

Enhanced performance in bulk heterojunction solar cells with alkylidene fluorene donor by introducing modified PFN-OH/Al bilayer cathode†

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We report bulk heterojunction solar cells with benzothiadiazole-containing polyalkylidene fluorene (PAFBT_oBT) donors made by introducing 2,4,7,9-tetramethyldec-5-yne-4,7-diol (Surfynol 104)-doped poly[9,9-bis(6'-(diethanolamino)hexyl)-fluorene] (PFN-OH) as an interfacial layer to enhance power conversion efficiency (PCE) and stability. Surfynol 104 has amphiphilic characteristics, and it supports the formation of a homogeneous interfacial layer on the photoactive layer. In addition, the application of the Surfynol 104-doped PFN-OH interfacial layer prevented the decrease in absorption of photons in the photoactive layer and improved the photocurrent density (J_{SC}) by increasing the electron mobility. Therefore, J_{SC} and the fill factor increased to 10.5 mA cm⁻² and 49%, respectively, and the calculated PCE was 4.8%. In addition, a modified bilayer cathode system was introduced to the PCDTBT and the P3HT-based PSCs, and the PCE improved to 5.3% and 3.9%, respectively. Moreover, the in-air stability was enhanced.

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1. Introduction

π -Conjugated polymer-based polymer solar cells (PSCs) offer the advantage of easy fabrication of light-weight devices with superior mechanical properties.^{1–3} Therefore, if spin-coating, ink jet printing, roll-to-roll printing, brush painting or stamping techniques are applied to the flexible substrate, light-weight and flexible, large-area photovoltaic devices can be fabricated inexpensively.^{4–9} However, the power conversion efficiency (PCE) of the PSCs at 8–9% remains too low for commercialization.^{10,11} Hence, studies have focused on improving PCE through the molecular structure design^{12,13} of a new donor polymer, the introduction of a bulk heterojunction (BHJ) system and the elucidation of BHJ device physics.¹⁴ To improve the PSC performance, research on device structure has recently focused on the optimization of photo-active layer formation and the introduction of an interfacial layer. For effective charge separation on the photo-active layer, a solvent with a different boiling point can be mixed during the manufacture of the polymer ink,¹⁵ or the carrier mobility can be enhanced by forming an interpenetrating polymer network after adding a processing additive.^{16–18} To improve the photon harvesting properties, a buffer layer with metal nanoparticles can be introduced,^{19,20} or a metal oxide layer can be inserted as an

optical spacer.²¹ Other studies have improved the electron accepting properties through the introduction of a self-assembled monolayer^{22,23} in order to tune the work function of the indium tin oxide (ITO) anode, which has been used as a transparent electrode, or insert an interfacial layer such as LiF or BaF₂ between the cathode and the photo-active layers.^{8,9,19,24} Because an interfacial layer such as LiF and BaF₂ is introduced through thermal evaporation, some difficulties are encountered in manufacturing high-efficiency all-solution processed PSCs. In the Cao group, therefore, the short-circuit current density (J_{SC}) and fill factor (FF) were reportedly improved by introducing an alcohol/water-soluble polymer by spin coating between the cathode and the photo-active layers.²⁵ In theory, because an alcohol/water-soluble polymer is not intermixed with an active layer (organic solvent soluble polymer), a multi-layer structure can be fabricated through a solution process. According to a study by Zhang *et al.*, even though the characteristics of the open circuit voltage (V_{OC}), J_{SC} and FF were improved because of the internal electric field induced by the use of poly(ethylene oxide) (PEO) as a cathode interfacial layer, the PCE was not significantly improved due to the insulating properties of PEO.²⁶ The conjugated polymers for an interfacial layer with alcohol/water-soluble characteristics of good electron conductivity include poly[(9,9-dioctyl-2,7-fluorene)-*alt*-(9,9-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene)] (PFN) and poly[9,9-bis(6'-(diethanolamino)hexyl)-fluorene] (PFN-OH).^{27,28} These two polymers dramatically improved the maximum brightness and power efficiency after being applied to polymer light-emitting diodes and white-polymer light-emitting diodes in advance.²⁹ He *et al.* and Zhang *et al.* improved the PCE by 65% and 80%,

