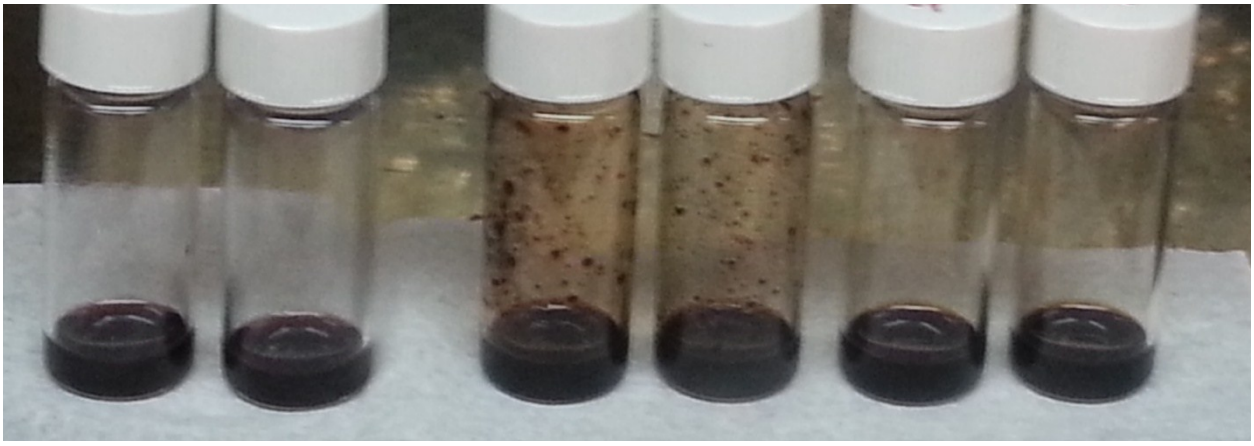
Table S1. Highest reported photovoltaic characteristics obtained using various halogen-free solvents ***for small-molecule blend systems***

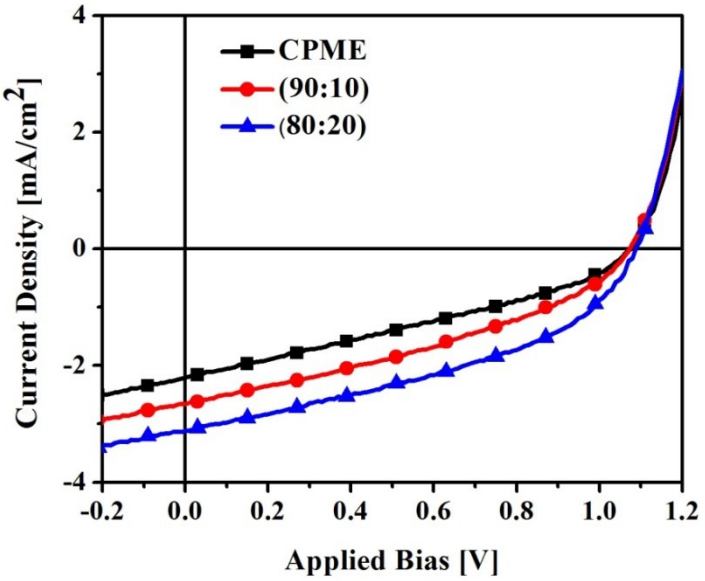
Solvent system	Blend system	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]	Reference
Benzaldehyde:mesitylene 80:20	N(Ph-2T-DCN-Et)/$PC_{71}BM$	8.37	0.96	46.68	3.75	[1]
2-MeTHF	X2:$PC_{61}BC_8$	12.30	0.72	55.00	5.10	[2]
THF with additive	SM:$PC_{71}BM$	11.23	0.91	48.00	4.96	[3]
Tol with SVA[(a)]	SMPV1:$PC_{71}BM$	12.55	0.89	63.03	7.04	Our work [4]
CPME:Tol (60:40)	SMPV1:$PC_{61}BM$	12.72	0.95	67.03	8.10	This study

[(a)] SVA: Solvent Vapor Annealing



$PC_{61}BM$ **$PC_{71}BM$** **ICBA**

Fig. S1 Solubility test: Photograph of three fullerene derivatives in CPME (10 mg mL^{-1}); stirred for 3 h at 60 °C.



Condition	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
CPME	2.21	1.08	31.59	0.754
90:10	2.66	1.07	35.49	1.01
80:20	3.12	1.09	40.87	1.39

Fig. S2 and **Table S2** present the photovoltaic characteristics of devices fabricated from SMPV1:ICBA processed using CPME alone and CPME:Tol solvent mixtures with various Tol contents. The device performances displayed here are the best obtained after optimization of the thicknesses.

