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COMMUNICATION

Conventional polymer solar cells with PCE > 9% by combination of methanol treatment and an anionic conjugated polyelectrolyte interface layer

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
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DOI: 10.1039/x0xx00000x

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The power conversion efficiency (PCE) of PTB7:PC₇₁BM polymer solar cell is improved up to 9.1% by a methanol treatment following with a water/alcohol soluble conjugated polyelectrolyte cathode interface layer, which is contributed by a combination effect of enriched PC₇₁BM ratio on the top surface in the active layer and the presence of the prefer dipole at the cathode interface.

Bulk heterojunction (BHJ) polymer solar cells (PSCs) have drawn great attention due to their advantages such as light weight, flexible properties and low-cost manufacturing based on roll-to-roll processing.¹⁻³ During the past few years, the power conversion efficiency (PCE) of PSCs has been improved rapidly for the development of new conjugated polymers,⁴⁻⁷ applying new device structures,⁸⁻¹¹ and interface engineering.¹²⁻¹⁴ Interface engineering is critical to the PSCs and the devices performance can be dramatically improved by incorporating a functional interfacial layer between active layers and electrodes.¹⁵ Varying interfacial materials, such as metal oxides,¹⁶⁻¹⁹ self assembled monolayers (SAMs)²⁰ and hydrophilic polymers²¹⁻²⁴ have been successfully applied by solution processing to enhance the PCE of the fabricated PSCs. Alternatively, water/alcohol soluble polyelectrolyte has attracted great attention for the PSCs because the intermixing between the active layer and the cathode interface layer can be avoided. Different kinds of water/alcohol soluble hydrophilic polymers²⁵, such as conjugated polyelectrolyte (CPE, including PFN, PFN-Br, P3TMAHT, PFCn6:K⁺),^{15,22-24} and non-conjugated polymer (PEO, PEI, PEIE)²⁶⁻²⁸ had been used as cathode interface layer (CIL) in PSCs, and significantly enhanced PCE has been achieved. By incorporating a PFN or a derivative with metallic backbone as a CIL, PCE over 9.0% has been obtained in inverted PTB7:PC₇₁BM PSCs.^{29,30}

It has been reported that the performance of PSCs could be enhanced by treating active layers with polar solvents before the deposition of metal electrodes.³¹⁻³⁵ The positive effects of the polar solvents are suggested including the optimization of the phase separation in the active layer and a possible influence of the interface between the active layer and the PEDOT:PSS layer underneath,³¹ an increase in built-in voltage across the device due to passivation of surface traps and a correspondingly increase of surface charge density.³² Normally, polar solvents, including methanol and ethanol,

are widely used to prepare CPE solutions. Low concentration is used to minimize thicknesses and prevent possible complications due to ion motion and concomitant redistribution of internal electric field in the devices. Is the improvement in performance of PSCs after CPE deposition due to a combination of the effects of methanol treatment and the presence of the thin CPE layer? These interesting phenomena and attractive effects need to be further understood.

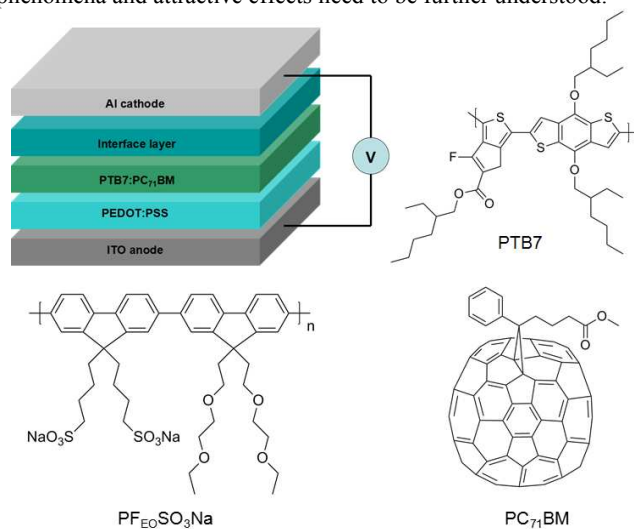


Figure 1. The structure of PTB7:PC₇₁BM PSCs and the chemical structure of PF_{EO}SO₃Na, PTB7 and PC₇₁BM.