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respectively, by introducing PFN to carbazole-quinoxalinebased PSCs and benzotriazole-containing polycarbazole-based PSCs.^{25,30} Both PFN and PFN-OH showed good conductivity with a conjugated polyfluorene backbone structure. In addition, amino groups in the side chain acted to inject electrons that had been spun off from the photo-active layer into the cathode, while the surfactant-like side chain and -OH group exhibited good solubility in the alcohol-based solvent. However, it has been reported that they are ineffective in poly(3-hexylthiophene, P3HT)- and poly(ρ -phenylenevinylene, PPV)-based PSCs. Even though they are effective in the PSCs of the N-heterocycle-containing polymer donor system, a low PCE of 3% or less has been observed.^{25,30} In addition, even though the photo-active layer and alcohol/water-soluble polymer should not be intermixed with each other, the small molecules of an active layer have been removed by alcohol or water.²⁹

In this study, we confirm that the photoactive layer and the interlayer are not intermixed with each other after adding 2,4,7,9-tetramethyldec-5-yne-4,7-diol (Surfynol 104, Air-Products, USA) as a surfactant into the PFN-OH (alcohol/water-soluble polymer solution) as an interfacial layer material. After improving the photon harvesting properties by preventing a decrease in the absorbance and forming a good film morphology, the efficiency was enhanced by improving J_{SC} and FF. In PSCs to which the poly[9-(1'-decylundecylidene)-2,7-fluorene-*alt*-5,5'-(4,7-bis(2-thienyl))-5,6-dioctyloxy-2,1,3-enzothiadiazole] (PAFBToBT) was introduced, a 60% increase of PCE (3.0% \rightarrow 4.8%) was observed. In addition, a 32% increase in PCE (4.0% \rightarrow 5.3%) was detected in poly[*N*-9'-heptadecanyl-2,7-carbazole-*alt*-5,5'-(4,7'-di-2-thienyl)-2',1',3'-benzothiadiazole] (PCDTBT)³¹-based PSCs. Furthermore, in the P3HT-based PSCs, but not in the N-heterocycle-containing polymer donor system, PCE (3.9%) was improved by 30% when our developed system was introduced, unlike the previous studies in which no marked effect was observed even though PFN-OH was introduced as an interfacial layer.

2. Experiment

2.1. Materials

Poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate) (PEDOT:PSS, AI 4083) as a hole transporting layer material was purchased from Clevios. P3HT, a donor material in the photo active layer, was purchased from Rieke Metals while the acceptor materials PC₆₁BM and PC₇₁BM were bought from Nano C. The Surfynol 104, which was used as an amphiphilic surfactant, was purchased from AirProducts. PAFBToBT (weight-average molecular weight (M_w): 37 kDa and M_w/M_n (M_n : number-average molecular weight): 2.07) was synthesized in accordance with the method in our previous study.³¹ PFN-OH (M_w : 15 kDa and M_w/M_n : 2.31) and PCDTBT (M_w : 35 kDa and M_w/M_n : 1.89) were synthesized in accordance with the method described in the literature.^{28,32} The chemical structures of Surfynol 104, PFN-OH, PAFBToBT, PCDTBT, P3HT, PC₆₁BM and PC₇₁BM are shown in Fig. 1.