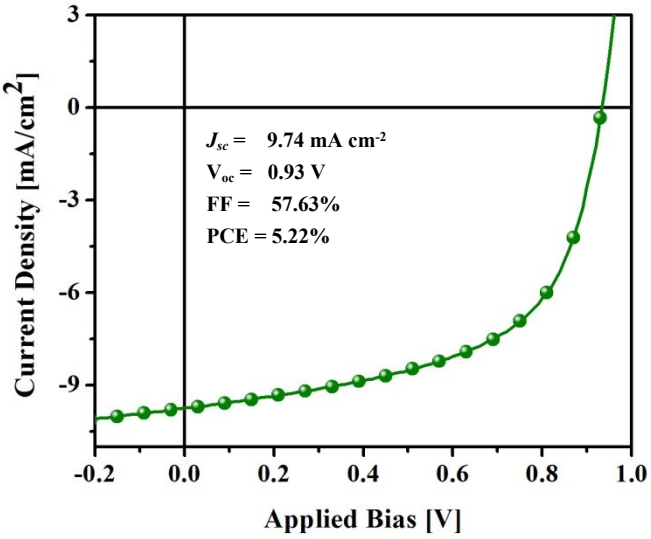


Fig. S3 *J–V* photovoltaic characteristics of an SMPV1:$PC_{61}BM$ device processed using Tol alone and without TA.

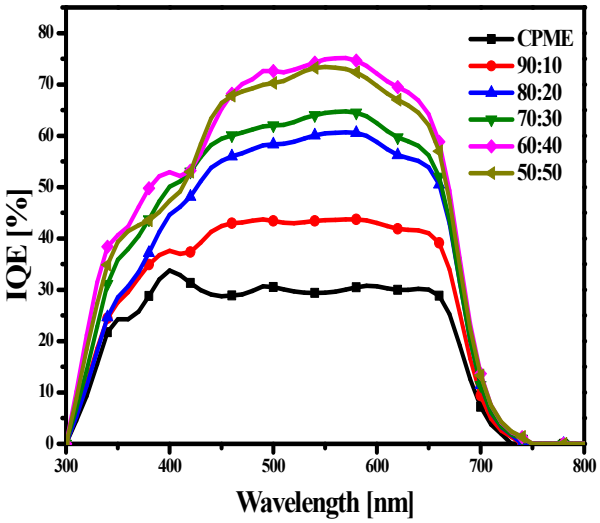


Fig. S4 IQE of SMPV1:$PC_{61}BM$ devices prepared using green solvent mixtures with various Tol contents.

