Supporting Information

Constructing Nanointerpenetrating Structure of PCDTBT:$PC_{70}BM$ Bulk Heterojunction Solar Cells Induced by Aggregation of $PC_{70}BM$ via Mixed-solvent Vapor Annealing

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Paper submitted to ***Journal of Materials Chemistry A***

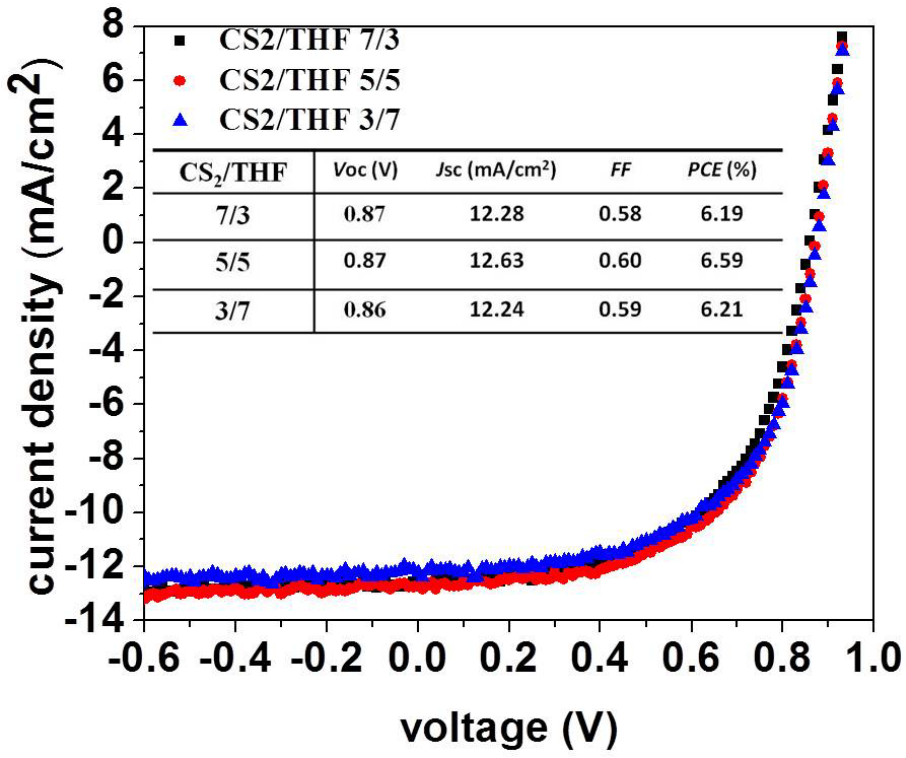
March 26, 2013

The estimated HOMO and LUMO energy levels from cyclic voltammetry for the PCDTBT used in this study is shown in Table S1, and its ^{1}H NMR information of is: ^{1}H NMR (400 MHz, ODCB-d_4): δ 8.11 (d, J = 3.5 Hz, 2H); 8.02 (d, J = 8.1 Hz, 2H); 7.94 (br, 2H); 7.74 (br, 2H); 7.56 (d, J = 7.8 Hz, 2H); 7.45 (d, J = 3.6 Hz, 2H); 4.73 (br, 1H); 2.42 (br, 2H); 2.05 (m, 2H); 1.23 (br, 8H); 1.22 (br, 16H); 0.70 (t, J = 6.8 Hz, 6H).

polymers	E_{ox}^{onset} (V)	E_{red}^{onset} (V)	HOMO (eV)	LUMO (eV)	Chemical band gap (eV)
PCDTBT	0.60	-1.50	-5.40	-3.30	2.10

Table S1. The HOMO and LUMO energy levels from cyclic voltammetry for PCDTBT.

The ratio of THF to CS_2 in mixed solvent has significant impact on the morphology of blend film as well. We used a series of mixed solvent with different ratios of THF to CS_2, including 7:3, 1:1 and 7:3, to treat the active layers of devices and tested its performances. The results showed that the device treated by the mixed solvent, THF:CS_2=1:1, has the best device performance, as shown in Figure S1.