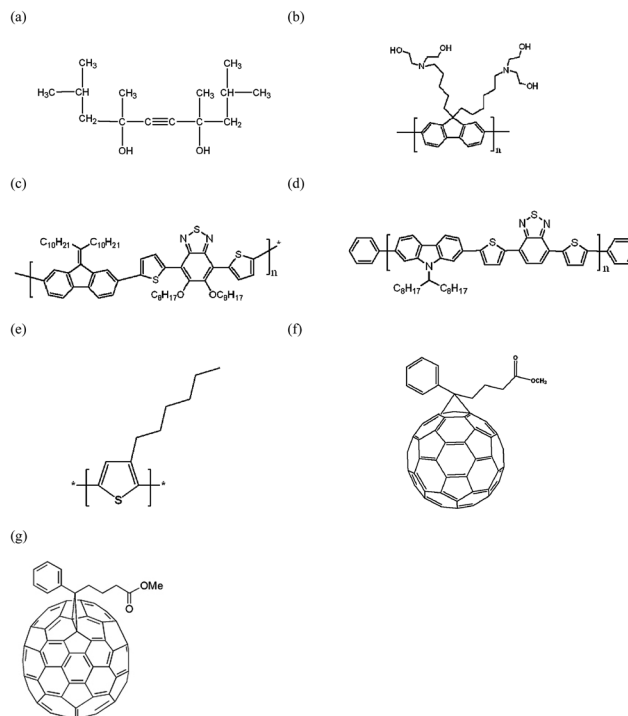


Fig. 1 The chemical structures of (a) Surfynol 104, (b) PFN-OH, (c) PAFBToBT, (d) PCDTBT, (e) P3HT, (f) PC₆₁BM and (g) PC₇₁BM.

2.2. Measurements

All of the thin films were fabricated using a GMC2 spin coater (Gensys), and their thicknesses were measured using an alpha step 500 surface profiler (KLA-Tencor). The morphology of the thin films were observed through atomic force microscopy (AFM, PSIA XE-100). The Raman spectroscopy measurements were performed using a T64000 (HORIBA Jobin Yvon). The current density-voltage (J - V) characteristics of the PSCs were measured using a Keithley 2400 source measure unit. The devices were evaluated at 298 K using a Class A Oriel solar simulator (Oriel 96000 150 W solar simulator) with a xenon lamp that simulates AM 1.5G irradiation (100 mW cm⁻²) from 400 to 1100 nm. The instrument was calibrated with a monocrystalline Si diode fitted with a KG5 filter to bring the spectral mismatch to unity. The calibration standard was calibrated by the National Renewable Energy Laboratory (NREL). The incident photon-to-current efficiency (IPCE) (Mc science) was measured. All devices were not encapsulated and stored in air for 600 hours in the dark for investigation of their long-term stability (Test ID: ISOS-D-1Shelf).³³

2.3. Fabrication and characterization of the PSCs

To clean the ITO glass (10 Ω sq⁻¹, Samsung Corning) and bare glass, they were sonicated in detergent (Alconox® in DI water, 10 wt%), acetone, isopropyl alcohol and DI water, in order, for 20 min and baked on a hot plate for 10 min at 100 °C. For the hydrophilic treatment of the ITO glass and bare glass surface, they were cleaned for 10 min in a UVO cleaner. On top of the ITO glass, the PEDOT:PSS was spin coated at 4000 rpm and a

40 nm-thick buffer layer was formed. Then, the solutions were annealed on the hot plate at 120 °C for 20 min to remove any residual solvent. In the case of an active layer, PAFBToBT and PCDTBT (donors) were mixed with PC₇₁BM (acceptor) in the ratio of 1 : 4. In addition, P3HT and PC₆₁BM were blended in the ratio of 1 : 0.6. The solutions were blended with an ODCB concentration of 1.5 wt% and spin-coated on the buffer layer to form a 130 nm-thick layer and then annealed at 120–160 °C for 10 min. To form a bilayer cathode, the PFN-OH was dissolved in methanol + DI water (93 : 7 v/v) + Surfynol 104 (0.1 wt%) at a concentration of 0.2 wt%. The solution was then spin coated onto the photo active layer to form a 5 nm-thick layer and then annealed at 80 °C for 10 min. To form the metal cathode, Al (5 Å s⁻¹, 100 nm) was thermally deposited in a high-vacuum (<10⁻⁷ torr) chamber. Finally, PSCs with an active area of 4 mm² were fabricated through encapsulation. For comparison, PSCs without a PFN-OH layer were also fabricated. The configuration of the cathode was BaF₂ (0.1 Å s⁻¹, 2 nm), Ba (0.2 Å s⁻¹, 2 nm) and Al (5 Å s⁻¹, 100 nm), which were thermally deposited in order in a high-vacuum chamber.

