Improvement of both efficiency and stability in organic photovoltaics by using water-soluble anionic conjugated polyelectrolyte interlayer

Kyung-Geun Lim a, Mi-Ri Choi a, Tae-Woo Lee b, * 

a Department of Materials Science and Engineering, Pohang University of Science and Technology (POSTECH), 77 Cheongam-Ro, Nam-Gu, Pohang, Gyeongbuk 37673, Republic of Korea 
b Department of Materials Science and Engineering, Seoul National University (SNU), 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Republic of Korea

ARTICLE INFO

Article history:
Received 25 January 2017
Received in revised form
27 March 2017
Accepted 29 April 2017
Available online 16 May 2017

Keywords:
Electron transport
Interface dipole
Lifetime
Organic photovoltaic

1. Introduction

Organic photovoltaics (OPVs) have advantages such as flexibility, low cost, and simple solution-process fabrication. However OPVs have insufficient power conversion efficiency PCE and half-life time LT50; these demerits must be solved for commercialization. Methods to achieve OPVs that have high PCE and long LT50 have been used such as controlling the morphology of the active layer [1–5], synthesizing photoactive materials with low bandgap or high transport mobility [6–12], and employing interlayers between the photoactive layer and electrodes [13–17].

Various kinds of interlayers can affect the PCE and LT50 critically and simultaneously. To introduce an efficient interlayer between the active layer and the negative electrode, vacuum-processed metal compounds (e.g., LiF, BaF2) and low-work-function metals (e.g., Ca, Ba) have been used to reduce the interfacial energy barrier of an Al top electrode [18–23]. Furthermore, recent research into solution-processed negative electrode interlayers that uses an orthogonal solvent that does not dissolve the photoactive layer has conducted to improve performance and reliability in the device using low-cost non-vacuum fabrication processes [24–31].

A cathode interlayer has been used to improve the PCE of OPVs. Materials used for solution-processing fabrication include insulating dipole polymers [26,30] and conjugated polyelectrolytes (CPEs) [31–49]. However, the LT50 under continuous illumination has not been mainly investigated for devices that have a solution-processed negative electrode interlayer, although the device reliability is critically important to commercialize the OPVs. In addition, the mechanism by which the dipole polymers builds the actual dipole moment at the interface has not been investigated clearly to understand and improve the device characteristics.

In this study, we used an ultrathin water-soluble CPE interlayer of poly[2,5-bis(3-sulfonatopropoxy)-1,4-phenylene, disodium salt-alt-1,4-phenylene] (PPP-OPSO3) [50,51] to achieve highly efficient and reliable OPVs, and investigated the interfacial dipole moment that originated from the distribution of ionic moieties at the interface between adjacent layers. A 50 under continuous simulated solar irradiation by 2.7 times despite the solution processing of water-dissolved PPP-OPSO3.

* Corresponding author.
E-mail address: twlees@snu.ac.kr (T.-W. Lee).

Available online 16 May 2017
Accepted 29 April 2017
Received in revised form
Available online 16 May 2017

Keywords:
Electron transport
Interface dipole
Lifetime
Organic photovoltaic

1. Introduction

Organic photovoltaics (OPVs) have advantages such as flexibility, low cost, and simple solution-process fabrication. However OPVs have insufficient power conversion efficiency PCE and half-life time LT50; these demerits must be solved for commercialization. Methods to achieve OPVs that have high PCE and long LT50 have been used such as controlling the morphology of the active layer [1–5], synthesizing photoactive materials with low bandgap or high transport mobility [6–12], and employing interlayers between the photoactive layer and electrodes [13–17].

Various kinds of interlayers can affect the PCE and LT50 critically and simultaneously. To introduce an efficient interlayer between the active layer and the negative electrode, vacuum-processed metal compounds (e.g., LiF, BaF2) and low-work-function metals (e.g., Ca, Ba) have been used to reduce the interfacial energy barrier of an Al top electrode [18–23]. Furthermore, recent research into solution-processed negative electrode interlayers that uses an orthogonal solvent that does not dissolve the photoactive layer has conducted to improve performance and reliability in the device using low-cost non-vacuum fabrication processes [24–31].

A cathode interlayer has been used to improve the PCE of OPVs. Materials used for solution-processing fabrication include insulating dipole polymers [26,30] and conjugated polyelectrolytes (CPEs) [31–49]. However, the LT50 under continuous illumination has not been mainly investigated for devices that have a solution-processed negative electrode interlayer, although the device reliability is critically important to commercialize the OPVs. In addition, the mechanism by which the dipole polymers builds the actual dipole moment at the interface has not been investigated clearly to understand and improve the device characteristics.

