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**Supporting Information** 

Water-dipping Effect of Branched Poly(ethylene imine) Interfacial Layers on the

Performance and Stability of Polymer: Nonfullerene Solar Cells

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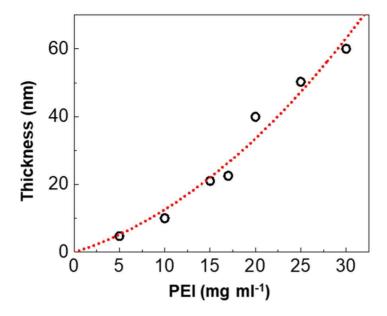
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**Table S1.** Extended summary of solar cell parameters (averaged values from more than 10 devices) for the inverted-type PM6:Y11 solar cells with the bPEI layers according to the bPEI thickness. Note that the minimum and maximum values are given in the bracket just below the average values.

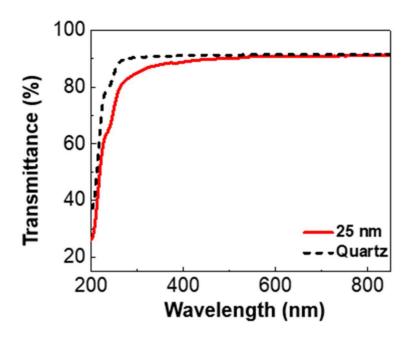
Darameter	bPEI Thickness (nm)										
Parameter	0	0.1	0.2	0.5	0.7	1.0	1.5	2.0	5.0		
V <sub>oc</sub>	0.38	0.84	0.86	0.86	0.86	0.85	0.85	0.84	0.61		
(V)	(0.27~0.45)	(0.82~0.85)	(0.85~0.87)	(0.86~0.87)	(0.85~0.86)	(0.85~0.86)	(0.83~0.86)	(0.82~0.85)	(0.50~0.76)		
J <sub>sc</sub>	15.99	19.09	19.44	19.84	19.68	19.81	19.00	13.67	0.05		
(mA cm <sup>-2</sup> )	(14.27~17.05)	(17.79~20.21)	(18.15~20.26)	(18.95~20.59)	(19.15~20.39)	(18.71~20.39)	(18.44~19.81)	(12.59~15.32)	(0.03~0.09)		
FF	40.58	56.73	60.18	62.24	60.11	56.89	52.09	33.22	19.58		
(%)	(34.01~43.95)	(53.33~59.52)	(56.93~62.91)	(59.40~69.23)	(56.52~61.64)	(52.44~61.96)	(48.10~54.72)	(29.86~36.72)	(17.15~20.66)		
PCE	2.49	9.05	10.05	10.54	10.12	9.62	8.39	3.79	0.01		
(%)	(1.49~3.16)	(8.49~9.80)	(9.30~10.55)	(10.00~11.03)	(9.80~10.41)	(8.92~10.02)	(7.80~8.76)	(3.11~4.42)	(0.00~0.01)		
R <sub>s</sub>	0.22	0.18	0.14	0.12	0.13	0.16	0.23	2.31	699.96		
(kΩ)	(0.17~0.28)	(0.13~0.28)	(0.10~0.18)	(0.10~0.16)	(0.12~0.19)	(0.10~0.23)	(0.18~0.32)	(1.08~5.13)	(270~1073)		
R <sub>SH</sub>	1.88	6.43	7.80	8.60	7.86	7.23	6.23	3.14	212.75		
(kΩ)	(0.84~2.48)	(4.57~8.03)	(6.59~9.17)	(7.51~9.63)	(7.06~8.94)	(5.74~8.68)	(4.39~7.71)	(2.61~3.54)	(75.1~296.5)		

**Table S2.** Extended summary of solar cell parameters (averaged values from more than 10 devices) for the inverted-type PM6:Y11 solar cells with the water-dipped bPEI layers according to the dipping (immersion) time (TDIP) of bPEI layers (initial thickness = 2.0 nm). Note that the minimum and maximum values are given in the bracket just below the average values.