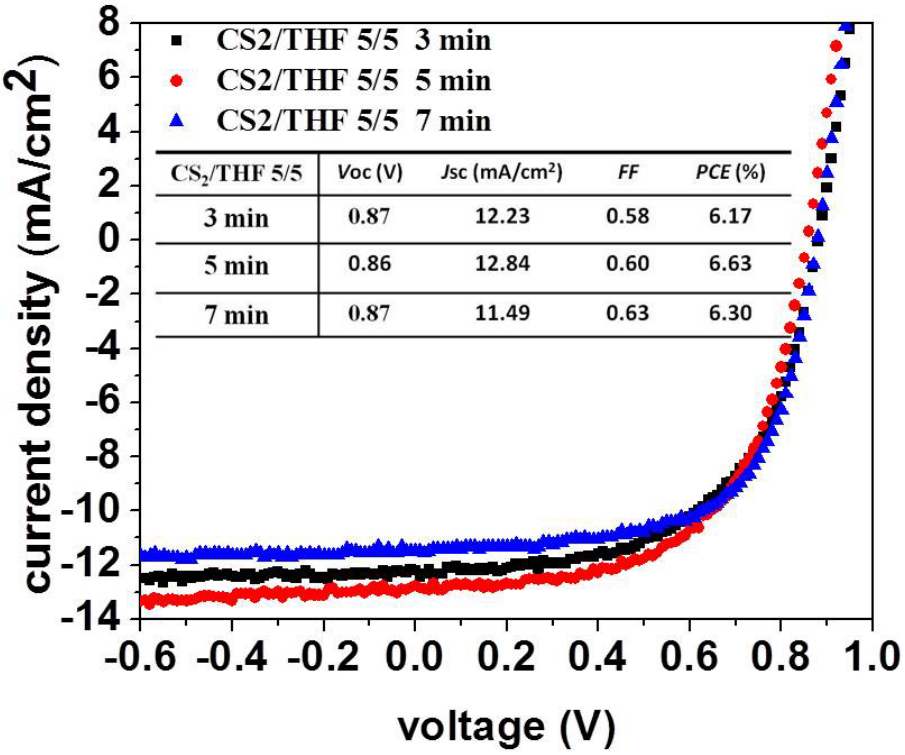


CS_2/THF	Voc (V)	Jsc (mA/cm²)	FF	PCE (%)
7/3	0.87	12.28	0.58	6.19
5/5	0.87	12.63	0.60	6.59
3/7	0.86	12.24	0.59	6.21

Figure S1 *I–V* curves for devices processed from PCDTBT:$PC_{70}BM$ (φ_{PC70BM}=71.4

wt%) films with different annealing treatment under AM 1.5 illumination. The mixed solvents have different ratios of THF to CS_2, including 7:3, 1:1 and 7:3. The vapor pressure is P=0.81 (25 °C) and the annealing time is 5 min.