In this study, a series PSCs based on poly[4,8-bis(2-ethylhexyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl-alt-ethylhexyl-3-urothithieno[3,4-b]thiophene-2-carboxylate-4,6-diyl] (PTB7) and [6,6]-phenyl C71-butyric acid methyl ester (PC₇₁BM) (the molecular structures is shown in Figure 1) are fabricated to probe possible influences by the polar solvent and CPEs. Methanol is chosen as a typical solvent because it is widely used as a solvent for conjugated polyelectrolytes.^{15,23} These experiments involved deposition of methanol atop the active layer followed by a sequence of steps similar to those for the CPE devices. An anionic CPE poly(9,9-bis(4-(sulfonatobutyl)-2,7-fluorene)-alt-2,7-(9,9-bis(2-(2-

(2-methoxyethoxy) ethoxyethyl)-fluorene) (PF_{EO}SO₃Na) is used as the CIL. The PCE of PTB7:PC₇₁BM PSCs increases in the sequence according to the interface modifications: methanol<Ca<PF_{EO}SO₃Na <methanol/PF_{EO}SO₃Na. A combination of methanol treatment followed by PF_{EO}SO₃Na layer gives the highest PCE of 9.1% by combination the effect of methanol treatment and the presence of the thin PF_{EO}SO₃Na layer.

The device configuration of PSCs:ITO/PEDOT:PSS(40 nm)/PTB7:PC₇₁BM/with or without CIL/Al (100 nm), is shown in Figure 1. The optimized concentration for PF_{EO}SO₃Na solution is found to be 0.25 mg/mL. The current density-voltage (J-V) curves for the optimized PTB7:PC₇₁BM PSCs with methanol treatment and PF_{EO}SO₃Na CIL along with other control devices are presented in Figure 2a. The key parameters of the PSCs, including short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF) and PCE, are summarized in Table 1. The PCE increases in the sequence according to the interface modifications: methanol<Ca<PF_{EO}SO₃Na<methanol/PF_{EO}SO₃Na. All the interfacial treatments improve the PCE of PTB7:PC₇₁BM PSCs in comparison with the control device without interface modification. A combination of methanol treatment followed by PF_{EO}SO₃Na CIL gives the highest PCE of 9.06%, with a J_{sc} of 17.1 mA cm⁻², a V_{oc} of 0.74 V, and a FF of 71.6%. The calculated J_{sc} by integrating of the external quantum efficiency (EQE) spectrum (Figure 2b) is 16.1 mAcm⁻², that is very close to the measured J_{sc}.

The PCE of the PSCs with methanol treatment on the active layer is 5.65% and is much higher than 3.95%, which from the devices without any interface modification. To study the modification of methanol treatment on the PTB7:PC₇₁BM films, we examine surface morphology by atomic force microscopy (AFM), surface potential by scanning Kelvin probe microscopy (SKPM), and surface composition by X-ray photoelectron spectroscopy (XPS). The surface morphology of PTB7:PC₇₁BM films before and after methanol treatment is shown in Figure 3a and 3b. No obvious change on film morphology and roughness is observed. And no obvious change in the film thickness is observed by profilometry after methanol treatment. However, the average surface potential of PTB7:PC₇₁BM films with methanol treatment is -266.43mV that is higher than -316.59mV of the pristine PTB7:PC₇₁BM film. Methanol treatment lifts the vacuum level on the metal side, which benefits to reduce the electron injection barrier at the organic/metal interface. The XPS survey of pure PTB7 film, pristine PTB7:PC₇₁BM film and PTB7:PC₇₁BM film with methanol pre-treatment is presented in the Figure S1. Sulfur is used as the characteristic element of PTB7 because there is no sulfur in PC₇₁BM. C/S atomic ratios are used to calculate the weight ratios of PC₇₁BM at the top surfaces of PTB7:PC₇₁BM film. The C/S ratios of pure PTB7 film, PTB7:PC₇₁BM films without or with methanol pre-treatment are 10.22, 14.43 and 15.81 respectively. The C/S ratios Table 1. Device performance of PSCs obtained with various interfacial treatments.

