Electronic Supplementary Information (ESI)

Critical Role of the External Bias in Improving the Performance of Polymer Solar Cells with a Small Molecule Electrolyte Interlayer

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Methods

Materials: EDTA-N was synthesized through the reaction of EDTA (Alfa Aesea) and triethylamine (Sinopharm Chemical Reagent Co., LTD, China) with a molar ratio of 1:2 at room temperature. After stirring overnight, the solution was evaporated at 40 ^{o}C. The precipitate was washed with acetone, tetrahydrofuran and then dried under vacuum. PTB7 and $PC_{71}BM$ were purchased from 1-Material Chemscitech Inc. (Canada), American Dye Source, Inc. (USA), respectively.

Device fabrication*:* The ITO coated glass was cleaned by ultrasonic treatment in deionized water, acetone and isopropanol for 15 minutes, respectively. Then, the pre-cleaned ITO substrate was dried with the flow of N_2 and further treated by UV-ozone for 20 minutes. The EDTA-N solution (1mg/mL in methanol) or PFN-4 (1mg/mL in methanol with 0.5% THF) was spin-coated on the pre-cleaned ITO glass at 4000 rpm for 60s. PTB7 (10mg) and $PC_{71}BM$ (15mg) were dissolved in 1mL mixed solvent of chlorobenzene/1,8 diiodoctane (97/3 by volume). Next, the PTB7:$PC_{71}BM$ solution was spin-coated on the EDTA-N coated ITO at 2000rpm for 120s and then transferred to vacuum chamber. Finally, 10nm MoO_3 and 100nm Al was deposited to form the anode. The device area is 4mm^2.

Device characterization: The J-V measurements were carried out using Keithley 2440 sourcemeter controlled by a computer. All the solar cells were measured under simulated AM 1.5G spectrum (100 mW/cm^2) with an Oriel So13A solar simulator.