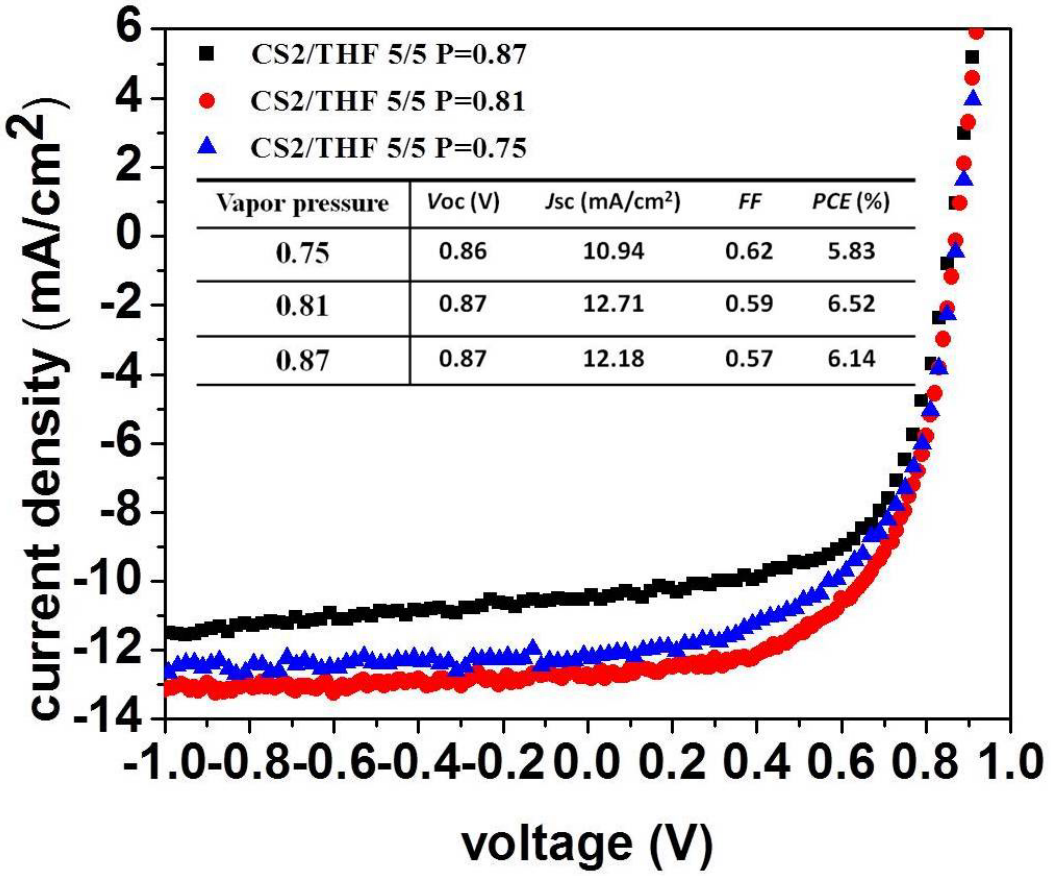
The annealing time are also an important parameter, the device were treated with different annealing time, including 3 min, 5min and 7 min, at the same vapor pressure. As shown in Figure S2, the device treated for 5 min showed the best performance.



CS_2/THF 5/5	Voc (V)	Jsc (mA/cm²)	FF	PCE (%)
3 min	0.87	12.23	0.58	6.17
5 min	0.86	12.84	0.60	6.63
7 min	0.87	11.49	0.63	6.30

Figure S2 *I–V* curves for devices processed from PCDTBT:$PC_{70}BM$ (φ_{PC70BM}=71.4 wt%) films with different annealing time, including 3 min, 5 min, 7 min, under AM 1.5 illumination. The mixed solvents have ratios of THF to CS_2 is 1:1. The vapor pressure is P=0.81 (25 °C) and the annealing time is 5 min.

The annealing pressure are also an important parameter, the device were treated with different vapor pressure, including P=0.75, 0.81 and 0.87 (25 °C). As shown in Figure S3, the device treated for P= 0.81(25 °C) showed the best performance.



Vapor pressure	Voc (V)	Jsc (mA/cm²)	FF	PCE (%)
0.75	0.86	10.94	0.62	5.83
0.81	0.87	12.71	0.59	6.52
0.87	0.87	12.18	0.57	6.14

Figure S3 *I–V* curves for devices processed from PCDTBT:$PC_{70}BM$ (φ_{PC70BM}=71.4 wt%) films with different vapor pressures during the annealing process, including P=0.75, 0.81 and 0.87 (25 °C), under AM 1.5 illumination. The mixed solvents have ratios of THF to CS_2 is 1:1, the annealing time is 5 min.

The ratio of donor to acceptor has profound influence on the morphology of active layer as well as the device performance. Here, three ratios of PCDTBT to $PC_{70}BM$, 1:1 (φ_{PC70BM}=50 wt%), 2:5 (φ_{PC70BM}=71.4 wt%) and 1:4 (φ_{PC70BM}=80 wt%), were annealed under the mixed solvent vapor (the ratio of THF to CS_2 is 1:1 and the annealing time is 5 min). The PCDTBT could self-organize into nanofibrils regardless of the fullerene content after the MSV-A treatment. However, the extent of phase separation is more homogeneous when the content of $PC_{70}BM$ is 71.4 wt% and 80 wt%, as shown in Figure S4. After the device performance test, it is clear that the device with 71.4 wt% PCBM content has the best performance, as shown in Figure S5, which may result from the enhanced photon absorption as shown in Figure S6.