In this study, we used an ultrathin water-soluble CPE interlayer of poly[2,5-bis(3-sulfonatopropoxy)-1,4-phenylene, disodium salt-alt-1,4-phenylene] (PPP-OPSO3) [50,51] to achieve highly efficient and reliable OPVs, and investigated the interfacial dipole moment that originated from the distribution of ionic moieties at the interface between adjacent layers. We studied how orientation of the ionic moiety and nano-morphological control of CPE layer affected dipole moment alignment to decrease the interfacial
energy barrier. The device with the PPP-OPSO3 interlayer had improved open circuit voltage $V_{oc}$, short circuit current $J_{sc}$, fill factor $FF$, and $PCE$, and significantly extended device reliability under continuous simulated solar irradiation.

2. Results and discussion

We used a water-soluble CPE, PPP-OPSO3, as the multifunctional ultrathin interlayer for the solution processed OPVs (Fig. 1). We investigated the photovoltaic characteristics of poly(3-hexylthiophene) (P3HT) (6,6)-phenyl C60-butyric acid methyl ester) (PC70BM) and poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benothiadiazole) (PCDTBT) (6,6)-phenyl C70-butyric acid methyl ester) (PC70BM) devices with PPP-OPSO3 interlayer. We used PCDTBT as low bandgap and deep HOMO photofunctional materials to show the universality of PPP-OPSO3 interlayer and a potential for better device efficiency. To amplify the effect of the PPP-OPSO3 interfacial layer on the device characteristics, a self-organized hole extraction layer (SOHEL) [52,53] based on poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) and a perfluorinated ionomer (PFI) was used as the hole extraction layer to achieve Ohmic contact with the deep HOMO level of the donor material, PCDTBT. An ultrathin PPP-OPSO3 interfacial layer was cast by spin-coating of water-dissolved PPP-OPSO3 solution on top of photoactive layers. We also used a conventional vacuum-deposited interfacial layer (LiF or Ca) to compare the device characteristics of the OPVs with PPP-OPSO3 interlayer.

The current density-voltage ($J$-$V$) characteristics of the P3HT:PC60BM and PCDTBT:PC70BM devices with PPP-OPSO3 interlayer were obtained under irradiation of air mass (AM)-1.5 global simulated sunlight at an intensity of 100 mW cm$^{-2}$ (Fig. 2a, c). $V_{oc}$ of the devices with a 3.5-nm-thick PPP-OPSO3 interlayer were 0.55 V for P3HT:PC60BM and 0.89 V for PCDTBT:PC70BM, which were significantly increased compared with that with Al only (0.44 V for P3HT:PC60BM and 0.81 V for PCDTBT:PC70BM). Moreover, $FF$ of the devices with PPP-OPSO3 interlayer were increased (62.6% for P3HT:PC60BM and 62.3% for PCDTBT:PC70BM) compared with the Al only (48.7% for P3HT:PC60BM and 51.9% for PCDTBT:PC70BM) due to the increased shunt resistance $R_{shunt}$ (from 230 to 340 $\Omega$ cm$^2$ for P3HT:PC60BM device and from 366.0 to 572.4 $\Omega$ cm$^2$ for PCDTBT:PC70BM device) and decreased series resistance $R_{series}$ (from 13.3 to 6.5 $\Omega$ cm$^2$ for P3HT:PC60BM device and from 16.4 to 6.6 $\Omega$ cm$^2$ for PCDTBT:PC70BM device). $J_{sc}$ of the PCDTBT:PC70BM devices showed very slight changes depending on interlayers as the comparable EQE results regardless of interlayers (Figure S1). Therefore, the corresponding $PCE$ of the devices were improved to 3.8% for P3HT:PC60BM and 6.7% for PCDTBT:PC70BM compared to the devices without the interlayer (2.1% and 5.0%, respectively). The $PCE$s of PPP-OPSO3/Al devices are higher than even that of LiF/Al and Ca/Al devices. The dark currents of the devices with PPP-OPSO3/Al were increased greatly compared with Al only devices (Fig. 2b, d) because of a better electron injection at the PPP-OPSO3/Al interface than Al only. The rectification ratio (forward-biased current/reverse-biased current) at 2.0 V in the dark $J$-$V$ characteristics was $-10^2$ for PCDTBT:PC70BM/PPP-OPSO3/Al device but only $-10^1$ for the device without the interlayer, and the device with Ca/Al. Furthermore, $PCE$ of P3HT:PC60BM device was slightly increased in the device with 3.5-nm-thick PPP-OPSO3 interlayer (3.8%) compared with that of 4.8-nm-thick (3.5%) due to the reduced $R_{series}$ of the P3HT:PC60BM/PPP-OPSO3 device with thickness of 3.5 nm (6.5 $\Omega$ cm$^2$) compared to the one with thickness of 4.8 nm (8.3 $\Omega$ cm$^2$). It is because ionic polymers have randomly-oriented dipole moments in the ionic aggregates of the bulk film [54]. So the overall dipole moment of the thick PPP-OPSO3 layer was reduced compared with the larger dipole moments at the interface with the adjacent layer of thin PPP-OPSO3. Because of these so-called interfacial dipole moments $\mu_{ID}$ at the interface with adjacent layers of CPE layers, a large shift and adjustment of energy level occurred at the cathode interface and the photoactive interface [31,55,56]. As a result of the energy level shift, the energy level offset $\phi$ at the interface was correlated with the dipole moments of interlayers with the adjacent layer as