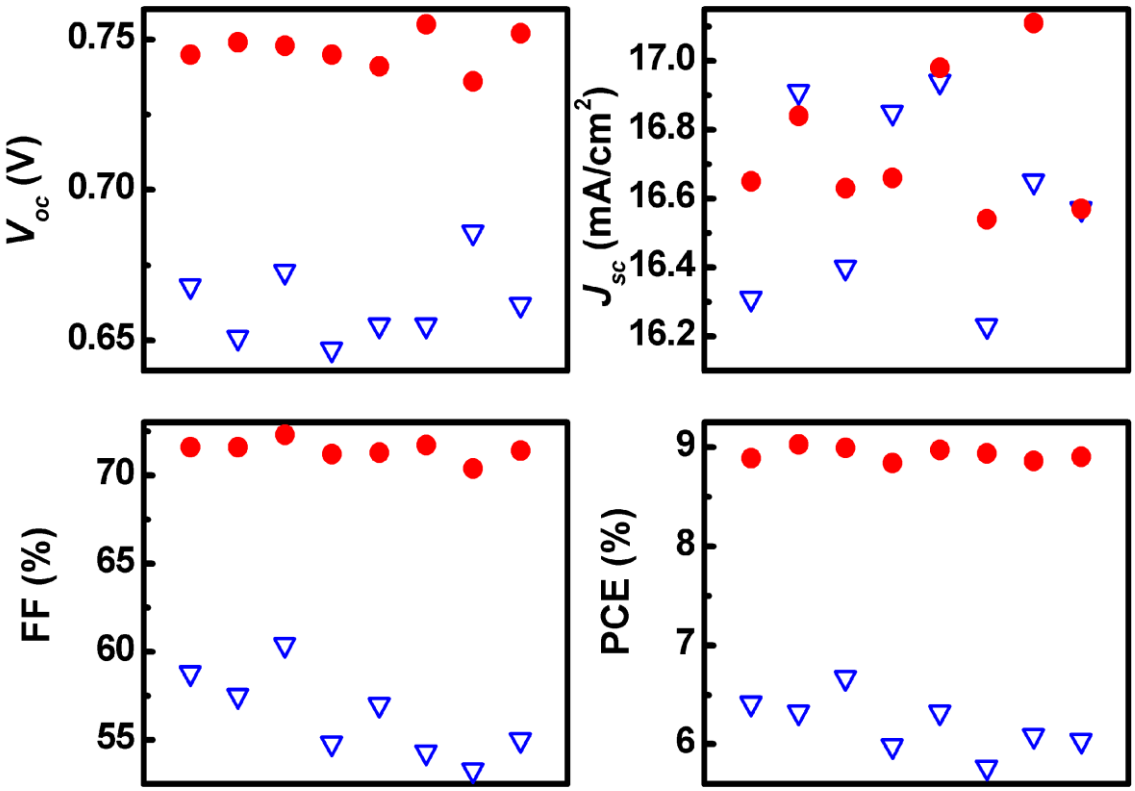

Fig. S1. The distribution of V_{oc}, J_{sc}, FF and PCE for PSCs with the EDTA-N interlayer before (blue triangle) and after pre-bias (red circle).

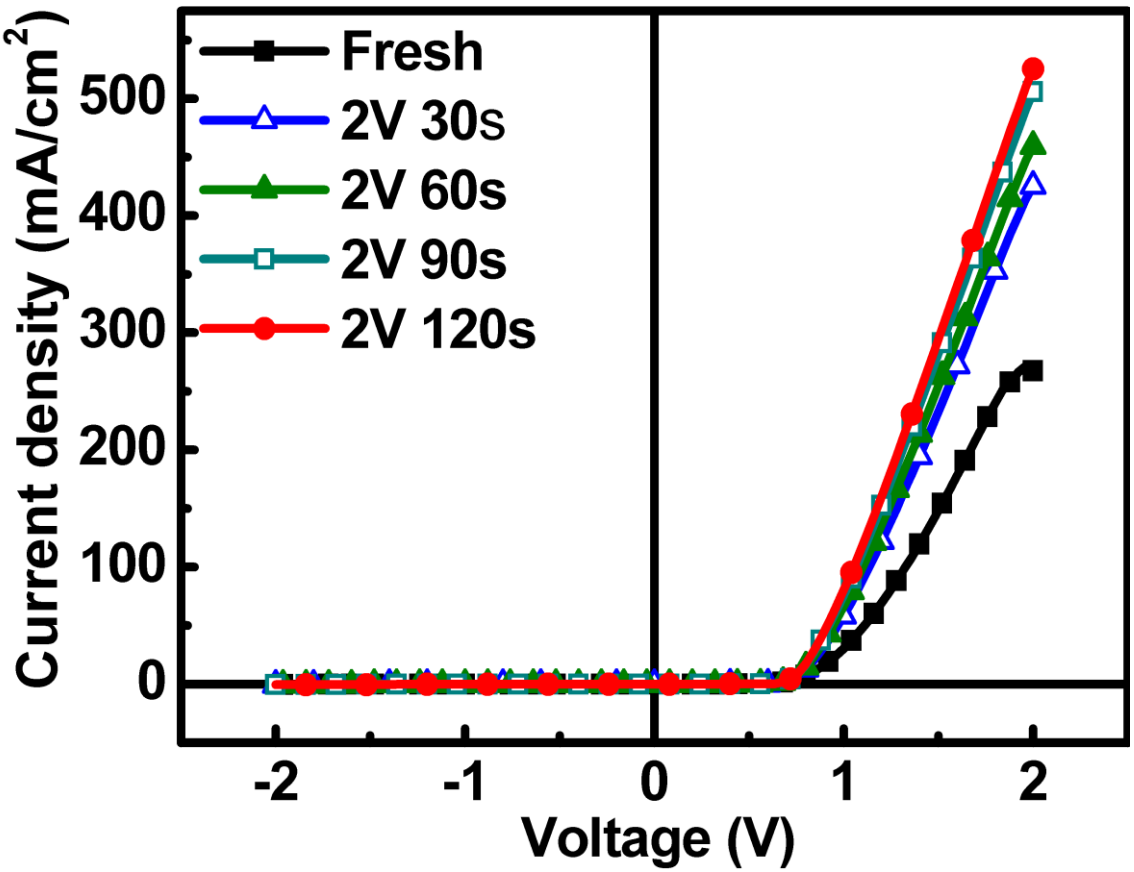

Fig. S2. The J-V curves (in dark) as the bias time is increased.