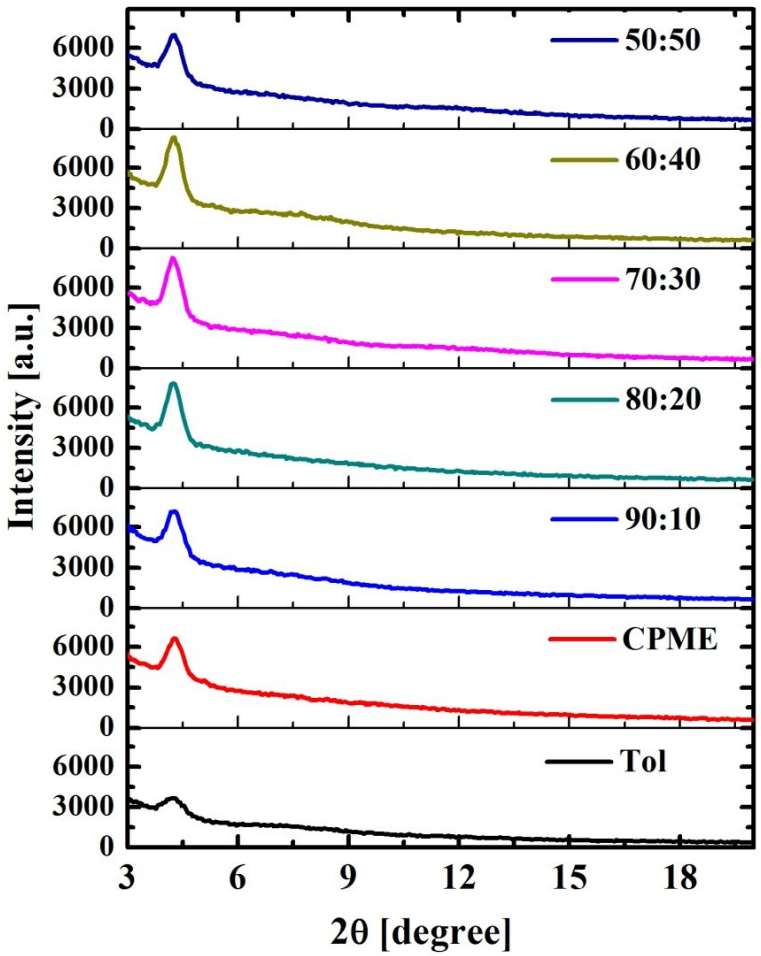


Fig. S5 XRD profiles of SMPV1:$PC_{61}BM$ active layers prepared using green solvent mixtures with various Tol contents.

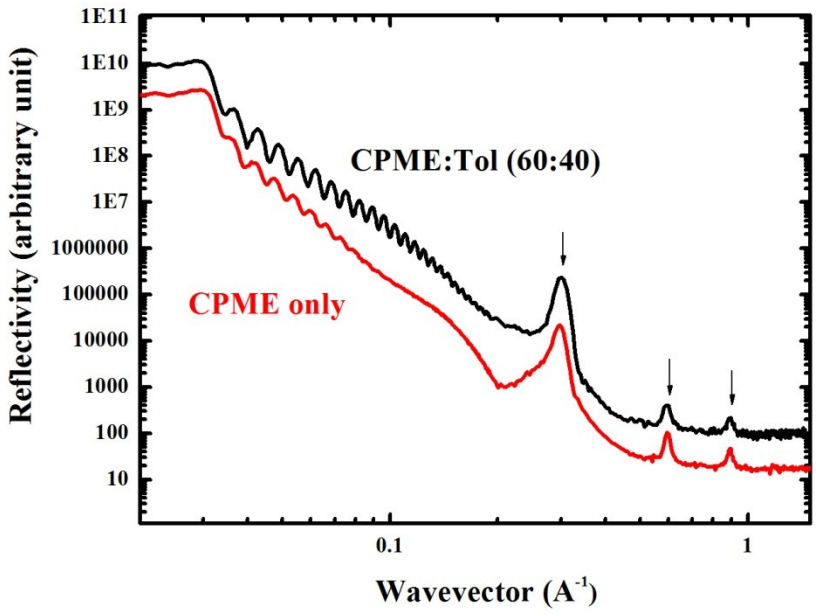


Fig. S6 X-ray reflectivity profiles of SMPV1:$PC_{61}BM$ active layers processed from CPME alone and from the 60:40 green solvent mixture. Arrows indicate the (100), (200), and (300) diffraction peaks of the stacking lattice spacing of SMPV1 crystallinity. The reflectivity profile with CPME only (red) has been shifted for clarity.