$$\Delta \phi = \frac{N_{\mu} \phi_{0}}{q \varepsilon_{\text{vac}}}$$

where $N$ is the surface dipole concentration, $\mu$ is the dipole moment, $\phi$ is the angle which the dipole makes to the surface normal, $\varepsilon_{\text{vac}}$ is the vacuum permittivity, and $r$ is the static dielectric constant [57–59]. Therefore, $\phi$ at the interface decreases linearly when the interlayer have a high surface dipole concentration, a stronger dipole moment, and a more normal angle toward the air surface of the layer.

To investigate how device characteristics were improved by the reduction in $\Delta \phi$ at the electron extraction contact by the PPP-OPSO3 interlayer, we analyzed the energy level alignment and the $\mu_{ID}$ of PPP-OPSO3 interlayer (Fig. 3). We investigated the vacuum level shift $\Delta \varepsilon_{\text{vac}}$ in the P3HT:PC60BM with our PPP-OPSO3 interlayer because the energy level alignment in the device originates from the energy state of adjacent layers and particularly by $\Delta \varepsilon_{\text{vac}}$ at the interlayers [31,55,56]. The secondary cut-off of P3HT:PC60BM thin film (17.26 eV) on the high binding energy state of ultraviolet photoelectron spectroscopy (UPS) spectra was shifted to higher binding energy depending on thickness of PPP-OPSO3 interlayer (17.32 eV for 4.8 nm, 17.47 eV for 3.5 nm) (Fig. 3a). Because the alkali-metal counter-ions (Na$^+$) interact intimately with the surrounding polar solvent (water) in dilute solution, they are preferentially arranged at the air surface side of the layer, whereas the sulfonated poly(p-phenylene) backbones are located at the photoactive layer [31]. Therefore, $\mu_{ID}$ which originates from the interfacial polarization at the intimate contact between the dipole layer and the adjacent layers points toward the photoactive layer, and $\varepsilon_{\text{vac}}$ is shifted as depicted in Fig. 3b. The net dipole moment is determined primarily by $\mu_{ID}$ at the intimate contact between the dipole layer and the metal or photoactive layer, not by intrinsic molecular dipoles $\mu_{MD}$ [31,60]. In addition, $\Delta \varepsilon_{\text{vac}}$ and resulting $\Delta \phi$ were larger at the interface between the photoactive layer and the PPP-OPSO3 interlayer with optimized thickness (3.5 nm) than at that with 4.8-nm thickness. As a result, the energy level offset at the electron extraction contact $\phi_e$ was reduced, and the difference of

![Fig. 1. Architecture of OPV device with PPP-OPSO3 interlayer and its chemical structure.](image-url)
effective work function between two electrodes, so called built-in potential ($V_{bi}$), was increased in the device; therefore $V_{oc}$ and $FF$ were increased in the device with PPP-OPSO3 interlayer as an efficient electron extraction layer [61].

