## **Electronic Supplementary Information**

## Improving efficiency of polymer solar cells via a treatment of methanol:water on the active layers

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(b)<sub>0-</sub> 0 h - 0 h -2 -2 100 ł 100 h Current density (mA/cm<sup>2</sup>) Current density (mA/cm<sup>2</sup>) 220 h - 220 h -4 -4 364 h 364 ł - 508 ł 508 ł -6 -6 -8 -8 -12 -12 -0.1 0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 -0.1 0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 Voltage (V) Voltage (V)  $(\mathbf{d})_0$  $(c)_{0}$ -0 h **—**0 h -2 -2 100 h 100 h Current density (mA/cm<sup>2</sup>) Current density (mA/cm<sup>2</sup>) 220 h 220 h -4 -4 364 h 364 1 508 1 508 -6 -6 -8 -8 -10 -12 -12 -0.1 0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9  $-0.1 \ 0.0 \ 0.1 \ 0.2 \ 0.3 \ 0.4 \ 0.5 \ 0.6 \ 0.7 \ 0.8 \ 0.9$ Voltage (V) Voltage (V)

Fig. S1 J-V curves of the encapsulated PSCs based on ITO/PEDOT:PSS/PCDTBT:PC71BM/Al (a), ITO/PEDOT:PSS/PCDTBT:PC71BM/LiF/Al (b), ITO/PEDOT:PSS/PCDTBT:PC71BM/methanol/Al (c) and ITO/PEDOT:PSS/PCDTBT:PC71BM/M:W=6:1/A1 (d).



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**Fig. S2** Normalized PCE (a), Jsc (b), Voc (c) and FF (d) *versus* time of the encapsulated PSCs. Blank: ITO/PEDOT:PSS/PCDTBT:PC<sub>71</sub>BM/Al; LiF: ITO/PEDOT:PSS/PCDTBT:PC<sub>71</sub>BM/LiF/Al; MT: ITO/PEDOT:PSS/PCDTBT:PC<sub>71</sub>BM/methanol/Al; M:W=6:1: ITO/PEDOT:PSS/PCDTBT:PC<sub>71</sub>BM/M:W=6:1/Al .

interfacial material	PCE (%)		$Jsc (mA/ cm^2)$		Voc (V)		FF	
	initial	final	initial	final	Initial	final	initial	final
Blank	5.64 ± 0.23	4.12 ±0.11	$\begin{array}{c} 11.57 \\ \pm \ 0.19 \end{array}$	$\begin{array}{c} 10.11 \\ \pm \ 0.13 \end{array}$	$\begin{array}{c} 0.84 \\ \pm \ 0.01 \end{array}$	0.79 ± 0.01	$\begin{array}{c} 0.58 \\ \pm \ 0.01 \end{array}$	$\begin{array}{c} 0.52 \\ \pm \ 0.01 \end{array}$
LiF	5.99 ± 0.14	4.48 ±0.22	$\begin{array}{c} 10.63 \\ \pm \ 0.09 \end{array}$	9.48 ± 0.11	$\begin{array}{c} \textbf{0.88} \\ \pm \ \textbf{0.01} \end{array}$	0.84 ± 0.01	0.64 ± 0.01	0.57 ± 0.01
MT	6.69 ±0.24	5.81 ±0.10	$\begin{array}{c} 11.67 \\ \pm \ 0.04 \end{array}$	$\begin{array}{c} 10.60 \\ \pm \ 0.12 \end{array}$	$\begin{array}{c} 0.88 \\ \pm \ 0.01 \end{array}$	$\begin{array}{c} \textbf{0.88} \\ \pm \ \textbf{0.01} \end{array}$	$\begin{array}{c} 0.65 \\ \pm \ 0.01 \end{array}$	$\begin{array}{c} 0.62 \\ \pm \ 0.01 \end{array}$
M:W=6:1	7.24 ± 0.22	6.08 ±0.04	12.44 ± 0.15	$\begin{array}{c} 11.48 \\ \pm \ 0.05 \end{array}$	$\begin{array}{c} 0.88 \\ \pm \ 0.01 \end{array}$	$\begin{array}{c} \textbf{0.88} \\ \pm \ \textbf{0.01} \end{array}$	0.66 ± 0.02	$0.60\pm\!\!0.01$

Table S1 Photovoltaic performance of encapsulated the PSCs obtained from Fig. S1.