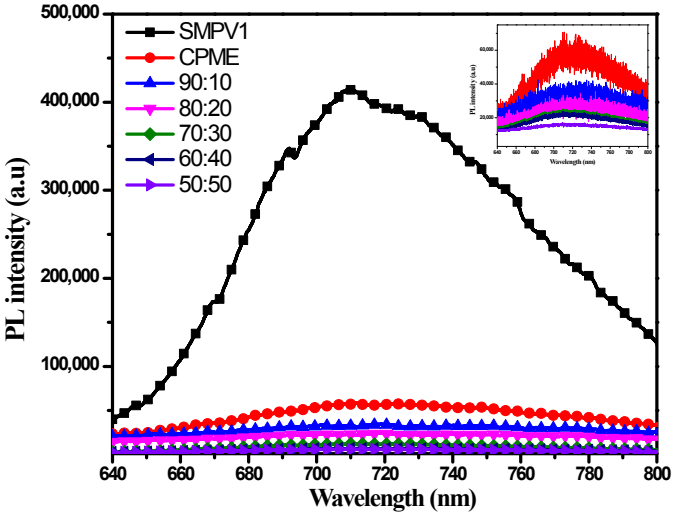
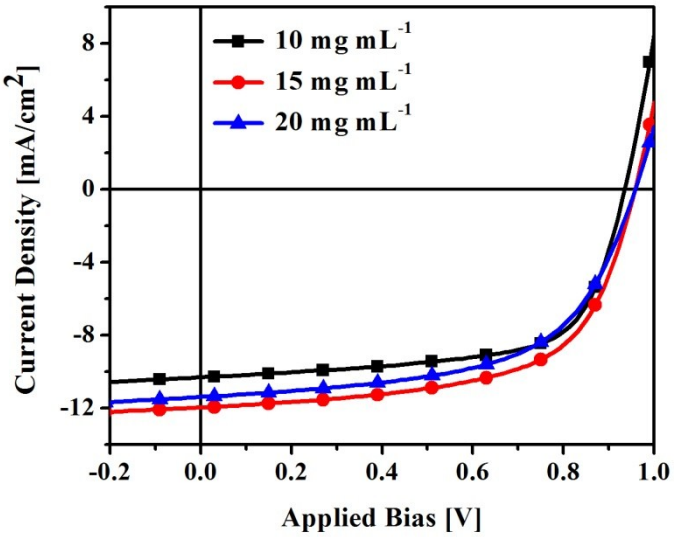
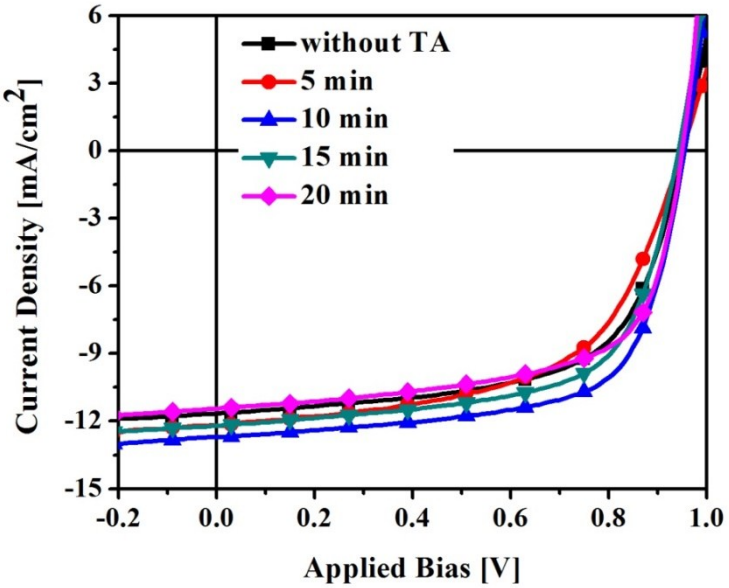


Fig. S7. PL spectra, measured using light from a green laser (532 nm), of neat SMPV1 and SMPV1:$PC_{61}BM$ films prepared using different volume ratios of CPME and Tol.



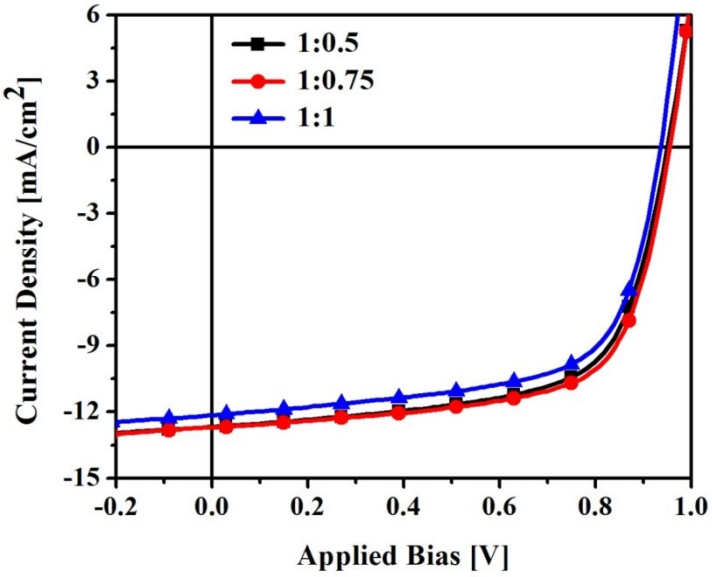
SMPV1 Conc. [mg mL^{-1}]	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
10	10.30	0.94	65.59	6.35
15	11.96	0.96	60.97	7.00
20	11.37	0.96	57.90	6.32

Fig. S8 and **Table S4** present the effect of various SMPV1 concentrations on the *J–V* photovoltaic characteristics of SMPV1:$PC_{61}BM$ films at a blend ratio of 1:0.75. The SMPV1:$PC_{61}BM$ blends were cast from the 60:40 green solvent mixture and were not subjected to TA. The device performances presented here are the best obtained after optimization of thicknesses.