We used atomic force microscopy (AFM) to investigate the surface morphology of the PPP-OPSO3 layer on the on P3HT:PC$_{60}$BM photoactive layer (Fig. 4a). The PPP-OPSO3 layers were deposited by spin-casting at 2000 rpm (Fig. 4b) and 4000 rpm (Fig. 4c) on bare P3HT:PC$_{60}$BM surface to control the thickness and morphology of the PPP-OPSO3 layer. The layers consisted of a number of molecular grains evenly distributed on the P3HT:PC$_{60}$BM surface (Fig. 4b–c). The grain size of PPP-OPSO3 layer was decreased as spin-speed increased (~30 nm for 2000 rpm and ~20 nm for 4000 rpm), because the PPP-OPSO3 grains are grown by a combination of ionic interaction between the ionic groups, repulsion against the hydrophobic polymer backbones [54], and the centrifugal force during spin-casting. We also measured AFM height images of PPP-OPSO3 interlayer on photoactive layer (Figure S2). When we increased the spin-speed, the ratio of the dispersion force (i.e. centrifugal force during spin-casting) over the attractive interaction between PPP-OPSO3 molecules was increased, then grain size and thickness PPP-OPSO3 layer were reduced. We compared ionic alignment of PPP-OPSO3 interlayers depending on morphology (Figure S3). Randomly orientated ionic molecules, which is formed in bulk ionic aggregates of PPP-OPSO3 interlayer with thick layer and large grains, reduce a net dipole moment of interlayer (Figure S3a). However the net dipole moment of PPP-OPSO3 interlayer with thin layer and small grains is increased because it is dominated by $\mu_{ID}$ at the intimate contact between PPP-OPSO3 interlayer and the metal or photoactive layer (Figure S3b). Furthermore, the direction of net dipole moment according to $\Delta EV_{oc}$ (pointing toward the active layer) is determined primarily by $\mu_{ID}$ (pointing toward the active layer), not by intrinsic molecular dipoles $\mu_{MD}$ (pointing toward the metal layer) (Fig. 3b). Therefore a large $\Delta EV_{oc}$ of the 3.5-nm-thick PPP-OPSO3 interlayer originated from its larger dipole moment than that of 4.8-nm-thick PPP-OPSO3 interlayer because the dipole molecule (sulfonated

Table 1

<table>
<thead>
<tr>
<th>Cathode interlayer</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>$FF$ [%]</th>
<th>$PCE$ [%]</th>
<th>$R_{shunt}$ [U cm$^{-2}$]</th>
<th>$R_{series}$ [U cm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>No interlayer (Al only)</td>
<td>0.44</td>
<td>9.7</td>
<td>48.7</td>
<td>2.1</td>
<td>230</td>
<td>13.3</td>
</tr>
<tr>
<td>LiF</td>
<td>0.53</td>
<td>10.2</td>
<td>64.9</td>
<td>3.5</td>
<td>537</td>
<td>7.1</td>
</tr>
<tr>
<td>PPP-OPSO3 (4.8 nm)</td>
<td>0.54</td>
<td>10.2</td>
<td>63.2</td>
<td>3.5</td>
<td>498</td>
<td>8.3</td>
</tr>
<tr>
<td>PPP-OPSO3 (3.3 nm)</td>
<td>0.55</td>
<td>11.0</td>
<td>62.6</td>
<td>3.8</td>
<td>340</td>
<td>6.5</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>Cathode interlayer</th>
<th>$V_{oc}$ [V]</th>
<th>$J_{sc}$ [mA cm$^{-2}$]</th>
<th>$FF$ [%]</th>
<th>$PCE$ [%]</th>
<th>$R_{shunt}$ [U cm$^{-2}$]</th>
<th>$R_{series}$ [U cm$^{-2}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>No interlayer (Al only)</td>
<td>0.81</td>
<td>11.8</td>
<td>51.9</td>
<td>5.0</td>
<td>366</td>
<td>16.4</td>
</tr>
<tr>
<td>Ca</td>
<td>0.89</td>
<td>11.6</td>
<td>58.3</td>
<td>6.2</td>
<td>528</td>
<td>7.3</td>
</tr>
<tr>
<td>PPP-OPSO3 (3.3 nm)</td>
<td>0.89</td>
<td>11.7</td>
<td>62.3</td>
<td>6.7</td>
<td>572</td>
<td>6.6</td>
</tr>
</tbody>
</table>

Fig. 2. Current density-voltage characteristics of the device with PPP-OPSO3 interlayer for P3HT:PC$_{60}$BM device (a) at 100 mW cm$^{-2}$, (b) in the dark; and for PCDTBT:PC$_{70}$BM device (c) at 100 mW cm$^{-2}$, (d) in the dark.
poly(p-phenylene) backbone and alkali-metal counter ions (Na\(^+\)) was randomly orientated within the ionic aggregates in the bulk PPP-OPSO\(_3\) layer. By this process, the 3.5-nm-thick PPP-OPSO\(_3\) interlayer showed large \(\Delta E_{\text{vac}} = 0.21\) eV and a consequent low \(\phi\) at the interface for better energy level alignment in the device.