Cathode	V _{oc} [V]	J _{sc} [mA cm ⁻²]	FF [%]	PCE [%]	R _s [Ω cm ²]	R _{sh} [kΩ cm ²]
None	0.52	13.8	55.3	3.95	8.39	0.43
Methanol	0.66	14.3	59.8	5.65	8.28	0.63
Ca	0.72	14.4	67.6	7.02	6.22	0.78
PF _{EO} SO ₃ Na	0.74	16.5	69.5	8.50	5.30	1.13
Methanol/PF _{EO} SO ₃ Na	0.74	17.1	71.6	9.06	2.45	5.46

10.22 of pure PTB7 film obtained from XPS measurement is close to the C/S ratio 10.25 from PTB7 molecular formula, implying that the measurement is reliable. After introducing PC₇₁BM, the C/S ratios of PTB7:PC₇₁BM films without or with methanol pre-treatment are increased, while the C/S ratios of PTB7:PC₇₁BM film with methanol pre-treatment increased more obviously. This means that PC₇₁BM is richer at the surface of PTB7:PC₇₁BM film after methanol pre-treatment, which would be beneficial for electron extraction in conventional device. It has been reported that minor changes are observed on the surface morphology and composition by treatment of polar solvents, including methanol, acetonitrile, and ethanol.³¹

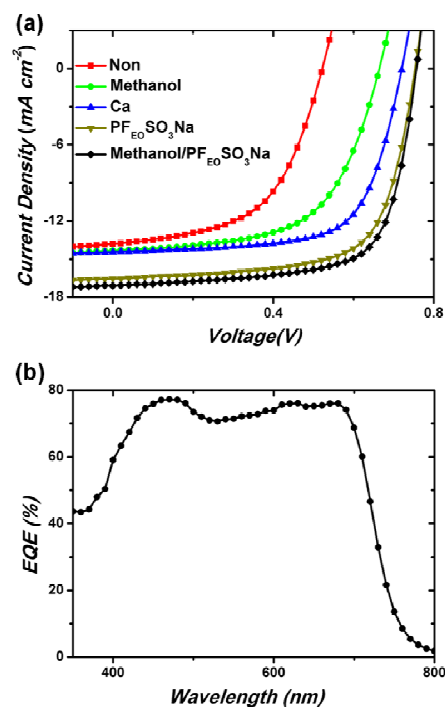


Figure 2. (a) The current density-voltage (J-V) characteristics of the PSCs with various treatments under AM 1.5G irradiation (100 mW cm⁻²); (b) EQE spectra of the solar cells with methanol pre-treatment and PF_{EO}SO₃Na cathode interface layer.