Annealing duration	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
Without TA	11.96	0.95	60.97	7.00
5 min	12.44	0.95	63.67	7.53
10 min	12.72	0.95	67.03	8.10
15 min	12.22	0.94	64.51	7.41
20 min	11.45	0.95	64.26	6.99

Fig. S9 and **Table S5** present the effect of the TA duration on the *J*–*V* photovoltaic characteristics of devices fabricated from SMPV1:$PC_{61}BM$ blends at the optimized blend ratio (1:0.75) and SMPV1 concentration (15 mg mL^{-1}). The SMPV1:$PC_{61}BM$ blends were cast from the 60:40 green solvent mixture and then thermally annealed at 80 °C for various durations. The device performances presented here are the best obtained after optimization of thicknesses.



Acceptor ratio	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
1:0.5	12.68	0.95	65.17	7.85
1:0.75	12.72	0.95	67.03	8.10
1:1	12.15	0.94	64.79	7.40

Fig. S10 and **Table S6** present the effect of various $PC_{61}BM$ ratios on the *J–V* photovoltaic characteristics of SMPV1:$PC_{61}BM$ blends prepared at the optimized SMPV1 concentration (15 mg mL^{-1}). The SMPV1:$PC_{61}BM$ blends were cast from the 60:40 green solvent mixture and then thermally annealed at 80 °C for various durations. The device performances presented here are the best obtained after optimization of thicknesses.

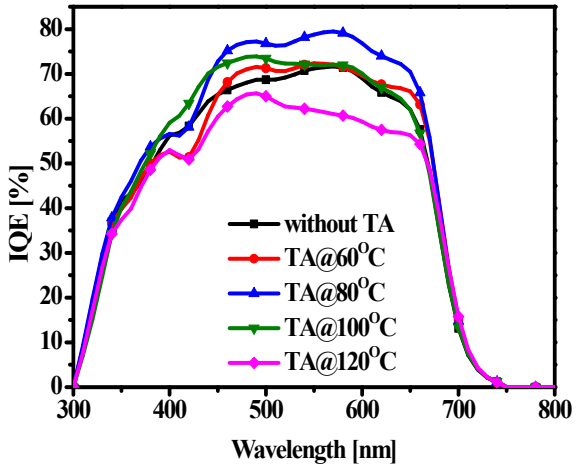


Fig. S11 IQE of SMPV1:$PC_{61}BM$ devices prepared using TA.

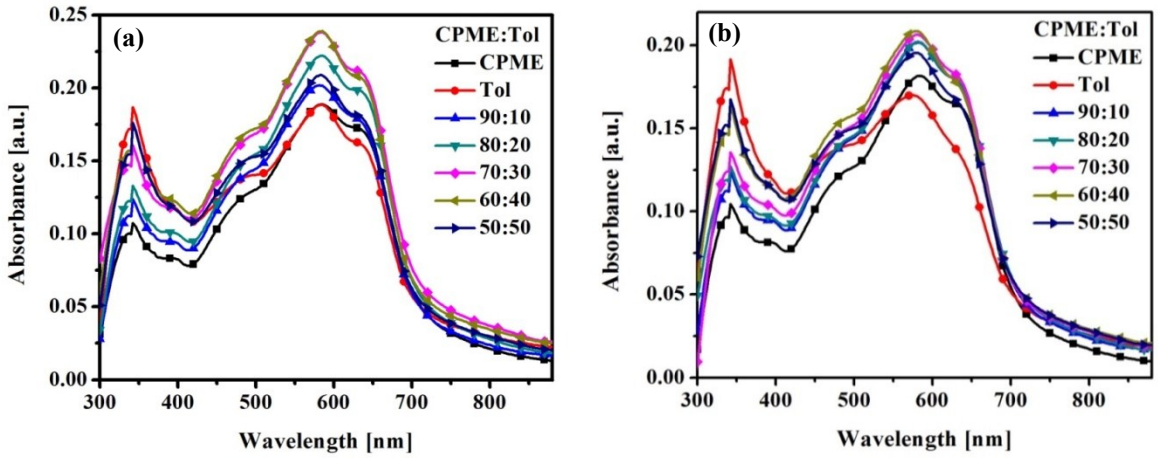


Fig. S12 UV–Vis absorption spectra of active layers processed from CPME and CPME:Tol solvent mixtures with various Tol contents: (a) thermally annealed at 80 °C for 10 min; (b) without thermal annealing.