To understand the energy level alignment and the \(V_{\text{oc}}\) increase in the device with PPP-OPSO\(_3\) interlayer, we measured C-V characteristics of the P3HT:PC\(_{60}\)BM devices and PCDTBT:PC\(_{70}\)BM devices (Fig. 5). The capacitances of devices increased as bias voltage increased to a maximum where the voltage is called as the ‘peak voltage’ \(V_{\text{peak}}\), and decreased drastically as voltage increased further; the decrease is due to recombination of majority space charges with injected opposite charges under open circuit (or flat band) condition [30]. Thus \(V_{\text{peak}}\) is correlated with \(V_{\text{bi}}\) as \([21,30,62]\). \(\text{LT}_{50} = V_{\text{peak}} - k_{B} T/\epsilon\) (2)

where \(k_{B}\) is the Boltzmann constant, \(T\) is the temperature and \(\epsilon\) is the elementary charge. At room temperature, \(V_{\text{peak}}\) is always smaller than \(V_{\text{bi}}\) due to the space charges near the electrodes. Therefore, the change of \(V_{\text{peak}}\) of the device at room temperature is considered as an effective measure to estimate the change in \(V_{\text{bi}}\).

The P3HT:PC\(_{60}\)BM device without interlayers had \(V_{\text{peak}} = 0.29\) V in the C-V curve, but the devices that had an LiF or PPP-OPSO\(_3\) interlayer showed significantly higher \(V_{\text{peak}} = 0.51\) and 0.53 V, respectively (Fig. 5a). \(V_{\text{peak}}\) of the PCDTBT:PC\(_{70}\)BM device with PPP-OPSO\(_3\) interlayer also had higher \(V_{\text{peak}} = 0.66\) V than the device with Al only (0.58 V) (Fig. 5b). The higher \(V_{\text{peak}}\) value in the device with PPP-OPSO\(_3\)/Al than that with Al only indicates the higher \(V_{\text{bi}}\) and corresponding \(V_{\text{oc}}\). As a result of energetic analysis and device behavior characterization, we conclude that the device with PPP-OPSO\(_3\) interlayer has lower \(\phi\) at the interface and the corresponding increased \(V_{\text{bi}}\), thus \(V_{\text{oc}}\) increased compared with that with Al only.

We also measured \(\text{LT}_{50}\) of P3HT:PC\(_{60}\)BM devices with and without the PPP-OPSO\(_3\) layer (Fig. 6). Device characteristics were recorded during stability measurement at intervals of 1 h under irradiation of AM-1.5 100 mW cm\(^{-2}\) light, N\(_2\)-filled atmosphere, and at 25.3 \(^{\circ}\)C in the temperature controlled chamber until the PCE had decreased by 50%. The devices were encapsulated with a glass lid by using a UV-curable epoxy resin in a N\(_2\)-filled glovebox. Under continuous illumination with simulated solar light (AM 1.5G, 100 mW cm\(^{-2}\)), \(\text{LT}_{50}\) of the P3HT:PC\(_{60}\)BM device with PPP-OPSO\(_3\) interlayers was greatly increased to 191 h (3.5-mm-thick layer) and 283 h (4.8-nm-thick layer) than that with Al only (107 h). In previous research, the P3HT:PC\(_{60}\)BM device with the 1-nm-thick BaF\(_2\) interlayer showed a greatly (approximately nine times) increased device \(\text{LT}_{50}\) under continuous simulated solar irradiation at 100 mWcm\(^2\) as compared with the device without an interfacial layer, despite highly hygroscopic property of metal fluoride (CsF, LiF, BaF\(_2\), etc.) film. Because metal electrode diffusion into the active layer during operation is one of major causes of the OPV degradation, BaF\(_2\) interlayer was used to block the diffusion of Al into the P3HT:PC\(_{60}\)BM layer [21]. \(\text{LT}_{50}\) was increased more in the device with 4.8-nm-thick PPP-OPSO\(_3\) interlayer than 3.5 nm despite the hydrophilic nature of the PPP-OPSO\(_3\) interlayer, because the PPP-OPSO\(_3\) interlayer might efficiently block the atomic migration of Al layer during operation.