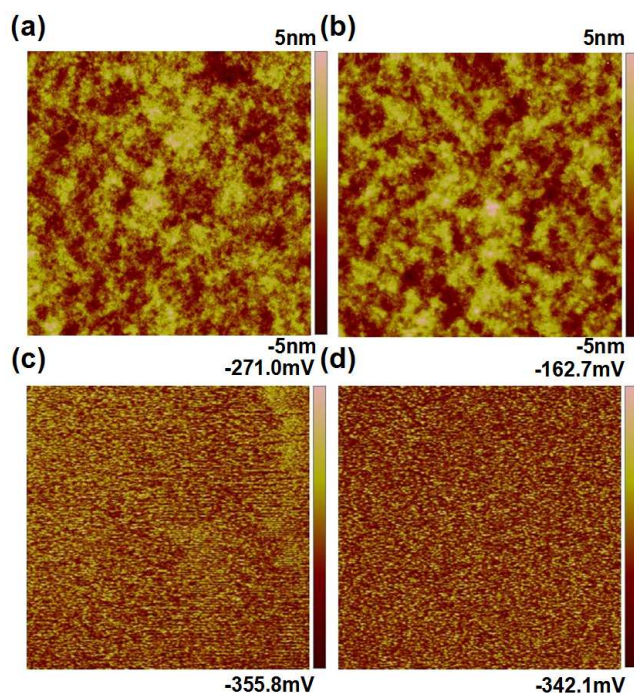


Figure 3. AFM height images ($5\mu\text{m}\times 5\mu\text{m}$) of PTB7:PC₇₁BM films with none treatment (a), with methanol treatment (b); Surface potential images ($1\mu\text{m}\times 1\mu\text{m}$) of PTB7:PC₇₁BM films with none treatment (c), with methanol pre-treatment (d).

In comparison with PTB7:PC₇₁BMPSCs using Ca cathode, simultaneous enhancement of V_{OC} (0.74V vs. 0.72V), J_{sc} (16.5mA cm^{-2} vs. 14.4mA cm^{-2}), FF (69.5% vs. 67.6%), and finally PCE (8.50% vs. 7.02%) is achieved for the PSCs with PF_{EO}SO₃Na CIL. Different to the morphology of PF_{EO}SO₃Na CIL on P3HT:PC₆₁BM PSCs,³⁶ a lot of holes with a radius of ~200-300 nm and a height of ~3-5 nm are observed in PF_{EO}SO₃Na CIL on PTB7:PC₇₁BM films (Figure 4a). The surface potential of PF_{EO}SO₃Na CIL (9.3 mV) is about 300 mV more positive than that of the active layer (Figure 4b) that provides a strong interfacial dipole layer between the cathode and the active layer and increase the V_{bi} . Thus a favorable electrical field was developed due to the interfacial dipole and would influence the charge transporting and extraction.

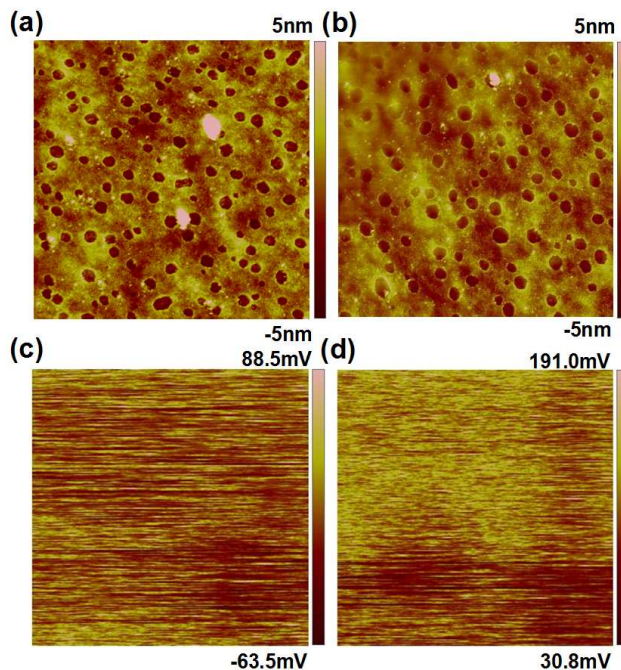


Figure 4. AFM height images ($5\mu\text{m}\times 5\mu\text{m}$) of PTB7:PC₇₁BM films with PF_{EO}SO₃Na CIL (a), with methanol treatment and PF_{EO}SO₃Na CIL (b); Surface potential images ($1\mu\text{m}\times 1\mu\text{m}$) of PTB7:PC₇₁BM films with PF_{EO}SO₃Na CIL (c), with methanol treatment and PF_{EO}SO₃Na CIL (d).