3. Results and discussion

In terms of configuration, PSCs were structured with ITO (10 Ω sq⁻¹, 170 nm)/PEDOT:PSS (40 nm)/active layer/cathode

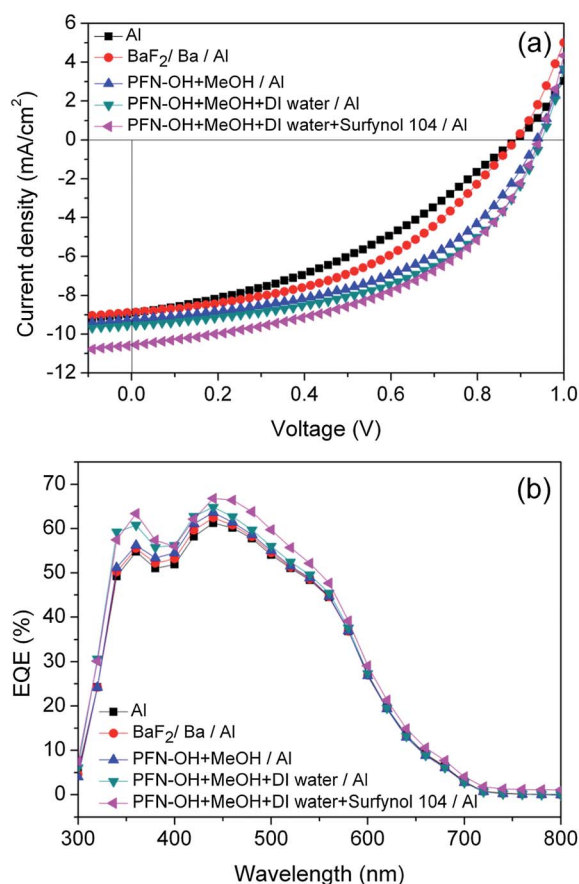


Fig. 2 (a) J - V characteristics and (b) external quantum efficiency (EQE) characteristics of PSCs with PAFBToBT:PC₇₁BM = 1 : 4 as the active layer when using various cathodes.

(Al (100 nm)) or (BaF₂ (2 nm)/Ba (2 nm)/Al (100 nm)) and ITO/PEDOT:PSS/active layer/modified PFN-OH layer (5 nm)/Al (100 nm). The J - V characteristics and external quantum efficiency (EQE) of the PSCs which used PAFBToBT as an active layer and introduced various cathodes are shown in Fig. 2 and the results are summarized in Table 1. Moreover, the J - V characteristics and EQE of the PSCs using the PCDTBT and the P3HT as an electron donor polymer are shown in Fig. S1 and S2†.

The V_{OC} , J_{SC} and FF values of the PSCs which used only Al as the cathode were 0.878 V, 8.9 mA cm⁻² and 38.7%, respectively, and the calculated PCE was 3.0%. However, when Surfynol 104 was added to PFN-OH at 0.1 wt%, the device performance was optimized and the calculated PCE was 4.8% (the optimization data of devices are shown in ESI Fig. S3†). This result was improved by about 60% compared to the reference device which was the applied Al anode. The important thing is that J_{SC} and FF significantly increased after adding Surfynol 104 to PFN-OH. Therefore, it is expected that the characteristics of the interfacial layer changed with the addition of Surfynol 104 to PFN-OH. For analysis of this change, various surface analyses were conducted.

As shown in Fig. 3, the root mean square (RMS) roughness of the surface morphology increased from 0.491 nm when PFN-OH was dissolved in methanol to 0.734 nm when PFN-OH was dissolved in the methanol and DI water-mixed solution because of the formation of larger agglomerate domains of PFN-OH molecules in the interfacial layer. The increased agglomerate domain size of the PFN-OH molecules improved the mobility in the agglomerate domain because PFN-OH has an amino group in the chain, and the mobility increased in the chain at the domain formation. However, the looseness of these agglomerate domains prevented their conductivity from increasing (Fig. 4(a)).³⁴ Hence, despite the increase in J_{SC} , FF slightly decreased because of the increased surface roughness after the formation of the agglomerate domain. As a result, PCE slightly increased from 4.1 to 4.2%.

