Supporting Information

Highly efficient polymer solar cells by step-by-step optimizing donor molecular packing and acceptor redistribution

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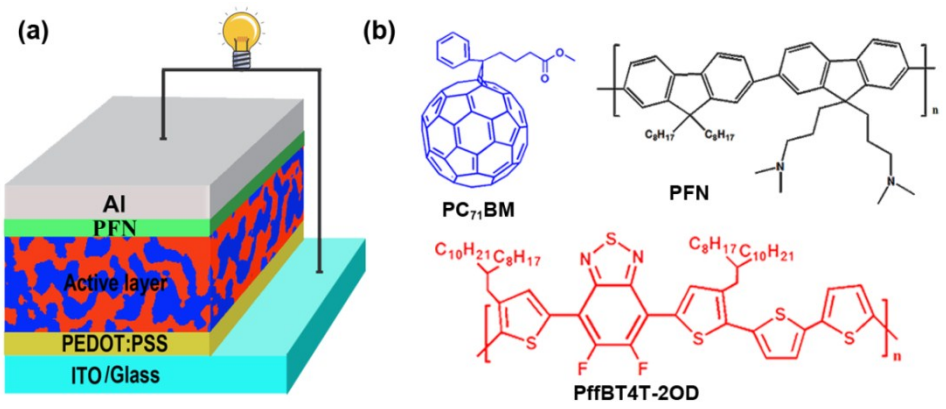


Fig. S1 (a) The schematic configuration of the PSCs; (b) the chemical structures of $PC_{71}BM$, PffBT4T-2OD and PFN.

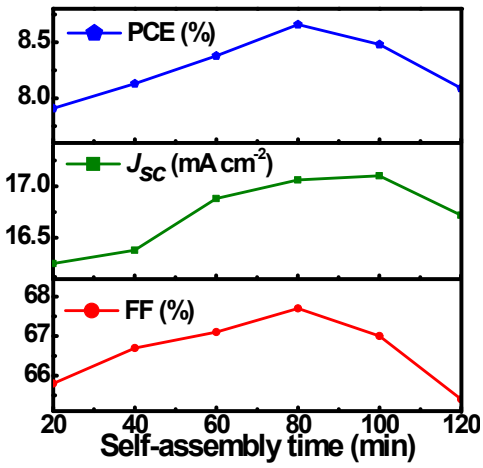


Fig. S2 The PCE, J_{SC} and FF dependence on self-assembly time.

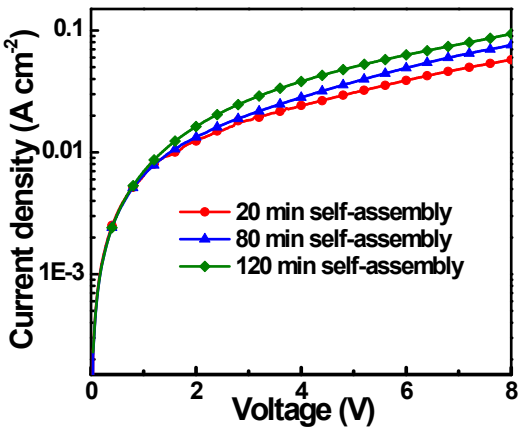


Fig. S3 The *J*-*V* curves of hole-only devices (ITO/PEDOT:PSS/active layer/MoO_3/Ag) with different self-assembly time.

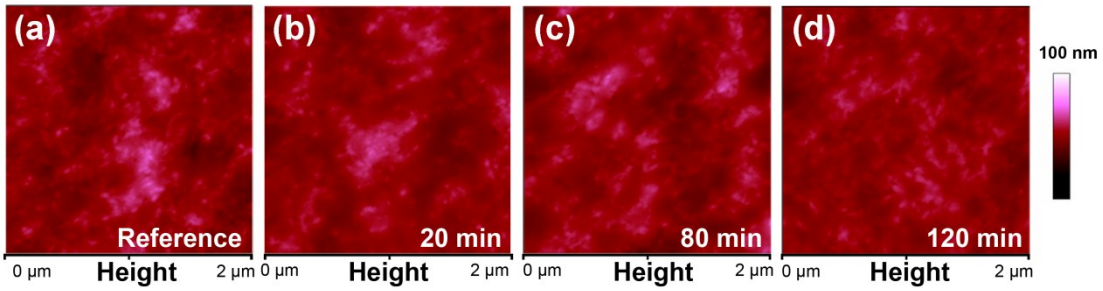


Fig. S4 AFM surface morphology images of PffBT4T-2OD:$PC_{71}BM$ blend films. (a) Reference blend film; (b-d) blend films with different self-assembly time (20 min, 80 min, 120 min).