A combination of methanol treatment followed by PF_{EO}SO₃Na CIL further improves the PCE of PTB7:PC₇₁BM PSCs up to 9.06%. The major improvement is attributed to J_{sc} (17.1mA cm^{-2} vs. 16.5mA cm^{-2}) and FF (71.6% vs. 69.5%), in comparison with PSCs using PF_{EO}SO₃Na as CILs. Although no obvious change on morphology and film thickness (Figure 4 a and b) is observed, the surface potential of PF_{EO}SO₃Na layer with methanol pre-treatment is measured to be 113.90mV that is about 100mV higher than the 9.30mV of PF_{EO}SO₃Na layer. These results indicate that a combination of methanol treatment followed by PF_{EO}SO₃Na layer can further improve the performance of PSCs by combination the effect of methanol treatment and the presence of the thin PF_{EO}SO₃Na layer although the PF_{EO}SO₃Na solutions use methanol as solvents. In addition, with a combination of methanol treatment and PF_{EO}SO₃Na layer, the series resistance (R_s) is reduced from 8.39 to $2.45\Omega\text{cm}^2$ and the shunt resistance (R_{sh}) is increased from $0.43\text{k}\Omega\text{cm}^2$ to $5.46\text{k}\Omega\text{cm}^2$, and the hole mobility is increased from $1.7\times 10^{-4}\text{cm}^2\text{V}^{-1}\text{s}$ to $4.0\times 10^{-4}\text{cm}^2\text{V}^{-1}\text{s}$, in comparison with PSCs without surface modification (Figure S3).

Conclusions

In conclusion, The PCE of PTB7:PC₇₁BM based PSCs in conventional configuration is achieved 9.1% by a combination of methanol treatment followed a PF_{EO}SO₃Na layer. The methanol treatment enriched the PC₇₁BM at the surface of PTB7:PC₇₁BM films and lifts the vacuum level on the metal side, which benefits to reduce the electron injection barrier at the organic/metal interface. The incorporation of an ultra thin PF_{EO}SO₃Na interlayer contributed a strong interfacial dipole, which improved the surface potential of the active layer and benefited to the charge collections. A combination of methanol treatment followed by PF_{EO}SO₃Na layer can further improve the performance of PSCs by combination the effect of methanol

treatment and the presence of the thin $\text{PF}_{\text{EO}}\text{SO}_3\text{Na}$ layer although the $\text{PF}_{\text{EO}}\text{SO}_3\text{Na}$ solutions use methanol as solvents. This result provides deeper insight to understand the mechanism of surface engineering by polar solvent processing and introduction of polyelectrolyte. Furthermore, this strategy may offer a simple and efficient method to improve PCEs of PSCs in laboratory study or industry fabrication.

Experimental Section

Device Fabrication: PTB7 was purchased from 1-Material Chemsitech Inc. (St-Laurent, Quebec, Canada) and used as received. The devices configuration was ITO/PEDOT:PSS/PTB7:PC₇₁BM/Ca/Al. PTB7: PC₇₁BM solution was prepared with a ratio of 1:1.5 by weight in o-dichlorobenzene/1,8-diiiodoctane (97:3 vol%). The PTB7:PC₇₁BM active layer with a thickness of 100 nm was prepared by spin-coating the o-dichlorobenzene solution at 1200 rpm for 90 second. The films were dried at 4×10^{-4} Pa for 30 min before directly subjecting to thermal evaporation or methanol treatment. Methanol was spin-coated at 2500rpm on the top of active layers. The $\text{PF}_{\text{EO}}\text{SO}_3\text{Na}$ was dissolved in methanol and the thickness of it was adjusted by the concentration of the solution. Ca (10 nm) and Al electrode (100 nm) were deposited onto active layers by thermal evaporation at 2×10^{-4} Pa with a metal mask. The area of metal electrodes was 6.6 mm².