Fig. 4 shows the mechanism of forming a lower surface roughness film of PFN-OH with Surfynol 104 compared to the pristine PFN-OH film. Surfynol 104 is an amphiphilic surfactant which consists of a hydrophobic alkyl backbone and hydrophilic hydroxyl group. Hence, hydrophobic/hydrophobic interactions such as van der Waals interactions and other multiple weak interactions take place in the hydrophobic backbone of the Surfynol 104 in PFN-OH and the hydrophobic photoactive layer surface.²³ Therefore, the surface of the photoactive layer became hydrophilic because of the hydroxyl group in Surfynol 104. As a result, hydrophilic PFN-OH can form a lower surface roughness film on the photoactive layer. Therefore, because a tight agglomerate domain (RMS: 0.564 nm) can be formed by creating a domain which is bigger than methanol but finer than the methanol and DI water mixed solution at the formation of the agglomerate domain of PFN-OH, the electrons that were generated in the photo active layer can be quickly extracted through the external circuit by increasing the conductivity of the PFN-OH thin film (Fig. 4(b)).

Charge mobility studies of the devices with a modified PFN-OH interfacial layer as the electron collection layer were

Table 1 Photovoltaic performances of various donor polymers using different cathodes

Polymer	Cathode	V_{oc} [V]	J_{sc} [mA cm^{-2}]	FF [%]	PCE [%]	R_s [$\Omega \text{ cm}^2$]
PANBToBT:PC ₇₁ BM (1 : 4)	Al (ref.)	0.878	8.9	38.7	3.0	53.7
	BaF ₂ /Ba/Al	0.878	8.9	45.7	3.6	35.8
	PFN-OH + MeOH/Al	0.930	9.3	47.5	4.1	21.3
	PFN-OH + MeOH + DI water/Al	0.939	9.6	47.1	4.2	18.5
	PFN-OH + DI water + Surfynol 104/Al	0.939	10.5	49	4.8	16.9
PCDTBT:PC ₇₁ BM (1 : 4)	Al	0.858	9.3	49.5	4.0	42.5
	PFN-OH + DI water + Surfynol 104/Al	0.959	9.7	58.5	5.3	16.3
P3HT:PC ₆₁ BM (1 : 0.6)	Al	0.616	7.7	62.6	3.0	17.2
	PFN-OH + DI water + Surfynol 104/Al	0.621	9.2	68.6	3.9	12.6

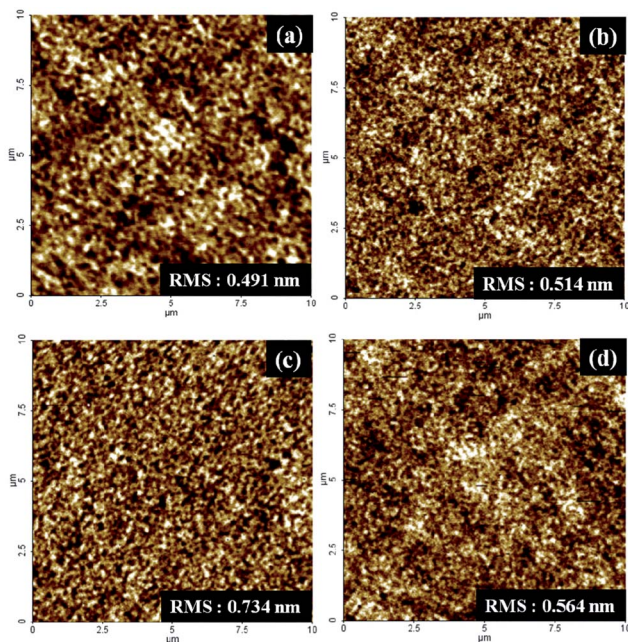


Fig. 3 AFM images of (a) PFN-OH + MeOH, (b) PFN-OH + DI water, (c) PFN-OH + MeOH + DI water and (d) PFN-OH + MeOH + DI water + Surfynol 104.