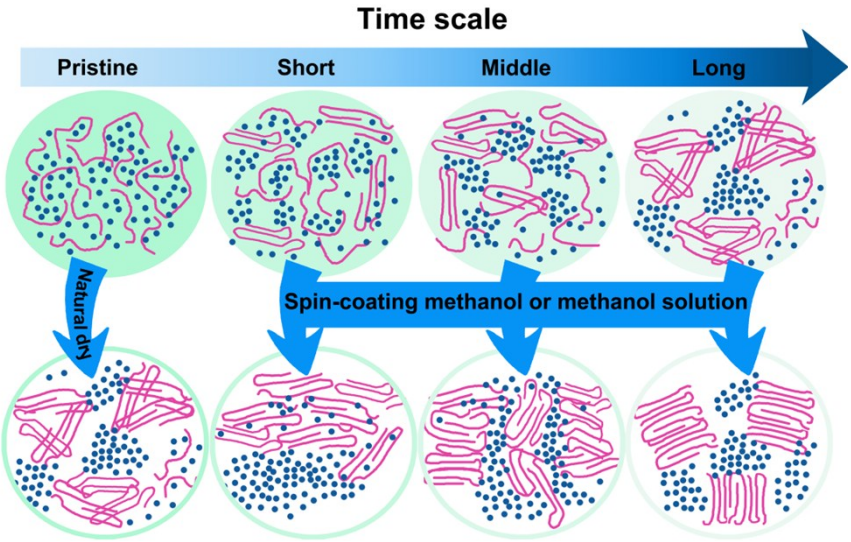


Fig. S5 schematic diagram of active layer evolutionary process (Line: PffBT4T-2OD, dot: $PC_{71}BM$).

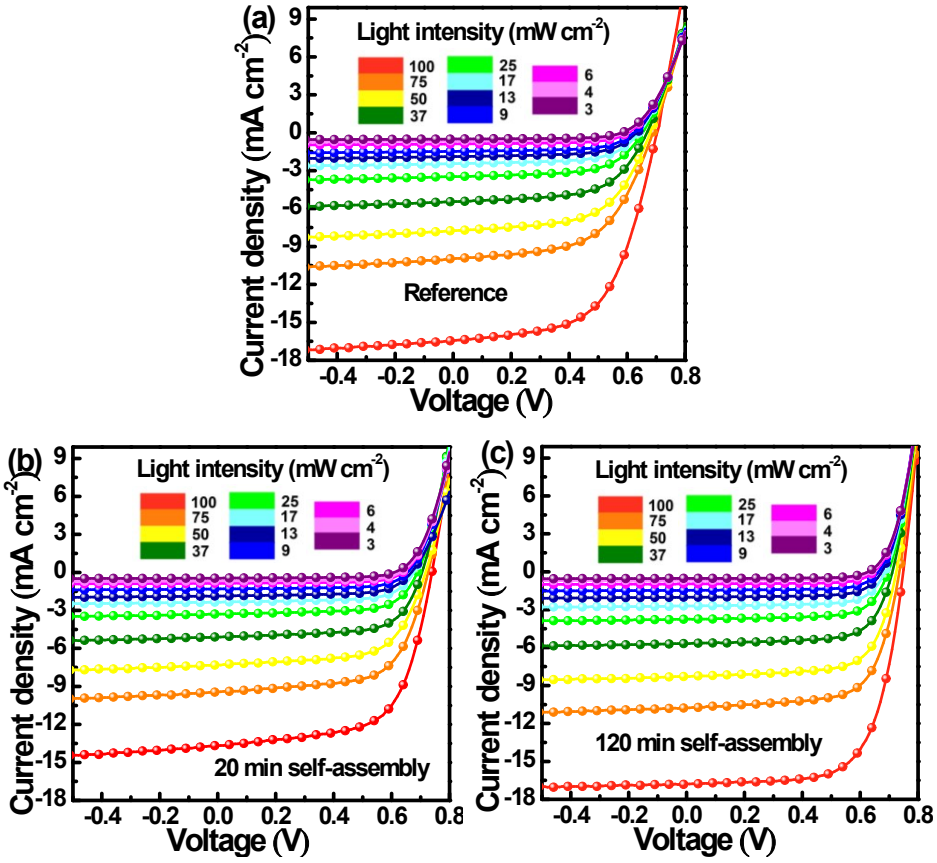


Fig. S6 The dependence of *J-V* curves on light intensity, a) the reference PSCs, b) PSCs with active layers undergoing 20 min self-assembly, c) PSCs with active layers undergoing 120 min self-assembly.

