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All-in-one solar cell: Stable, light-soaking free, solution processed and efficient diketopyrrolopyrrole based small molecule inverted organic solar cells



Fang Jeng Lim^{a,b}, Ananthanarayanan Krishnamoorthy^{b,*}, Ghim Wei Ho^{a,**}

^a Department of Electrical and Computer Engineering, National University of Singapore, Blk EA #06-10, 9 Engineering Drive 1, 117575 Singapore, Singapore ^b Solar Energy Research Institute of Singapore (SERIS), National University of Singapore, 7 Engineering Drive 1, 117574 Singapore, Singapore

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ABSTRACT

Organic solar cells (OSC) based on diketopyrrolopyrrole (DPP) small molecule have achieved relatively high efficiency (7%) in recent times. 2,5-di(2-ethylhexyl)-3,6-bis-(5"-n-hexyl-[2,2',5',2"]terthiophen-5-yl)-pyrrolo[3,4-c]pyrrole-1,4-dione (SMDPPEH) is the workhorse material for small molecule OSC as it has good solution-processing capability. However, there was no previous report on improving the device stability in inverted organic solar cells (IOSC) by using this material. Furthermore, the degradation and light-soaking behavior of this material in IOSC are also not well-addressed. In this work, we have fabricated a stable, light-soaking free, solution-processed and efficient SMDPPEH:PC₆₁BM based IOSC for the first time. Fluorosurfactant modified PEDOT:PSS and fluorinated TiO_x (F-TiO_x) transport layers were used to circumvent the inherent processability and light-soaking issues. An exclusive study on the device stability and light-soaking characteristics were also carried out for the first time. The final device provides the following merits: (i) comparable material stability to P3HT polymer, suggesting a potential for further development of DPP materials for high-efficiency devices; (ii) F-TiO_x can be used universally to fabricate a light-soaking free device with a wide range of photoactive materials from polymers to small molecules and; (iii) higher device with a wide range of to the non-inverted counterpart were obtained when the modified transport layers were used.

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1. Introduction

Solution processed organic solar cells (OSC) have made significant progress in recent times with device efficiency reaching 10% [1,2]. However, the device stability of OSCs still needs improvement if they have to be used in outdoor conditions. One way of improving the device stability is by employing the inverted architecture. In this architecture, the hole and electron transport layer positions are interchanged, resulting in the charge carriers being collected in the opposite direction across the device compared to its non-inverted counterpart. Inverted organic solar cells (IOSC) provides better stability compared to non-inverted devices through the following key modifications: (a) shifting of the hygroscopic PEDOT:PSS away from the ITO surface to prevent unintended etching and (b) by replacing the low work function

** Corresponding author. Tel.: +65 6516 8121.

E-mail addresses: serkran@nus.edu.sg,

kananthaz@gmail.com (A. Krishnamoorthy), elehgw@nus.edu.sg (G.W. Ho).

metal contact (Al) with a high work function metal (Ag) to prevent oxidation [3,4]. Impressive studies have been carried out on P3HT: $PC_{61}BM$ based devices, to understand its degradation behavior under standard operating conditions [5–8].

Small molecule based photoactive materials can be a suitable candidate for the purpose of commercialization and large scale production. In fact, Heliatek GmbH announced a record 12% efficiency for its organic solar cells based on small molecules (oligomers) recently [9]. Relative to their polymer counterparts, small molecules hold several advantages: (i) uniform and defined molecular structures, reducing batch-to-batch variation [10,11]; (ii) more versatile and ease of modification of the chemical structure [12,13]; (iii) higher charge mobility [14] and (iv) generally higher open-circuit voltage [15,16]. Small molecule based organic solar cells (SMOSC) have been widely adopted in OSC as photoactive layer to achieve an efficiency of over 9% [16-19]. Diketopyrrolopyrrole (DPP) is a commonly utilized chromophore in organic electronics [10,20-22]. DPP is an attractive building block because of its facile synthetic modifications, i.e. substitution of solubilizing alkyl groups and aromatic groups for energy level

^{*} Corresponding author. Tel.: +65 6516 7434.

tuning [15]. Due to the rationale of the conjugated structure, it has a greater tendency to crystallize, resulting in a high mobility. This property is desirable in OSC to enable better control of the morphology for optimal charge transport properties [23]. OSC with device efficiency of 7% was achieved using solution-processed DPP based donor small molecules [22].