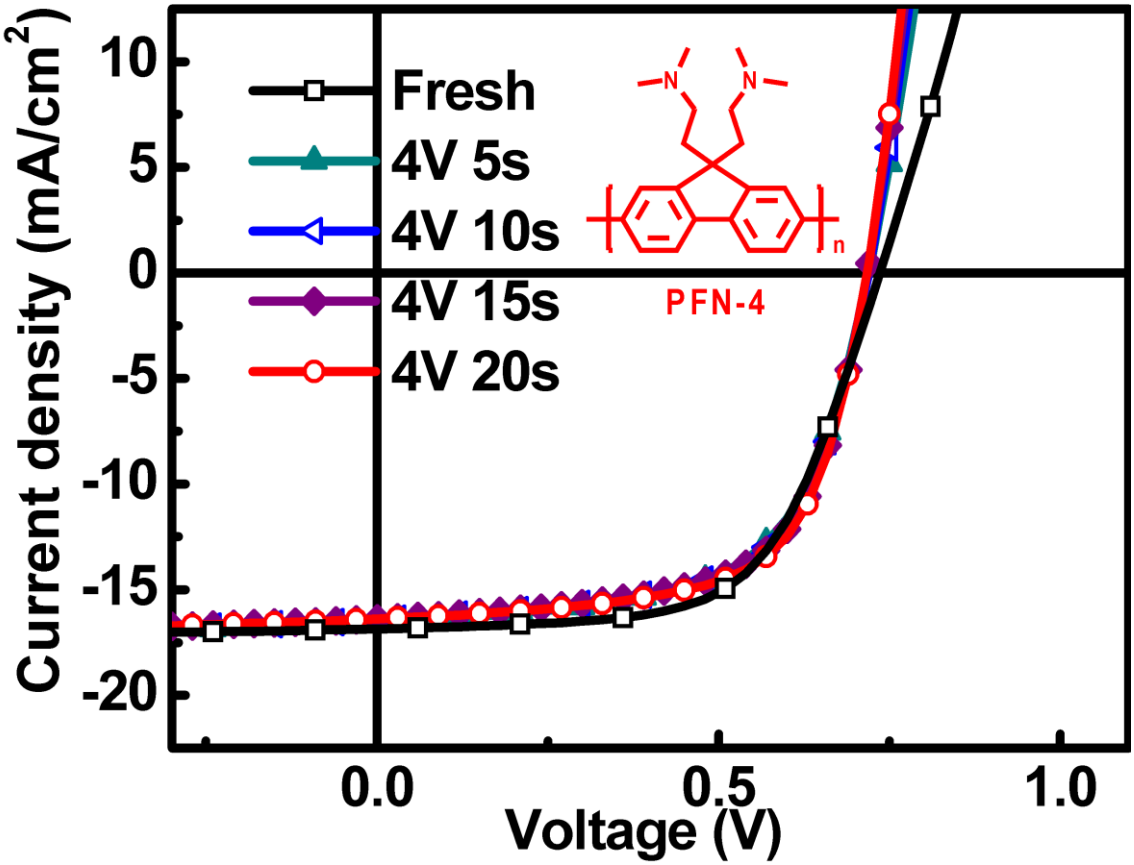

Fig. S3. The performance of PSCs with the PFN-4 interlayer under 4V bias.