Characterization and Measurement: The current density-voltage curves for the PTB7:PC₇₁BM PSCs were characterized under an illumination of AM 1.5 G at 100 mWcm⁻² (Oriel solar 3A simulator) with a computer-controlled Keithley 2400 source measure unit. Solar simulator illumination intensity was determined by a monocrystal silicon reference cell (M-91150V, with KG5 filter certificated by NREL). EQE was characterized on the QTest Station 2000 ADI system (Crowntech, Inc., USA). Atomic force microscopy (AFM) images and scanning Kelvin probe microscopy (SKPM) images were obtained using a Bruker Metrology Nanoscope III-D atomic force microscope. XPS measurements were performed using a VG ESCALAB MK2 system with a monochromatized Al K α under a pressure of 5×10^{-7} Pa.

Acknowledgements

We thank the financial support by National Natural Science Foundation of China (nos. 51073063, 21274048, 21374120) and National Significant Program (2013CB922104), J. Zhang acknowledges the support by 100 Talents Program of the Chinese Academy of Sciences.

Notes and references

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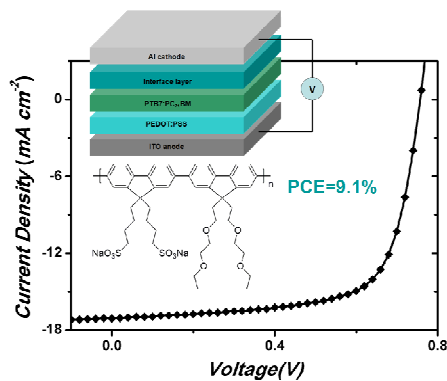
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Conventional polymer solar cells with PCE > 9% by combination of methanol treatment and an anionic conjugated polyelectrolyte interface layerTao Yuan,^a Dong Yang,^b Xiaoguang Zhu,^a Lingyu Zhou,^b Jian Zhang,^{b*} Guoli Tu^{a,*} and Can Li^b

The power conversion efficiency of PTB7:PC₇₁BM polymer solar cell is improved up to 9.1% by a combination of methanol treatment followed a water/alcohol soluble conjugated polyelectrolyte thin layer, which is the result of the joint effect of methanol treatment and the presence of the conjugated polyelectrolyte thin layer.

Supporting Information

Conventional polymer solar cells with PCE > 9% by methanol pre-treatment and incorporation an anionic conjugated polyelectrolyte interface layer

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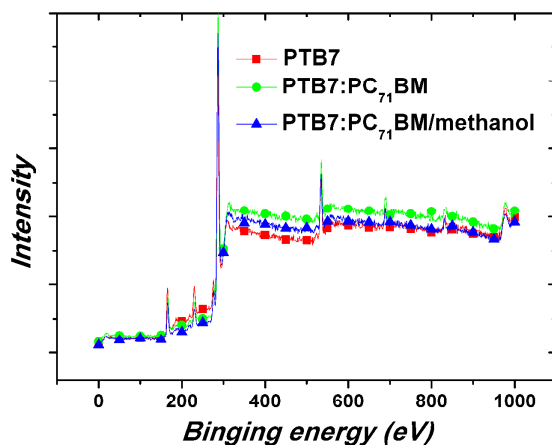


Figure S1. XPS survey of the top surfaces at various conditions.