Among the family of DPP molecules, 2,5-di(2-ethylhexyl)-3,6bis-(5"-n-hexyl-[2,2',5',2"]terthiophen-5-yl)-pyrrolo[3,4-c]pyrrole-1,4-dione (SMDPPEH), is one material variation that has easy solution-processing capability [10]. The solubility of the material originates from the hexyl and ethyl-hexyl side chains at the thiophene terminals and DPP building block respectively. These alkyl side chains act as the solubilizing groups in the material, enabling decent solubility in organic solvents such as chloroform and chlorobenzene [10,24–26]. The terthiophene groups attached to the DPP backbone is crucial to make the molecule more planar and well-ordered, which results in high carrier mobility compared to non-thiophene substituents counterparts [24]. To date, typical device efficiency of 2.8% was reported when SMDPPEH:PC₆₁BM was utilized as a photoactive layer in the conventional device architecture [24,27]. Farahat et al. have reported a device efficiency of 4.5% by using (3-chloropropyl)trimethoxysilane as an additive to the photoactive blend SMDPPEH:PC₆₁BM [25]. However, there have been fewer reports of IOSC utilizing small molecules as photoactive layer. Few of which includes thermal evaporated SubPc:C₆₀ system [28,29] and p-DTS(FBTTh₂)₂:PC₇₁BM [30], without much information on the DPP based small molecule systems. Furthermore, the study of this small molecule material, which has a less complicated configuration, is essential to provide a deeper understanding on the behavior of the DPP functional group in inverted architecture.

Though inverted organic solar cells (IOSC) usually exhibits better device stability compared to the conventional OSC under ambient conditions, there are still two inherent issues: (i) wettability issue and (ii) light-soaking issue. Firstly, coating of PEDOT:PSS onto the photoactive layer remains to be a serious technical challenge involved in the fabrication of these devices. The hydrophobic nature of the underlying photoactive layer produces a high surface tension upon contact with the hydrophilic PEDOT:PSS, causing a serious wettability issue. Without the aid of additives, PEDOT:PSS can hardly be coated onto the photoactive layer, resulting in low device efficiency even though it may give stable device lifetime. As a result, additives are generally used to modify the wettability of PEDOT:PSS on photoactive layers [31-34]. However, these methods often cause deterioration of device efficiencies due to the requirement of additional UV-ozone treatment on the photoactive layer to enable proper film quality [35,36]. Secondly, a reversible light-soaking treatment is required when n-type oxide is used as a selective electron transport layer (ETL) in IOSC. Since this is a reversible effect [37–39], the device has to be activated repeatedly at each dark-light cycle (every morning if used in outdoor application) before it can function in full capacity. Hence, this effect should be addressed for improved device practicality. A typical device with TiO_x or ZnO as electron transport layer requires 10-15 min under AM1.5G to reach its maximum efficiency [40-42]. Impurity-modified metal oxides have also been used by various groups to address the light soaking issue [41,43]. Recently, we have reported the use of DupontTM Capstone® FS-31 (CFS-31) modified PEDOT:PSS as HTL and fluorinated TiO_x (F-TiO_x) as ETL to overcome the wettability and light-soaking issues in P3HT:PC61BM and PTB-7:PC71BM based inverted organic solar cells [41,44,45]. We have identified that both transport layers were able to consistently provide its respective functions in polymeric photoactive layers but their performances in a small molecule system remains unclear. Thus, it is important to evaluate the compatibility of these transport layers in a small molecule based IOSC.

In this work, SMDPPEH:PC₆₁BM based inverted organic solar cell was fabricated using CFS-31 modified PEDOT:PSS as hole transport layer and F-TiO_x as electron transport layer for the first time by overcoming the wettability and light-soaking issues. We have investigated the device stability and light-soaking characteristics of this material in inverted organic solar cell. Different sets of device were exposed to air in dark, light in N₂ environment, light in ambient condition and prolonged light-soaking treatment. It was found that the small molecule is relatively stable in all the three degradation conditions, and that the F-TiO_x electron transport layer significantly reduces the device light-soaking time.

