**Conventional polymer solar cells with power conversion efficiencies increased to >9% by a combination of methanol treatment and an anionic conjugated polyelectrolyte interface layer**

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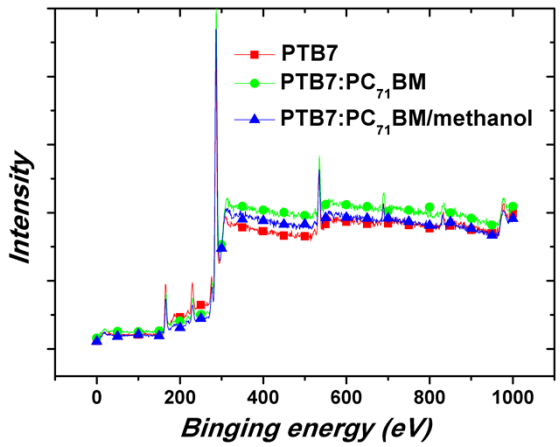


**Figure S1.** XPS survey of the top surfaces at various conditions.

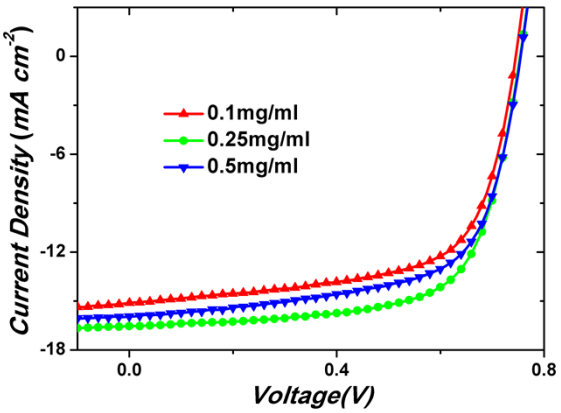


**Figure S2.**The current density-voltage (*J-V*) characteristics of the PSCs with $PF_{EO}SO_3Na$ interlayer spin-coated at different solutions under AM 1.5G irradiation (100 mW $cm^{-2}$).

The $PF_{EO}SO_3Na$ was dissolved in methanol, and the thickness of $PF_{EO}SO_3Na$ layer was optimized by varying the concentrations of its methanol solutions from 0.1 mg/ml to 0.5 mg/ml with fixed spin-coating speed and was measured by AFM. The optimized concentration of spin-coated $PF_{EO}SO_3Na$ interlayer was 0.25mg/mL. The *J*sc and *FF* of the resulting PSCs were highly dependent on the thickness of $PF_{EO}SO_3Na$. When spin-coated from 0.1mg/mL solution, the $PF_{EO}SO_3Na$ film could only cover a small part of the active layer, which led to a moderate enhancement. When the concentration of $PF_{EO}SO_3Na$ was further increased to 0.5mg/mL, the performance was reduced because the $PF_{EO}SO_3Na$ film was too thick and acted as an insulating layer. The detailed devices characteristics with different [$PF_{EO}SO_3Na$] were summarized in Table S1.

 

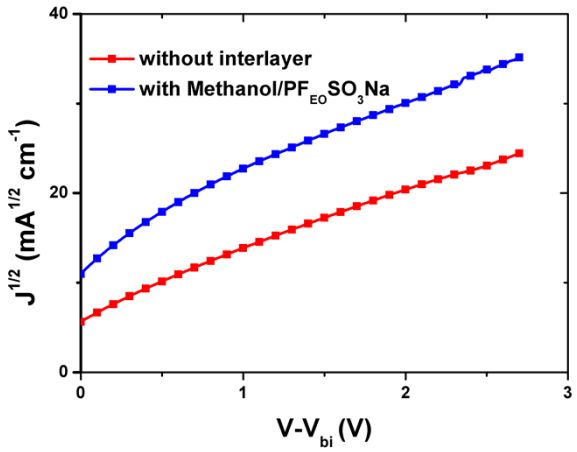


**Figure S3.** J-V curves of the hole mobility devices with methanol and $PF_{EO}SO_3Na$ cathode interface layer or without interlayer.

To confirm the effect of methanol treatment and $PF_{EO}SO_3Na$ layer on charge transport property, hole only devices with configuration of ITO/PEDOT:PSS/PTB7:$PC_{71}BM$/MoO3/Au with or without methanol treatment and $PF_{EO}SO_3Na$ layer were constructed and their hole mobility was calculated from the space charge limited current (SCLC) J-V curves obtained in the dark (Figure S3). SCLC can be characterized by the Mott-Gurney square law: $J = \frac{9}{8}\varepsilon_r\varepsilon_0\mu_0\frac{V^2}{L^3}$, in which $\varepsilon_0$ is the vacuum permittivity, $\varepsilon_r$ is the dielectric permittivity of the active layer, L is the thickness of the active layer and $\mu_0$ is the hole mobility. In pristine PTB7:$PC_{71}BM$ devices, the hole mobility was $1.7\times10^{-4}$ $cm^{-2}$ $V^{-1}$ s. After combination of methanol treatment and $PF_{EO}SO_3Na$ layer, the hole mobility was increased to $4.0\times10^{-4}$ $cm^{-2}$ $V^{-1}$ s, which suggested that the hole transport in devices with methanol treatment and $PF_{EO}SO_3Na$ layer was improved.

**Table S1.** Device performance of PSCs obtained with different [$PF_{EO}SO_3Na$].

| Cathode | $V_{oc}$ [V] | $J_{sc}$ [mA $cm^{-2}$] | *FF* [%] | PCE [%] |
|---|---|---|---|---|
| 0.1mg/mL | 0.74 | 15.1 | 65.8 | 7.36 |
| 0.25mg/mL | 0.74 | 16.5 | 69.5 | 8.50 |
| 0.5mg/mL | 0.75 | 15.9 | 65.5 | 7.83 |