Douguestou	T <sub>DIP</sub> (min)									
Parameter	0	10	30	60	90					
V <sub>oc</sub>	0.84	0.87	0.88	0.88	0.88					
(V)	(0.82~0.85)	(0.87~0.88)	(0.86~0.89)	(0.87~0.88)	(0.87~0.88)					
J <sub>sc</sub>	13.67	20.06	20.14	19.92	19.80					
(mA cm <sup>-2</sup> )	(12.59~15.32)	(19.49~20.81)	(19.02~21.62)	(19.00~20.67)	(19.05~20.61)					
FF	33.22	52.67	57.96	55.66	54.04					
(%)	(29.86~36.72)	(51.26~53.45)	(53.92~61.73)	(52.47~58.13)	(53.06~54.93)					
PCE	3.79	9.22	10.25	9.70	9.39					
(%)	(3.11~4.42)	(8.66~9.58)	(9.79~10.76)	(9.33~10.36)	(9.12~9.71)					
R <sub>s</sub>	2.31	0.24	0.15	0.19	0.23					
(kΩ)	(1.08~5.13)	(0.22~0.25)	(0.12~0.21)	(0.15~0.22)	(0.20~0.25)					
R <sub>sH</sub>	3.14	5.80	8.86	8.10	7.70					
(kΩ)	(2.61~3.54)	(4.23~6.90)	(5.82~16.50)	(5.28~13.53)	(5.72~10.08)					



**Figure S1.** The thickness of bPEI films as a function of bPEI solution concentration. The bPEI films were spin-coated at 4000 rpm for 60 using bPEI solutions (30, 25 20, 17, 15, 10, and 5.0 mg ml<sup>-1</sup>). Note that the film thickness was measured using a surface profilometer. The thickness of thinner bPEI films (layers), which were prepared from dilute solutions (2.0, 1.5, 1.0, 0.7, 0.5, 0.2 and 0.1 mg ml<sup>-1</sup>), was estimated on the basis of the prediction curve (red line).



**Figure S2.** Optical transmittance spectrum of the 25 nm-thick bPEI films coated on a quartz substrate: (see the black dashed line for the quartz substrate only).

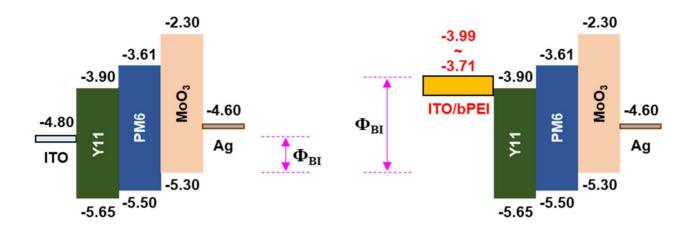


Figure S3. Comparison of flat energy band diagrams for the PSCs with (right) or without (left) the bPEI interfacial layers. Note that the built-in electric field (Φ<sub>BI</sub>) was approximated from the energy levels: (left) between the work function of ITO and the HOMO energy level of MoO<sub>3</sub>; (right) between the work function of bPEI-coated ITO (ITO/bPEI) and the HOMO energy level of MoO<sub>3</sub>.