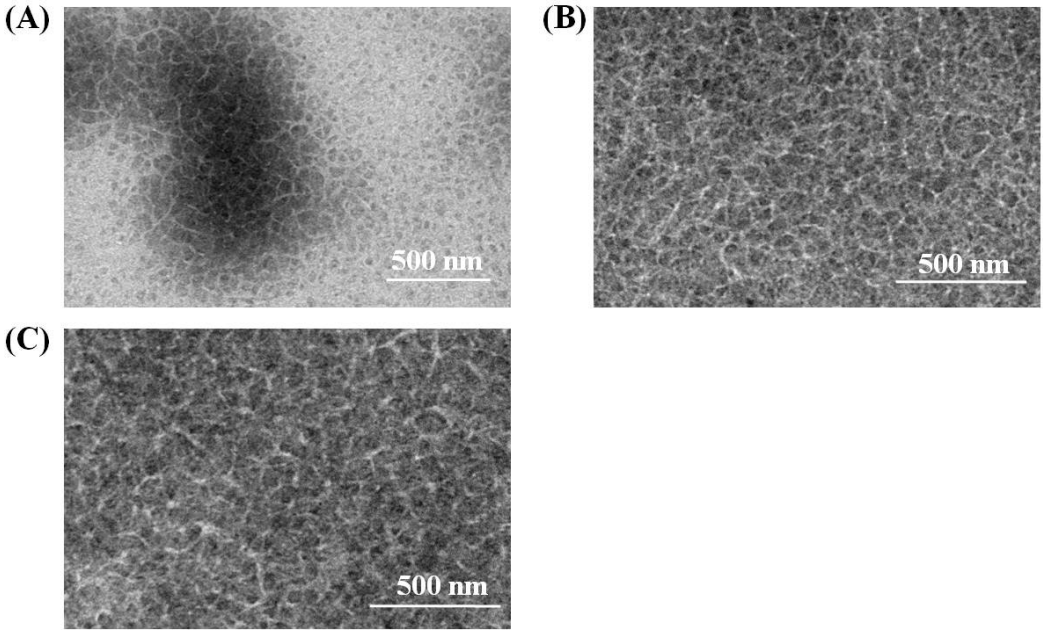
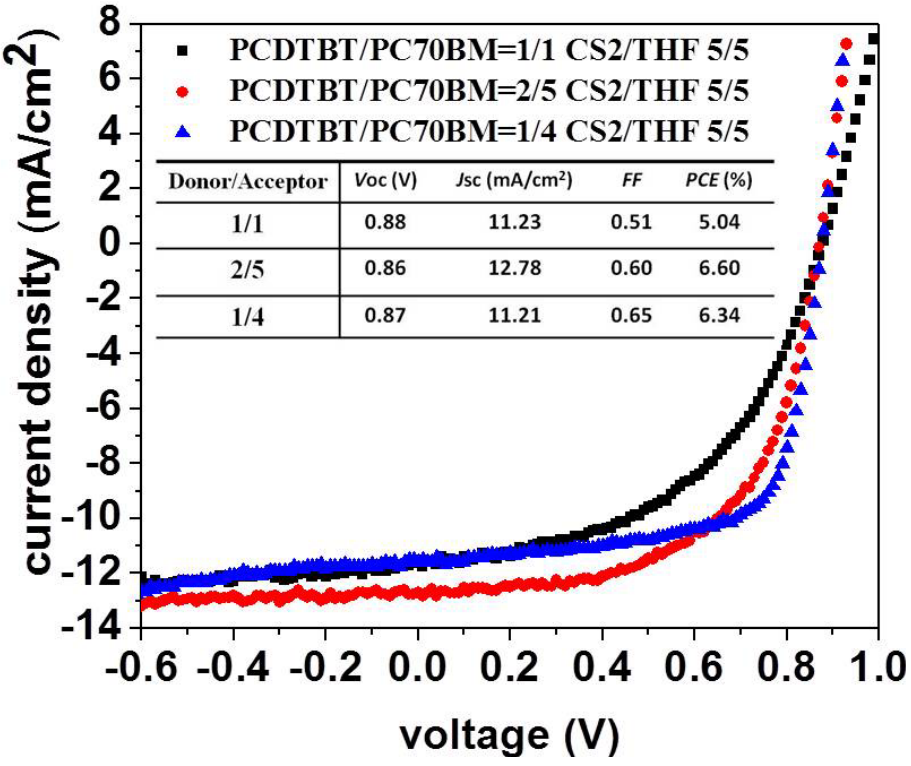