2. Materials and methods

2.1. Materials

Chemical bath deposited F-TiO_x was prepared from ammonium hexafluorotitanate ((NH₄)₂TiF₆, 99.99%, Sigma Aldrich) and boric acid (H₃BO₃, \geq 99.99%, Sigma Aldrich) as precursors. For sol gel-TiO_x, Titanium isopropoxide (TTIP, 97%, Sigma Aldrich), acetylacetone (AA, Sigma Aldrich) and isopropanol (IPA, reagent grade, Aik Moh Paints & Chemical Pte Ltd.) were used. Regioregular poly (3-hexylthiophene-2,5-diyl) (P3HT, >98%, Sigma Aldrich), poly ({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}) (PTB-7, 1-Material) and 2,5-di(2-ethylhexyl)-3,6-bis-(5"-nhexyl-[2,2',5',2"]terthiophen-5-yl)-pyrrolo[3,4-c]pyrrole-1,4-dione (SMDPPEH, 1-Material) were used as donor materials. Phenyl-C₆₁butyric acid methyl ester (PC₆₁BM, Nano-C) and phenyl-C₇₁butyric acid methyl ester (PC₇₁BM, Nano-C) were used as acceptor materials. Dichlorobenzene (DCB, Sigma Aldrich) and chlorobenzene (CB, Sigma Aldrich) were used as the solvent for donors and acceptors. 1,8-diiodooctane (DIO, Sigma Aldrich) was used as a solvent additive for PTB-7:PC71BM. Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS, Clevios P VP AI4083, Ossila) were used as hole transport layer. Capstone[®] FS-31 (DupontTM) was added into PEDOT:PSS prior to spin coating. Silver (Ag) metal was purchased from K.J. Kurt Lesker & Co. P3HT:PC₆₁BM and PTB-7:PC71BM IOSC were fabricated as control devices for the degradation study and the light-soaking study. All the above mentioned materials were used as received.

2.2. Solution preparation

The precursor solution for F-TiO_x films were prepared by mixing appropriate concentration of ammonium hexafluorotitanate $((NH_4)_2TiF_6, 99.99\%, Aldrich)$ and boric acid (H_3BO_3) . Both solutions were stirred separately for at least 10 min at room temperature before mixing. The stirred solutions were mixed and placed into a pre-heated bath with temperature at 40 °C before immersing ITO substrates into the bath for F-TiO_x deposition. The deposited film was finally annealed at 180 °C for 1 h. The precursor solution for sol–gel TiO_x was prepared by mixing titanium isopropoxide, acetylacetone, iso-propanol in volume ratio of 1:0.5:10.

P3HT:PC₆₁BM blend was prepared in the ratio of 1:0.8 (15 mg/ ml of P3HT, 12 mg/ml of PC₆₁BM) in DCB. PTB-7:PC₇₁BM blend was prepared in the ratio of 1:1.5 (12.5 mg/ml of PTB-7, 18.75 mg/ml of PC₇₁BM) in CB (96%) and DIO (4%). SMDPPEH:PC₆₁BM blend was prepared in the ratio of 1:1 (10 mg/ml of both SMDPPEH and PC₆₁BM) in CB. All mixed solution were stirred and heated at 60 °C overnight in a N₂ filled glove box prior to spin coating.

2.3. Device fabrication

Both conventional (non-inverted) and inverted bulk heterojunction organic solar cells based on P3HT:PC₆₁BM, PTB-7:PC₇₁BM and SMDPPEH:PC₆₁BM were prepared on pre-patterned tin doped indium oxide coated glass substrates (ITO, Xinvan Technology Ltd.). The sheet resistance of the ITO (thickness: 90 ± 10 nm) is approximately 15–20 Ω/\Box . The substrates were pre-cleaned using a detergent solution, followed by successive ultrasonication in de-ionized water, isopropanol and acetone for 15 min each. The pre-cleaned substrates were dried in oven at 60 °C for two hours. For inverted device with sol-gel TiO_x as ETL 80 nm of precursor solution was spun on ITO substrates and left hydrolvzed in air for 2 h. For inverted device with $F-TiO_x$ as ETL, 80 nm of fluorinated TiO_x (F-TiO_x) was deposited onto ITO by immersing the ITO substrate into a chemical bath which comprised of 0.1 M ammonium hexafluorotitanate ((NH₄)₂TiF₆) and 0.2 M boric acid (H₃BO₃) at 40 °C for 90 min. All coated films were annealed at 180 °C for 1 h before transferring into the N₂ filled glove box. For SMDPPEH:PC₆₁BM based device, 100 nm of organic film was spun onto TiO_x at 850 rpm for 60 s through a 0.2 μ m PTFE filter without any thermal annealing or solvent-annealed treatments. For P3HT:PC₆₁BM based device, 200 nm of organic film was spun onto TiO_x at 800 rpm for 30 s through a 0.45 μm PTFE filter and the wet film was then annealed at 140 °C for 1 min prior to coating of PEDOT:PSS. For PTB-7:PC71BM based device, 100 nm of organic film was spun onto TiO_x at 1600 rpm for 20 s through a 0.2 µm PTFE filter and the resultant film was then annealed at 60 °C for 5 min prior to coating of PEDOT: PSS. 70 nm of PEDOT:PSS blended with CFS-31 (PEDOT:PSS-CFS-31) with various volume ratios was then coated onto the active layer in air through a 0.45 µm cellulose filter and annealed at 140 °C for 1 min in the N_2 filled glove box, as reported in our earlier work [44]. Ag metal (100 nm) was then thermally evaporated at 4×10^{-6} mbar through a pre-designed shadow mask, resulting in an active device area of 9 mm². The completed device architecture is $ITO/TiO_x/pho$ toactive layer/PEDOT:CFS-31/Ag.