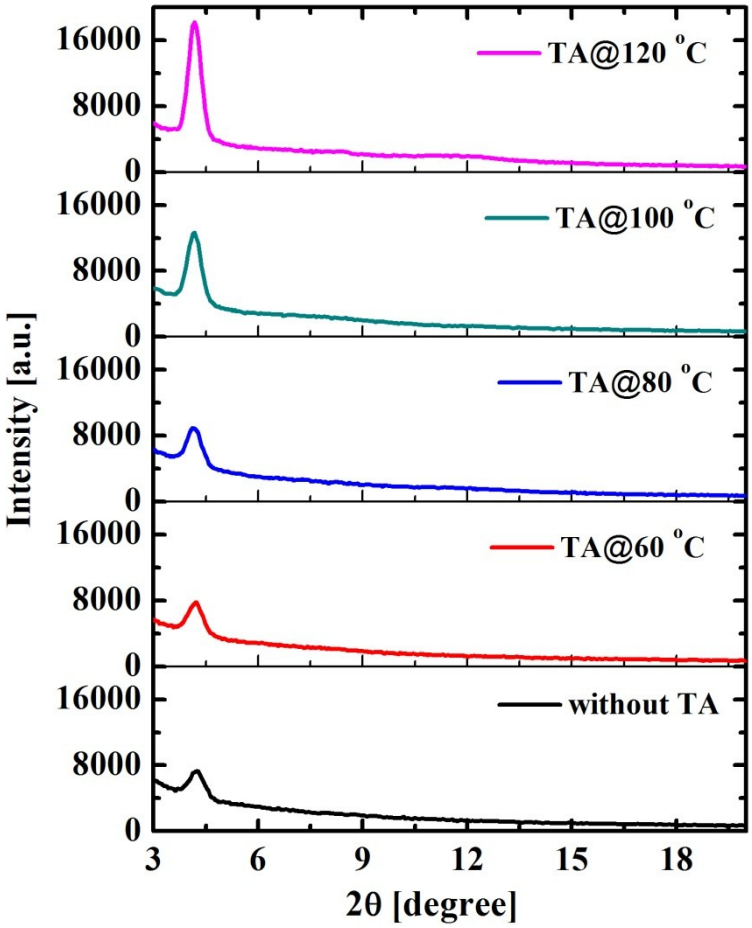
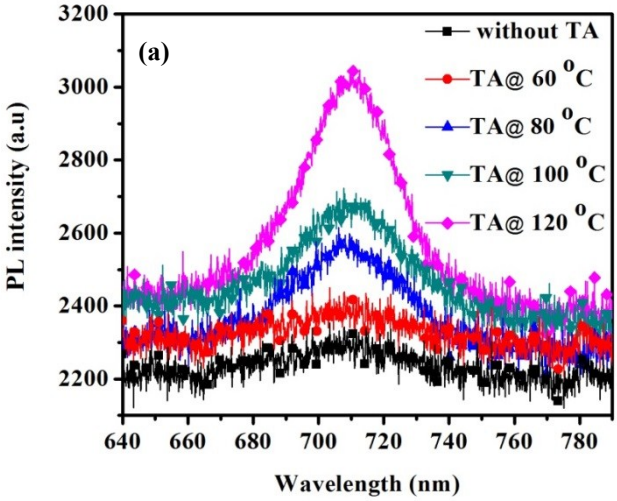
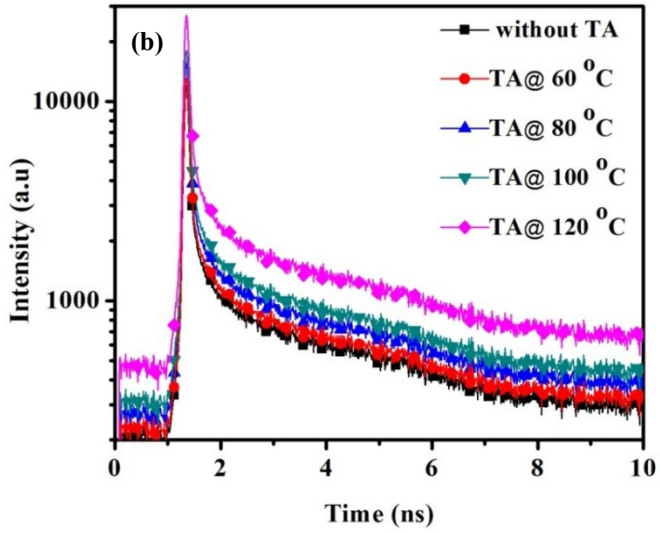


Fig. S13 XRD profiles of SMPV1:$PC_{61}BM$ active layers processed from the 60:40 green solvent mixture and then thermally annealed at various annealing temperatures for 10 min.