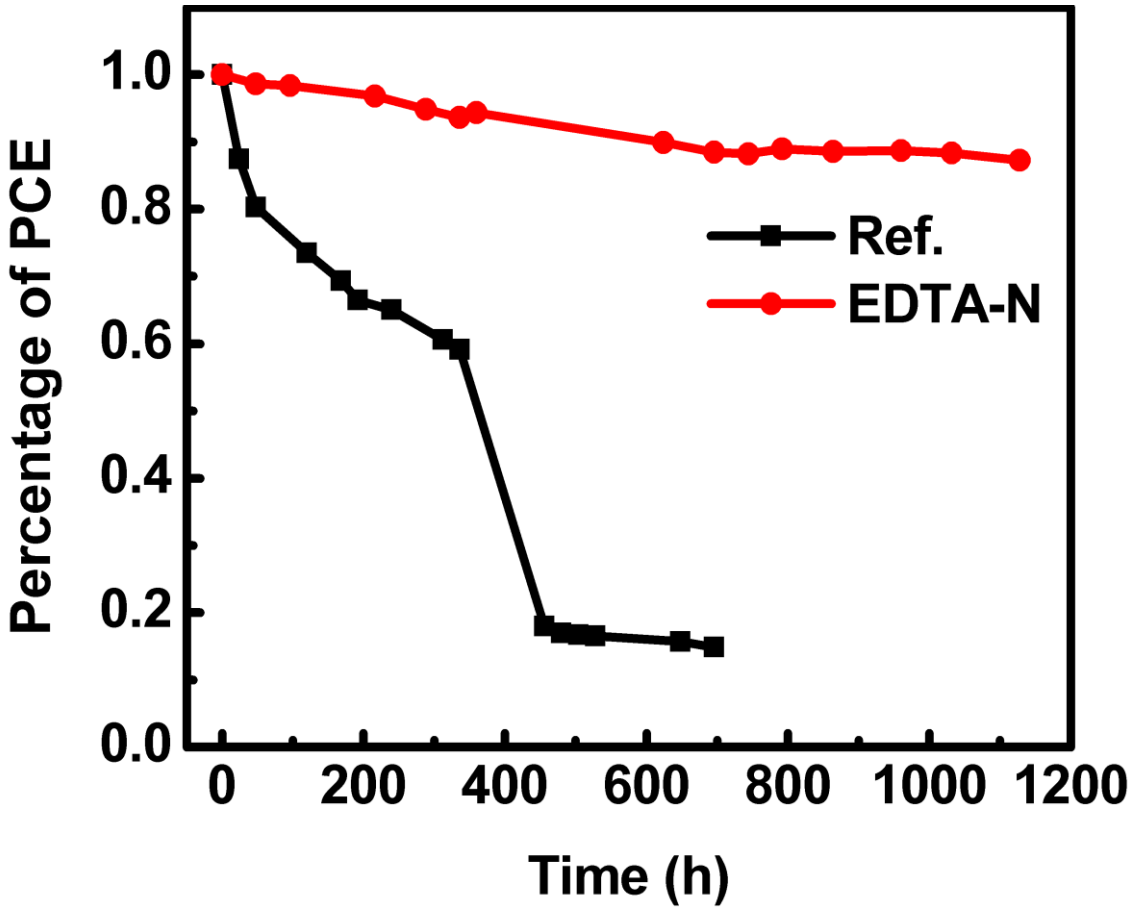

Fig. S4. The stability of PSCs with the EDTA-N interlayer, compared with reference conventional devices.