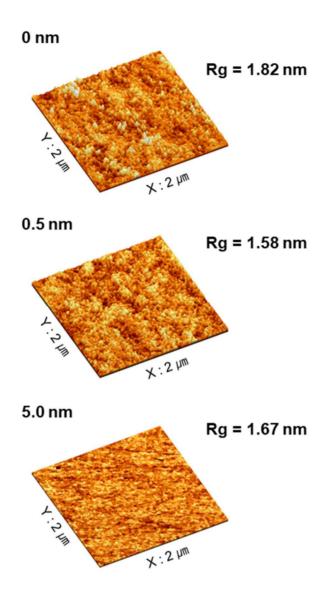
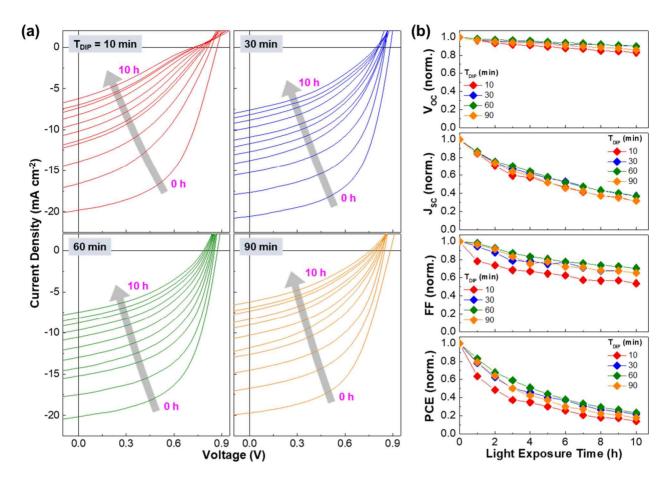
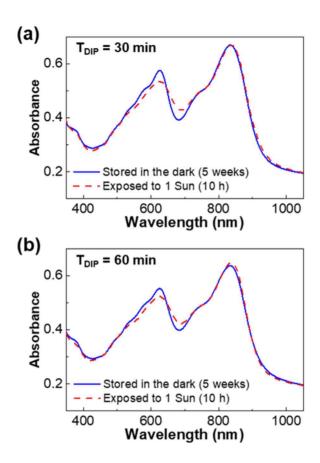


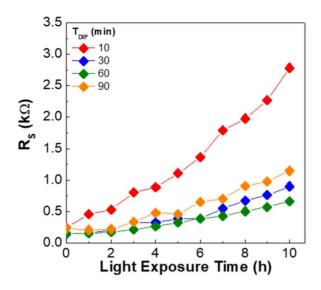
Figure S4. Height-mode AFM images (2  $\mu$ m x 2  $\mu$ m) for the bPEI-coated ITO surfaces according to the thickness of bPEI layers. Note that Rg denotes the root-mean-square (rms) roughness values.



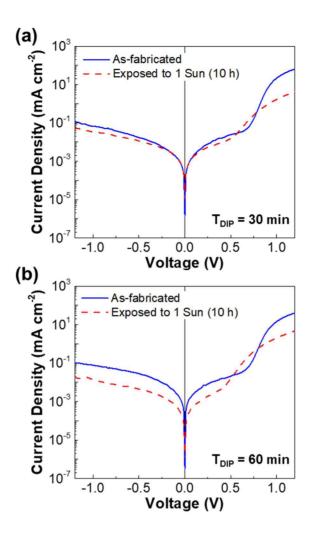
**Figure S5.** Stability of the PM6:Y11 solar cells with the water-dipped bPEI interlayers ( $T_{DIP} = 0, 30, 60, 90 \text{ min}$ ) under 1 sun condition for 10 h according to the dipping time: (a) J-V curves, (b) relative (normalized, initial state = 1.0) parameter values as a function of light exposure time.



**Figure S6.** Optical absorption spectra (original data, unnormalized) of the PM6:Y11 films (glass/ITO/bPEI/PM6:Y11) that were stored for 5 weeks in the dark (blue solid lines) and exposed to the 1 sun condition for 10 h (red dashed lines): (a)  $T_{DIP} = 30$  min, (b)  $T_{DIP} = 60$  min.



**Figure S7.** Change of series resistance ( $R_S$ ) as a function of light exposure time for the PM6:Y11 solar cells with the water-etched bPEI interlayers ( $T_{DIP} = 10, 30, 60, 90 \text{ min}$ ).



**Figure S8.** Dark J-V curves (semi-logarithmic scale) before and after exposure to 1 sun condition (10 h) for the PM6:Y11 solar cells with the water-etched bPEI interlayers: (a) dipping time  $(T_{DIP}) = 30 \text{ min}$ , (b)  $T_{DIP} = 60 \text{ min}$ .