(a)
without TA
TA@ 60 °C
TA@ 80 °C
TA@ 100 °C
TA@ 120 °C
PL intensity (a.u)
Wavelength (nm)


(b)
without TA
TA@ 60 °C
TA@ 80 °C
TA@ 100 °C
TA@ 120 °C
Intensity (a.u)
Time (ns)

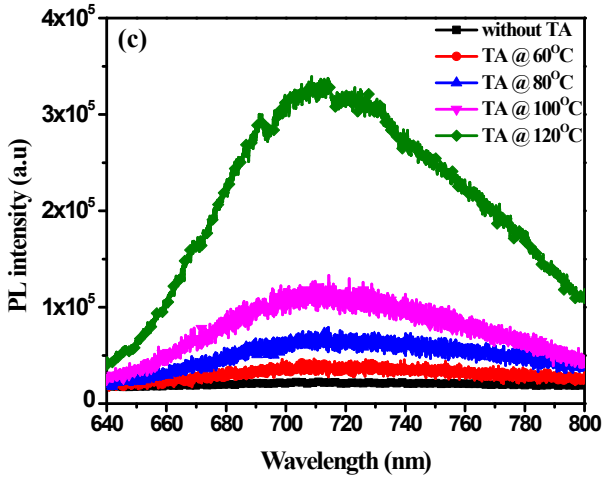

(c)
without TA
TA @ 60°C
TA @ 80°C
TA @ 100°C
TA @ 120°C
PL intensity (a.u)
Wavelength (nm)

Fig. S14 (a, c) PL and (b) corresponding TRPL spectra of SMPV1:$PC_{61}BM$ active layers, measured under excitation with light from (a, b) 266- and (c) 532-nm lasers; the films had been processed from the 60:40 green solvent mixture and then thermally annealed at various annealing temperatures for 10 min.

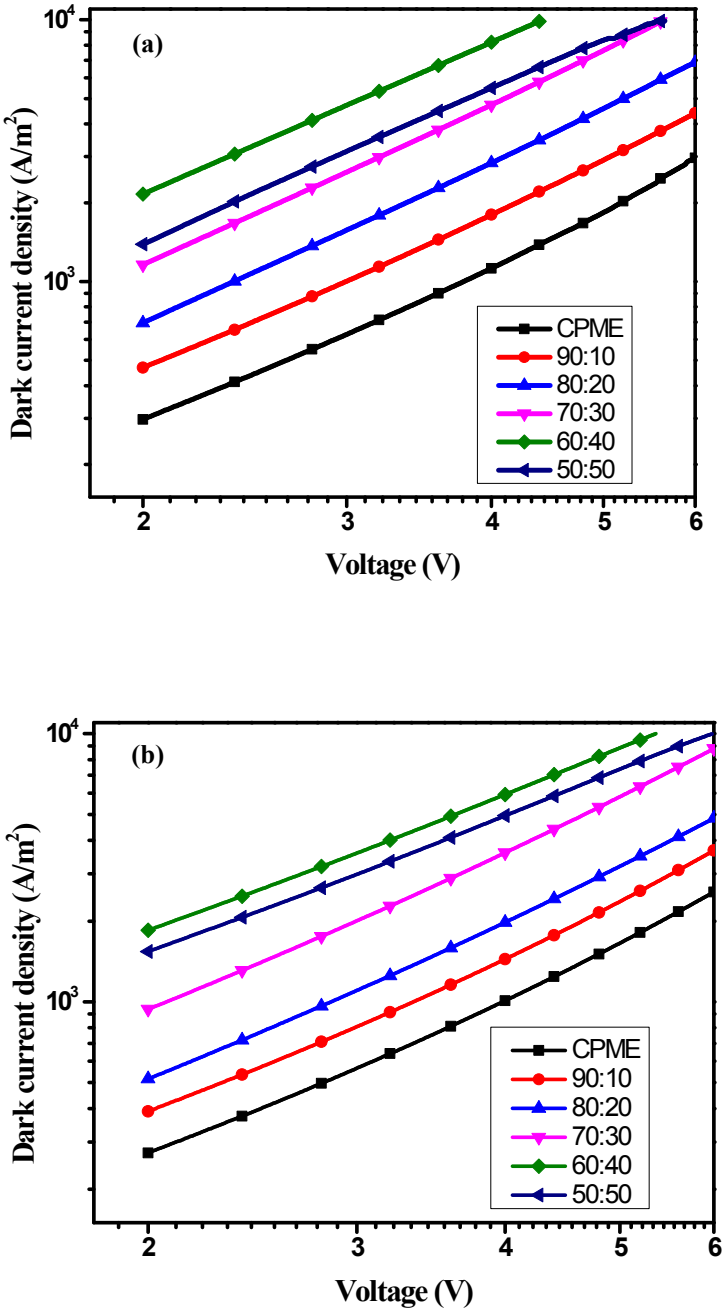


Fig. S15 (a) electron- and (b) hole-only devices of SMPV1:$PC_{61}BM$ active layers prepared using green solvent mixtures with various Tol contents.