Figure S4 TEM images of PCDTBT: $PC_{70}BM$ blend films with different fullerene content after the M-SVA treatment, (A) φ_{PC70BM}=50 wt%, (B) φ_{PC70BM}=71.4 wt% and (C) φ_{PC70BM}=80 wt%. The mixed solvents have ratios of THF to CS_2 is 1:1. The vapor pressure is P=0.81 (25 °C) and the annealing time is 5 min.



Donor/Acceptor	Voc (V)	Jsc (mA/cm²)	FF	PCE (%)
1/1	0.88	11.23	0.51	5.04
2/5	0.86	12.78	0.60	6.60
1/4	0.87	11.21	0.65	6.34

Figure S5 *I–V* curves for devices processed from PCDTBT:$PC_{70}BM$ films with

different fullerene content after the M-SVA treatment under AM 1.5 illumination. The mixed solvents have ratios of THF to CS2 is 1:1. The vapor pressure is P=0.81 (25 °C) and the annealing time is 5 min.

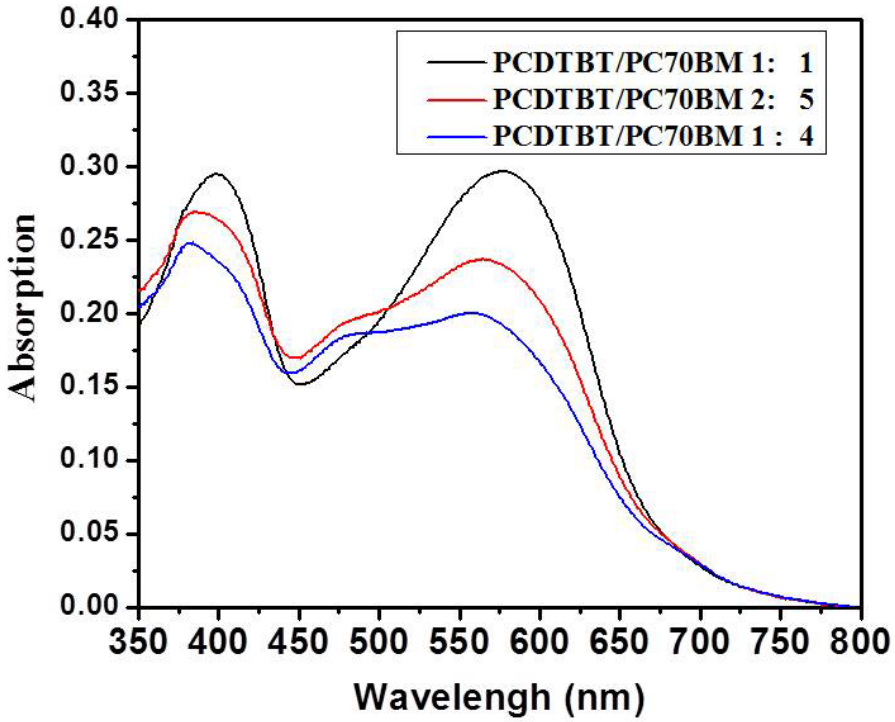


Figure S6 Absorption spectra for PCDTBT: $PC_{70}BM$ blend films with different fullerene content after the M-SVA treatment. The mixed solvents have ratios of THF to CS2 is 1:1. The vapor pressure is P=0.81 (25 °C) and the annealing time is 5 min.