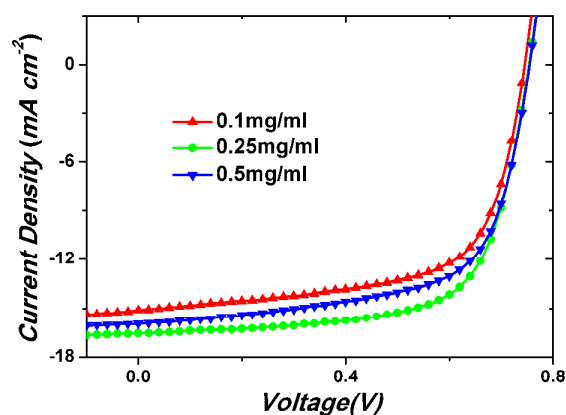


Figure S2. The current density-voltage (J - V) characteristics of the PSCs with $\text{PF}_{\text{EO}}\text{SO}_3\text{Na}$ interlayer spin-coated at different solutions under AM 1.5G irradiation (100 mW cm^{-2}).

The $\text{PF}_{\text{EO}}\text{SO}_3\text{Na}$ was dissolved in methanol, and the thickness of $\text{PF}_{\text{EO}}\text{SO}_3\text{Na}$ 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 $\text{PF}_{\text{EO}}\text{SO}_3\text{Na}$ interlayer was 0.25 mg/mL. The J_{sc} and FF of the resulting PSCs were highly dependent on the thickness of $\text{PF}_{\text{EO}}\text{SO}_3\text{Na}$. When spin-coated from 0.1 mg/mL solution, the $\text{PF}_{\text{EO}}\text{SO}_3\text{Na}$ film could only cover a small part of the active layer, which led to a moderate enhancement. When the concentration of $\text{PF}_{\text{EO}}\text{SO}_3\text{Na}$ was further increased to 0.5 mg/mL, the performance is reduced because the $\text{PF}_{\text{EO}}\text{SO}_3\text{Na}$ film is too thick and acted as an insulating layer. The detailed devices characteristics with different $[\text{PF}_{\text{EO}}\text{SO}_3\text{Na}]$ are summarized in Table S1.

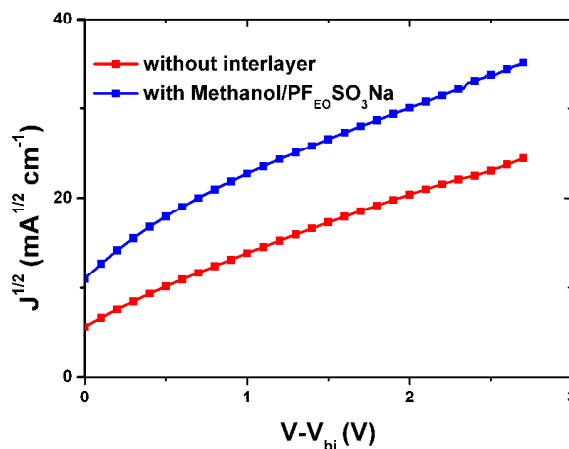


Figure S3. J-V curves of the hole mobility devices with methanol and PF_{EO}SO₃Na cathode interface layer or without interlayer.

To confirm the effect of methanol treatment and PF_{EO}SO₃Na layer on charge transport property, hole only devices with configuration of ITO/PEDOT:PSS/PTB7:PC₇₁BM/MoO₃/Au with or without methanol treatment and PF_{EO}SO₃Na layer were constructed and their hole mobility was calculated from the space charge limited current (SCLC) J-V curves obtained in the dark (Figure S4). SCLC can be

characterized by the Mott-Gurney square law: $J = \frac{9}{8} \epsilon_r \epsilon_0 \mu_0 \frac{V^2}{L^3}$, in which ϵ_0 is the vacuum permittivity, ϵ_r is the dielectric permittivity of the active layer, L is the thickness of the active layer and μ_0 is the hole mobility. In pristine PTB7:PC₇₁BM devices, the hole mobility was $1.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}$. After combination of methanol treatment and PF_{EO}SO₃Na layer, the hole mobility was increased from $1.7 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}$ to $4.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}$, which suggests that the hole transport in devices with methanol treatment and PF_{EO}SO₃Na layer was improved.

Table S1. Device performance of PSCs obtained with different [PF_{EO}SO₃Na].

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