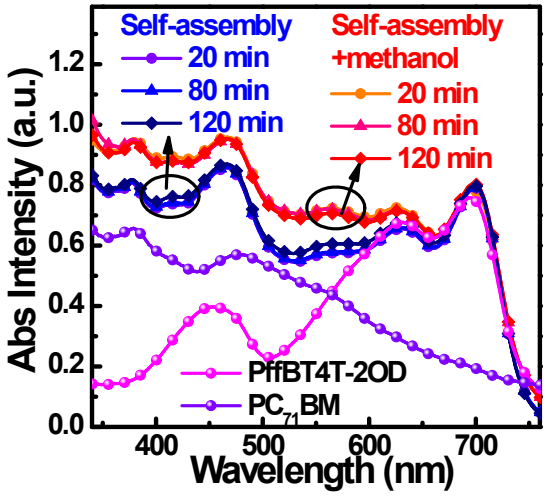


Fig. S7 Absorption spectra of neat PffBT4T-2OD film, neat $PC_{71}BM$ film and their blend films with different self-assembly time, some films were treated by methanol, and the others were not treated by methanol.

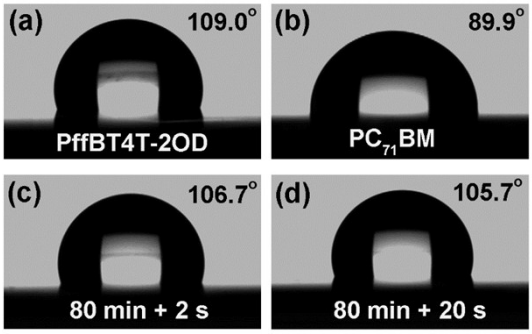


Fig. S8 Water contact angle images of neat PffBT4T-2OD film (a), neat $PC_{71}BM$ film (b) and blend films with 2 s or 20 s methanol soaking (c, d).

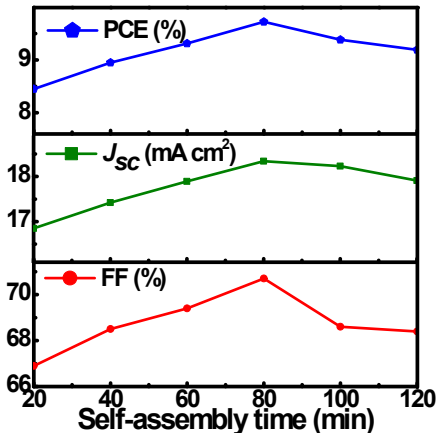


Fig. S9 The FF, J_{sc} and PCE of PSCs dependence on self-assembly time.

The mole number ratio of $PC_{71}BM$ ($C_{82}H_{14}O_2$) to PffBT4T-2OD ($C_{62}H_{88}F_2N_2S_5$) can be calculated by using the following formula:

$$\frac{n_C}{n_S} = \frac{82 \times n_{PC_{71}BM} + 62 \times n_{PffBT4T-2OD}}{5 \times n_{PffBT4T-2OD}} \quad (1)$$

Where $n_{PC_{71}BM}$ and $n_{PffBT4T-2OD}$ are mole number of $PC_{71}BM$ and PffBT4T-2OD molecule. The weight ratio of $PC_{71}BM$ to PffBT4T-2OD can be determined by using the following formula:

$$\frac{W_{PC_{71}BM}}{W_{PffBT4T-2OD}} = \frac{n_{PC_{71}BM} \times M_{PC_{71}BM}}{n_{PffBT4T-2OD} \times M_{PffBT4T-2OD}} \quad (2)$$

Where $M_{PC_{71}BM}$ and $M_{PffBT4T-2OD}$ are the molar mass of $PC_{71}BM$ molecule and repeated unit of PffBT4T-2OD molecule.