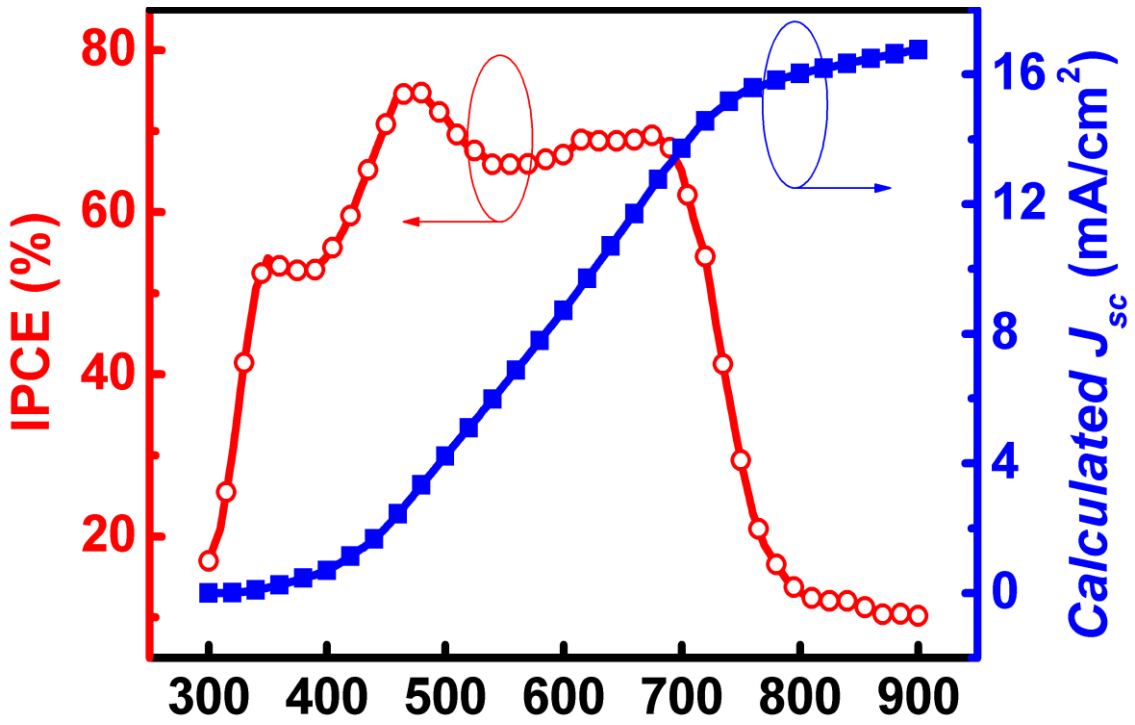

Fig. S5. The IPCE of PSCs with EDTA-N interlayer measured in air, the calculated J_{sc} is 16.76 mA/cm^2 in agreement with the average measurement J_{sc} (16.75 mA/cm^2).