**Fig. S3** Ultraviolet photoelectron spectra of bare Al (black line), Al treated by 100% methanol (red line) and Al treated by M:W=6:1 in the secondary electron cutoff range.

Electron-only devices	Hole-only devices µ <sub>h</sub>		
μ <sub>e</sub>			
$[cm^2 V^{-1} s^{-1}]$	$[cm^2 V^{-1} s^{-1}]$		
2.66×10-4	1.77×10 <sup>-5</sup>		
3.28×10-4	4.03×10 <sup>-5</sup>		
4.50×10-4	5.24×10 <sup>-5</sup>		
5.05×10-4	6.16×10 <sup>-5</sup>		
4.11×10 <sup>-4</sup>	4.92×10 <sup>-5</sup>		
	Electron-only devices $\mu_e$ [cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> ] 2.66×10 <sup>-4</sup> 3.28×10 <sup>-4</sup> 4.50×10 <sup>-4</sup> 5.05×10 <sup>-4</sup> 4.11×10 <sup>-4</sup>		

Table S2 Electron and hole mobilities from electron-only and hole-only devices.

Electron-only device: ITO/Al/LiF/PCDTBT:PC<sub>71</sub>BM/ST/LiF/Al; Hole-only device: ITO/PEDOT:PSS/PCDTBT:PC<sub>71</sub>BM/ST/MoO<sub>x</sub>/Al (ST : solvent treatment).



**Fig. S4** *J-V* curves of the PSCs based on ITO/PEDOT:PSS/PTB7:PC<sub>71</sub>BM/Al under AM1.5G illumination at intensity of 100 mW cm<sup>-2</sup>.

Voc	FF	PCE [%]		Rs	Rsh
[V]	FF	Max.	Aver.	$[\Omega \text{ cm}^2]$	$[\Omega \ cm^2]$
0.680	0.53	5.72	5.52	11.29	330.0
0.725	0.62	7.42	7.30	7.38	388.1
0.735	0.63	7.80	7.48	6.50	614.6
0.730	0.64	7.74	7.57	6.62	611.9
0.720	0.61	7.45	7.23	6.90	426.6
	Voc [V] 0.680 0.725 0.735 0.730 0.720	Voc [V] FF   0.680 0.53   0.725 0.62   0.735 0.63   0.730 0.64   0.720 0.61	Voc [V] FF PCE   0.680 0.53 5.72   0.725 0.62 7.42   0.735 0.63 7.80   0.730 0.64 7.74   0.720 0.61 7.45	Voc [V] FF $PCE [\%]$ 0.680 0.53 5.72 5.52   0.725 0.62 7.42 7.30   0.735 0.63 7.80 7.48   0.730 0.64 7.74 7.57   0.720 0.61 7.45 7.23	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

Table S3 Performances of the PSCs based on PTB7:PC71BM derived from Fig. S4.

<sup>c</sup> Device structure: Device 1: [ITO/PEDOT:PSS/PTB7:PC<sub>71</sub>BM/A1], Device 2: [ITO/PEDOT:PSS/PTB7:PC<sub>71</sub>BM/ Methanol/A1], Device 3: [ITO/PEDOT:PSS/PTB7:PC<sub>71</sub>BM/M:W=9:1/A1], Device 4: [ITO/PEDOT:PSS /PTB7:PC<sub>71</sub>BM/M:W=6:1/A1], Device 5: [ITO/PEDOT:PSS/PTB7:PC<sub>71</sub>BM/M:W=3:1/A1].