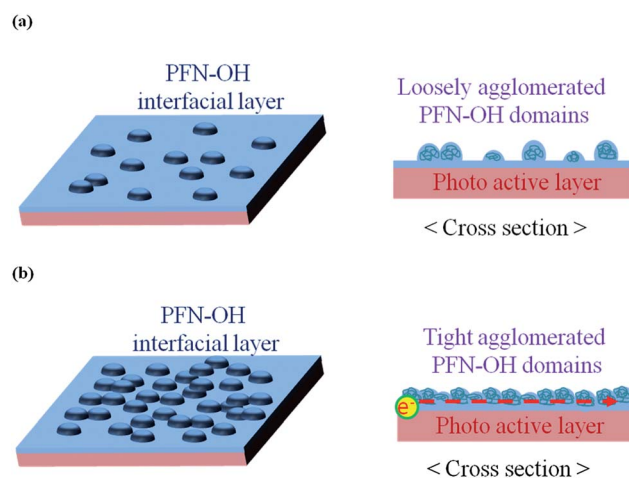


Fig. 4 (a) Loosely agglomerated domains of PFN-OH by adding DI water to a PFN-OH solution in methanol (left) and cross section of PFN-OH interfacial layer with loosely agglomerated domains (right). (b) Tight agglomerated domains of PFN-OH by adding Surfynol 104 to a PFN-OH solution in methanol + DI water (left) and cross section of PFN-OH interfacial layer with tight agglomerated domains (right). The electrons that were generated in the photo active layer can be quickly extracted through the external circuit.

conducted with electron-only devices using space charge limited current (SCLC) methods.³⁵ Electron-only devices were fabricated with a diode configuration of ITO/Cs₂CO₃/PAFBToBT:PC₇₁BM/with or without modified PFN-OH/Al. The graphs of the logarithm of JL^3/V^2 versus the square root of the mean electric field are shown in Fig. 5. The electron mobility of the devices with PCDTBT and P3HT are shown in Fig. S4.† The electron mobility of the pristine device was calculated to be $1.66 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, whereas the device with a modified PFN-OH layer had a value as high as $3.73 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The electron mobility was about 2-fold higher than that of the pristine device. Because of the high electron mobility of the device with modified PFN-OH, therefore, the R_s decreased from $53.7 \Omega \text{ cm}^2$ to $16.9 \Omega \text{ cm}^2$.

To study the structural properties of the Surfynol 104 doped PFN-OH layer on the photoactive layer, Raman spectra were measured for the pristine PFN-OH + MeOH/PAFBToBT, and the

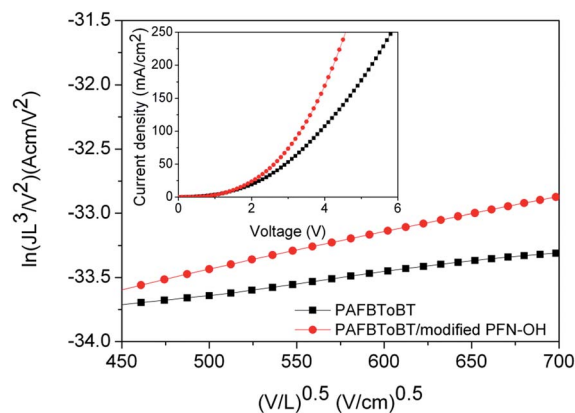


Fig. 5 The logarithm of JL^3/V^2 versus the square root of the mean electric field of electron-only devices measured in the dark. (Inset: J - V characteristics of electron-only devices).

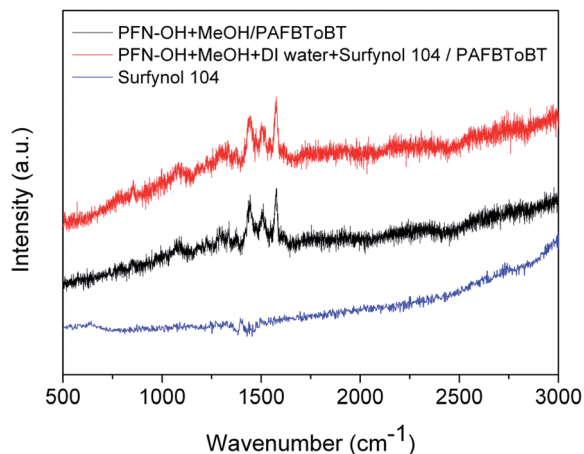


Fig. 6 Raman spectra of PFN-OH + MeOH/PAFBToBT, Surfynol 104 doped PFN-OH + MeOH + DI water/PAFBToBT and Surfynol 104.