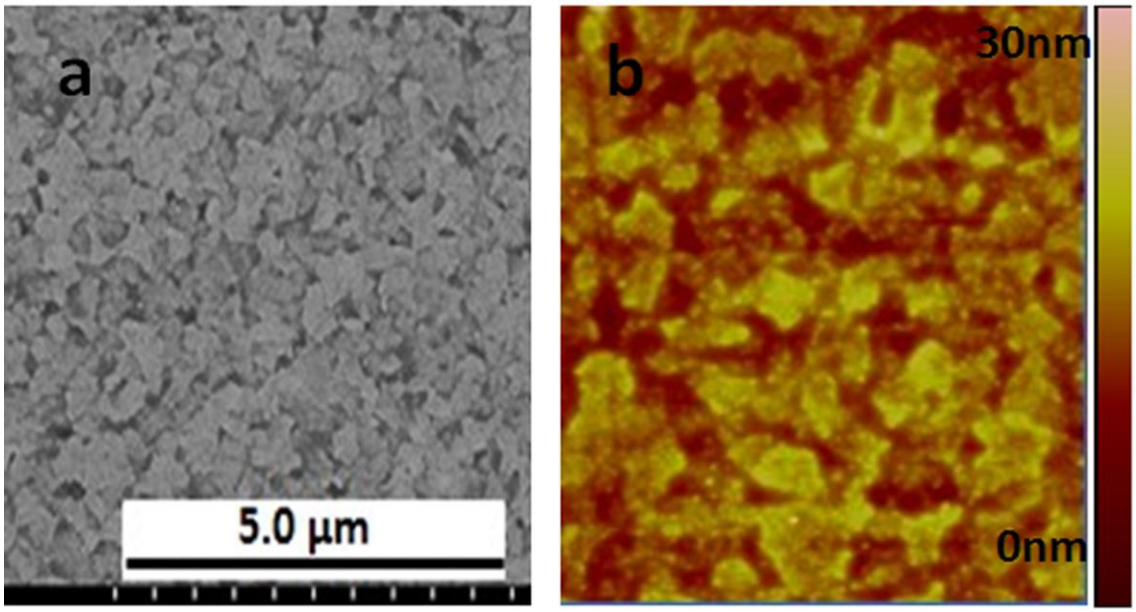

Fig. S6. The SEM (a) and AFM (b) image EDTA-N on ITO. The scanning scale for AFM (tapping mode) is 2.5 µm×2.5µm and the root mean square (RMS) of EDTA-N coated ITO is 2.58 nm, indicating a rather smooth surface.

Table S1. The parameters variation of PSCs with EDTA-N interlayer under 0.5V pre-bias.

V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	Time (s)
0.655	16.94	57.0	6.32	0
0.681	16.93	59.3	6.83	60
0.694	16.93	60.5	7.11	120
0.702	16.99	61.5	7.33	180
0.709	16.93	62.2	7.47	240
0.713	16.96	63.0	7.62	300
0.717	16.93	63.5	7.71	360
0.721	17.02	63.8	7.82	420
0.723	16.98	64.3	7.89	480

Table S2. The parameters variation of PSCs with EDTA-N interlayer under 1V pre-bias.

V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	Time (s)
0.647	16.85	54.8	5.98	0
0.705	16.87	59.7	7.10	30
0.710	16.89	60.2	7.22	60
0.715	16.91	60.6	7.33	90
0.719	16.88	61.2	7.43	120
0.722	16.93	61.6	7.53	150
0.727	16.92	62.2	7.64	210
0.729	16.86	63.1	7.75	240
0.730	16.87	63.7	7.84	270
0.732	16.92	63.8	7.91	300
0.735	16.85	64.2	7.95	330

Table S3. The parameters variation of PSCs with EDTA-N interlayer under 2V pre-bias.

V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	Time (s)
0.673	16.40	60.4	6.67	0
0733	16.41	67.2	8.08	30
0.739	16.39	68.9	8.34	60
0.741	16.37	69.8	8.47	90
0.744	16.43	70.2	8.58	120
0.745	16.40	70.5	8.62	150

Table S4. The parameters variation of PSCs with EDTA-N interlayer under 4V pre-bias.

V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	Time (s)
0.651	16.91	57.5	6.32	0
0.731	16.86	67.9	8.38	5
0.740	16.78	69.8	8.67	10
0.749	16.84	71.6	9.03	15
0.751	16.74	71.5	8.99	20

Table S5. The parameters variation of PSCs with EDTA-N interlayer for repeated measurements with scan bias -1.5~1.5V.

V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	Times
0.686	16.65	53.3	6.09	1
0.709	16.70	56.7	6.72	2
0.718	16.72	58.5	7.02	3
0.722	16.75	59.8	7.23	4
0.725	16.77	60.6	7.37	5
0.726	16.74	61.5	7.47	6
0.727	16.75	62.0	7.55	7
0.728	16.74	62.6	7.62	8
0.728	16.76	62.9	7.67	9
0.728	16.75	63.2	7.71	10

Table S6. The parameters variation of PSCs with EDTA-N interlayer under different scan bias range.

V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	Scan range
0.729	16.40	68.5	8.19	-1.5~4V
0.668	16.31	58.8	6.41	-1.5~1.5V
0.657	16.12	55.5	5.88	-4~1.5V

Table S7. The parameters variation of PSCs with PFN-4 interlayer under 4V bias.

V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	Time (s)
0.736	16.84	62.0	7.69	0
0.720	16.51	61.8	7.35	5
0.719	16.40	62.9	7.42	10
0.717	16.35	63.9	7.49	15
0.717	16.36	65.3	7.66	20