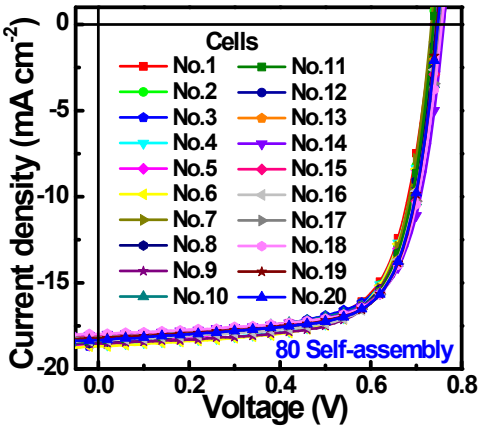
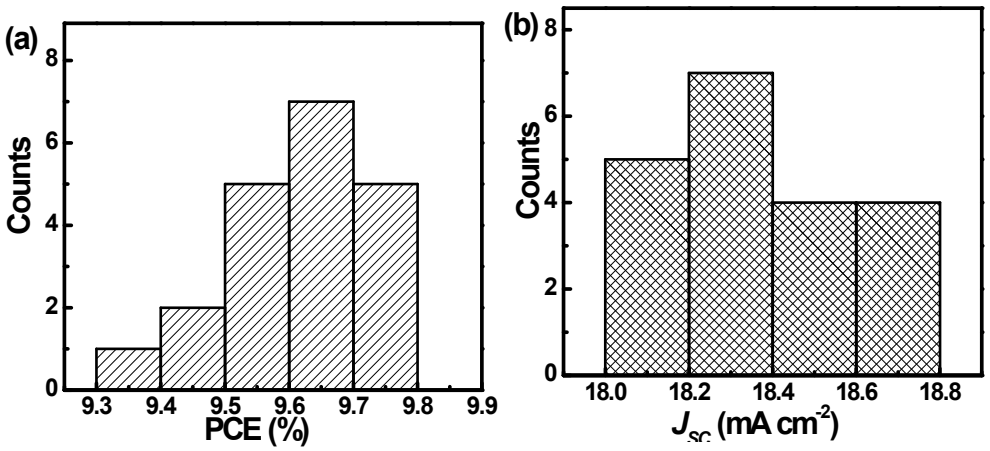


Fig. S10 *J-V* curves of PSCs with active layer undergoing 80 min self-assembly, 20s methanol soaking and PFN interfacial layer.

Table S1 Key photovoltaic parameters of PSCs with active layer undergoing 80 min self-assembly, 20s methanol soaking and PFN interfacial layer.

Cells	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)	Cells	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
No.1	18.39	0.74	69.0	9.39	No.11	18.57	0.76	68.5	9.67
No.2	18.64	0.75	67.7	9.47	No.12	18.24	0.75	70.7	9.67
No.3	18.58	0.74	69.0	9.49	No.13	18.13	0.75	71.2	9.68
No.4	18.65	0.75	68.2	9.54	No.14	18.01	0.76	70.8	9.69
No.5	18.45	0.73	71.1	9.57	No.15	18.12	0.75	71.3	9.69
No.6	18.61	0.74	69.5	9.57	No.16	18.33	0.75	70.6	9.70
No.7	18.69	0.75	68.4	9.59	No.17	18.18	0.75	71.2	9.71
No.8	18.49	0.74	70.1	9.59	No.18	18.02	0.76	71.0	9.72
No.9	18.35	0.75	70.1	9.65	No.19	18.21	0.75	71.2	9.72
No.10	18.36	0.74	71.1	9.66	No.20	18.34	0.75	70.7	9.72



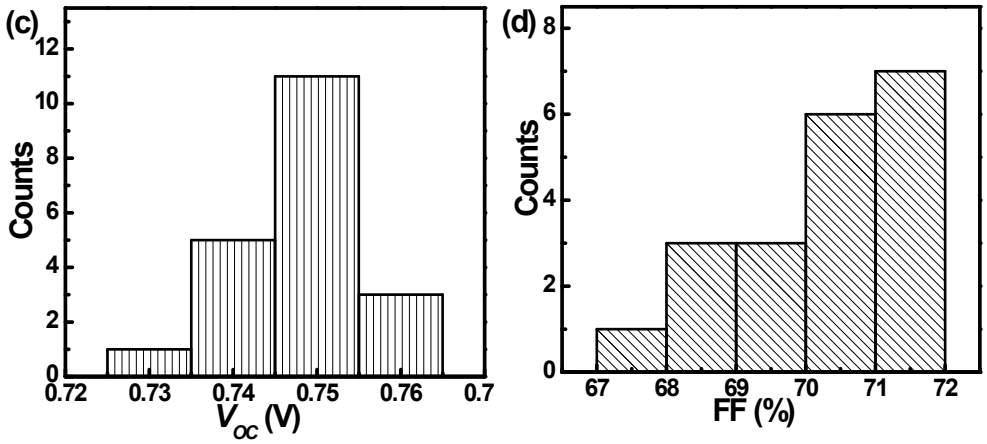


Fig. S11 Statistical histograms of key photovoltaic parameters for the 20 PSCs with 80 min self-assembly, 20 s methanol soaking and PFN interfacial layer.