In addition, the device with PPP-OPSO\(_3\) did not show any overshooting phenomenon of PCE as a function of time. During operational stability measurement, we could not observe the increase of current density at an initial stage which usually originates from ion motion of ionic interfacial polymer layer in polymer optoelectronics [63].

3. Conclusion

A water-soluble ultrathin poly(2,5-bis(3-sulfonatopropoxy)-1,4-phenylene, disodium salt-alt-1,4-phenylene) (PPP-OPSO\(_3\)) layer can increase power conversion efficiency PCE and half-lifetimes \(\text{LT}_{50}\) in bulk-heterojunction polymer solar cells such as poly(3-hexylthiophene) (P3HT) [6,6]-phenyl C\(_{60}\)-butyric acid methyl ester) (PC\(_{60}\)BM) and poly[N-9′-heptadecanyl-C,4,7,10,13,16 hexa-cyclooctadeca-5,8,11,14,17-penta-1,4-diene-9-carboxylate-alt-5,5-(4′,7′-di-2′-thienyl-2′,1′,3′-benzothiadiazole) (PCDTBT) [6,6]-phenyl C\(_{70}\)-butyric acid methyl ester) (PC\(_{70}\)BM). We systematically investigated the mechanism of energetic alignment of PPP-OPSO\(_3\) interlayer and controlled the dipole moment by adjusting the PPP-OPSO\(_3\) nano-morphology. Thereby, we demonstrated that the built-in potential in the device was significantly improved depending on the interfacial dipole moment of PPP-OPSO\(_3\), which was
determined by molecular arrangement of ionic moieties at the intimate contact between the dipole layer and the metal or photovoltaic layer. We also demonstrated the device operational stability was also improved according to the nano-morphological effects of PPP-OPSO3 interlayer. As a result, a PCDTBT:PC70BM device with a 3.5-nm-thick PPP-OPSO3 interlayer/Al showed a remarkably improved PCE (6.7%) compared with the device with Al only (5.0%) and a device with a conventional vacuum-processed Ca/Al interlayer (6.2%). LT50 also significantly increased from 107 h (without a CIL) to 283 h for the P3HT:PC60BM device with 4.8-nm-thick PPP-OPSO3 interlayer/Al.

4. Experimental section

Device Fabrication: A PEDOT:PSS layer (35 nm) was spin cast on top of a pre-patterned indium tin oxide (ITO) substrate, baked at 200 °C for 10 min, then transferred to a nitrogen glove box. The active layer of ~200 nm thickness was deposited by spin-coating P3HT:PC60BM solution (in 1:1 wt ratio) dissolved in 1,2-dichlorobenzene. PCDTBT:PC70BM solution (in a 1:4 wt. ratio) dissolved in 1,2-dichlorobenzene was spin-cast to form ~80-nm-thick film. To fabricate solution-processed interlayers, a solution of 1.5 mg mL−1 PPP-OPSO3 in water was spin-coated on top of the photoactive layers to achieve different thicknesses of 4.8 nm (spin rate 2000 rpm) or 3.5 nm (4000 rpm), then dried at 50 °C for 10 min. The Ca or LiF interlayer was evaporated thermally on the photoactive layer at a deposition rate of 0.2 Å s−1 under a high vacuum (<5 × 10−7 Torr), and the Al cathode was deposited sequentially: first, 20-nm thickness at a deposition rate of 1 Å s−1, then 80-nm thickness at 3 Å s−1 under high vacuum (<5 × 10−7 Torr). The photoactive area (0.06 cm2) was defined by using metallic shadow masks. The devices were encapsulated with a glass lid by using a UV-curable epoxy resin in a N2-filled glovebox.

Device Characterization: J–V characteristics were recorded using a computer-controlled Keithley 2400 Source Meter under...
Acknowledgements

This research was supported by the Nano Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (MSIP, Korea) (NRF-2014M3A7B4051747). This work was also supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (Ministry of Science, ICT & Future Planning) (NRF-2016R1A3B1908431).

Appendix A. Supplementary data

Supplementary data related to this article can be found at [http://dx.doi.org/10.1016/j.mtener.2017.04.005](http://dx.doi.org/10.1016/j.mtener.2017.04.005).

References