Table S7 electron- and hole-only mobilities of SMPV1:$PC_{61}BM$ active layers prepared using green solvent mixtures with various Tol contents.

CPME:Toluene [volume ratio]	μ_e **[$cm^2V^{-1}s^{-1}$]**	μ_h **[$cm^2V^{-1}s^{-1}$]**	μ_e/μ_h
CPME	3.22×10^{-5}	1.08×10^{-5}	2.98
90:10	4.61×10^{-5}	2.18×10^{-5}	2.12
80:20	6.38×10^{-5}	3.64×10^{-5}	1.75
70:30	9.22×10^{-5}	7.57×10^{-5}	1.21
60:40	2.15×10^{-4}	1.89×10^{-4}	1.13
50:50	1.31×10^{-4}	1.61×10^{-4}	0.81

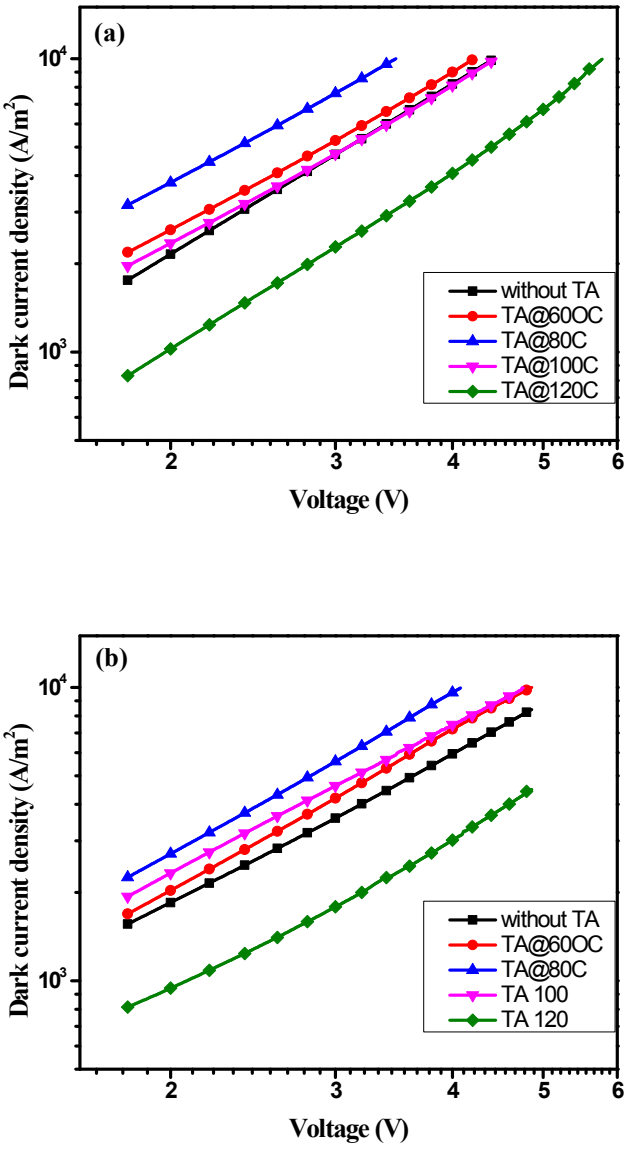


Fig. S16 (a) electron- and (b) hole-only devices of SMPV1:$PC_{61}BM$ active layers processed from the 60:40 green solvent mixture and then thermally annealed at various annealing temperatures for 10 min.

Table S8 electron- and hole-only mobilities of SMPV1:$PC_{61}BM$ active layers processed from the 60:40 green solvent mixture and then thermally annealed at various annealing temperatures for 10 min.

Temperature	μ_e **[$cm^2V^{-1}s^{-1}$]**	μ_h **[$cm^2V^{-1}s^{-1}$]**	μ_e/μ_h
without TA	2.15×10^{-4}	1.89×10^{-4}	1.13
60 °C	2.63×10^{-4}	2.54×10^{-4}	1.03
80 °C	3.81×10^{-4}	3.83×10^{-4}	0.99
100 °C	2.36×10^{-4}	2.57×10^{-4}	0.91
120 °C	8.52×10^{-5}	9.71×10^{-5}	0.87

Supporting References

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