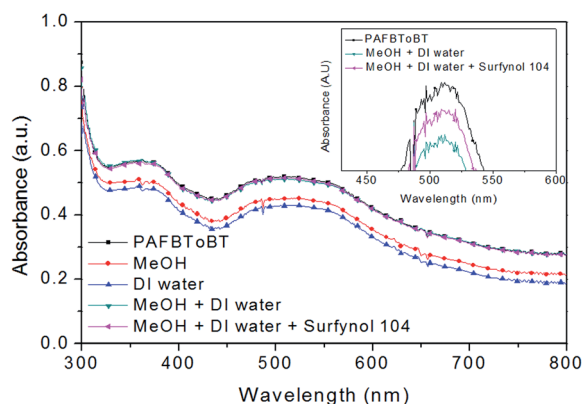


Fig. 7 UV-absorption spectra of PAFBToBT, and the equivalent films treated with methanol, methanol + DI water and methanol + DI water + Surfynol 104. Inset shows the region around 500 nm in greater detail.

Surfynol 104 doped PFN-OH + MeOH + DI water/PAFBToBT, as shown in Fig. 6. The spectrum of the Surfynol 104 doped PFN-OH + MeOH + DI water/PAFBToBT was very similar to the corresponding spectrum of the pristine PFN-OH + MeOH/PAFBToBT. From Raman spectroscopy it was revealed that the Surfynol 104 was removed from the PFN-OH layer when PFN-OH was annealed at 80 °C. Therefore, we confirmed that the electron mobility of the interfacial layer does not change due to the Surfynol 104 in the presence of the PFN-OH film.

Fig. 7 shows the UV-absorption spectra of the PAFBToBT film treated with methanol, methanol + DI water and methanol + DI water + Surfynol 104. According to Fig. 7, almost no change was observed in the absorbance of the PAFBToBT film washed with the methanol, DI water and Surfynol 104-mixed solution. Therefore, PFN-OH was treated with the Surfynol 104 solution introducing an interfacial layer, without decreasing the photon harvesting properties.

Fig. 8 shows the result of the air stability test on the PSCs which introduced the Al cathode and Surfynol 104-doped PFN-OH/Al bilayer cathode, which was performed for 600 h. In

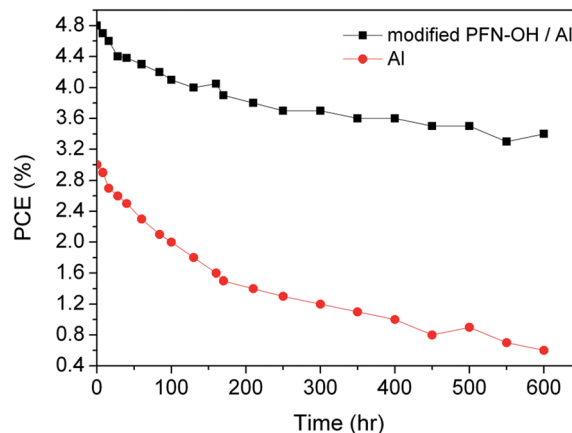


Fig. 8 PCE as a function of storage time for PAFBToBT based PSCs fabricated with an Al cathode and the Surfynol 104-doped PFN-OH/Al bilayer cathode in air under ambient conditions (no encapsulation).

the modified PFN-OH based devices, 37% degradation was observed after 600 hours. In the reference PSC, however, PCE decreased up to about 1/5 of the beginning value during the same period. It has been confirmed that the long-term stability was increased through the introduction of the modified PFN-OH to the cathode electrode.

4. Conclusion

PAFBToBT-based PSCs have been fabricated by introducing surfactant-doped PFN-OH for enhancing the PCE and the stability. Surfynol 104 has amphiphilic characteristics, and it supported the formation of a homogeneous interfacial layer on the photoactive layer. In addition, the application of the Surfynol 104-added PFN-OH interfacial layer prevented the decrease in absorption of photons in the photoactive layer and improved J_{SC} by increasing the electron mobility. Therefore, J_{SC} and FF were increased to 10.5 mA cm^{-2} and 49%, respectively, and the calculated PCE was 4.8%. In addition, when a modified bilayer cathode system was introduced to the PCDTBT and the P3HT-based PSCs, the PCE was improved to 5.3% and 3.9%, respectively. Moreover, the in-air stability was enhanced.

Acknowledgements

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