2.4. Device characterization

The current density-voltage (j-V) measurements were obtained under 1 sun illumination (ABET technologies Sun 2000 Solar Simulator) and a Keithley 2400 sourcemeter. The intensity was calibrated using a silicon reference cell (Fraunhofer ISE). The light-soaking treatment was done using the same lamp source, where the devices were continuously illuminated and data were periodically acquired. The thicknesses of all layers were measured using cross section SEM image by using JEOL FEG JSM 6700F field emission SEM operating at 15 keV. All the fabrication steps, except coating of TiO_x and PEDOT:PSS, were performed inside a glove box of N₂ atmosphere (Charslton Technologies, ≤ 1 ppm moisture and O₂). Cell degradation studies were carried out in various conditions; dark condition in air (25 °C, relative humidity 55%, ISOS-D-1 shelf scheme [46]), exposure to AM1.5G illumination in N₂ filled glove box and continuous AM1.5G illumination in air. Lightsoaking experiment was conducted by monitoring the i-V characteristics in-situ while illuminating the freshly prepared device under AM1.5G illumination at 25 °C, less than 1 ppm of moisture and oxygen. The UV-vis absorption spectra were acquired using Agilent Cary 7000 Universal Measurement Spectrophotometer in the wavelength range from 300 nm to 800 nm. Investigation of chemical bonds for various organic polymers and small molecules were obtained by Raman spectroscopy. The characterizations were done using Renishaw inVia microscope with $50 \times$ magnification in a back-scattering configuration. The excitation source was a 514 nm (Ar ion) laser, spectra were obtained with a laser power of 0.25 mW with an acquisition time of 15 s.



Fig. 1. (a) Inverted device architecture of SMDPPEH:PC₆₁BM based organic solar cells fabricated in this work; (b) chemical structure of 2,5-di(2-ethylhexyl)-3,6-bis-(5"-n-hexyl-[2,2',5',2"]terthiophen-5-yl)-pyrrolo[3,4-c]pyrrole-1,4-dione (SMDPPEH) and; (c) corresponding energy band diagram of the IOSC device.

3. Results and discussion

Fig. 1 shows the device configuration of SMDPPEH:PC₆₁BM based IOSC used in this work, the chemical structure of SMDPPEH and the corresponding energy band diagram. To better understand the degradation behavior and light-soaking characteristics of the small molecules based IOSC, IOSCs with P3HT:PC₆₁BM and PTB-7: PC₇₁BM photoactive layers were also fabricated and used as control devices. The degradation study was conducted in three different conditions: (i) dark in air; (ii) illuminated in N₂ environment and; (iii) illuminated in air. The light-soaking study was conducted with continuous illumination in N₂ filled glove box while acquiring its *j*-*V* characteristics in-situ.

3.1. Effect of PEDOT:PSS:CFS-31 on the device performance

The IOSC device was first evaluated by coating PEDOT:PSS:CFS-31 hole transport layer (HTL) at different annealing conditions and concentration of CFS-31. Previously when P3HT:PC₆₁BM [44] and PTB-7:PC₇₁BM [45] devices were used, 5.5 v/v% of PEDOT:PSS:CFS- 31 as HTL with annealing temperature of 140 °C gave the most optimized device performance. However, when SMDPPEH donor is used, the previously adopted treatment becomes non-optimal because the annealing temperature is higher than the glasstransition temperature of SMDPPEH (126 °C) [13,47]. The function of thermal annealing is to remove the residual moisture in the PEDOT:PSS layer. However, in OSC, this process also involves the annealing of the underlying photoactive layer, and annealing at 140 °C would disrupt the chemical structure of the small molecule; it is therefore mandatory to strike a balance between the removal of moisture in PEDOT:PSS and maintaining the annealing temperature below the material glass transition point. Extensive studies have shown that the annealing of PEDOT:PSS:CFS-31 at 100 °C for 10 min in SMDPPEH:PC₆₁BM IOSC devices could produce an optimal device efficiency up to 1.9% (see Section A.1 in Appendix for detailed optimization procedure). Despite the well-optimized annealing condition, the device efficiency was still lower than the commonly reported values (2.8%) [24,27].

The device efficiency is further increased by varying the concentration of CFS-31 fluorosurfactant in PEDOT:PSS. Fig. 2a and b shows the summary of device efficiency and the j-V characteristics of the IOSC when various CFS-31 concentrations were used (for detailed device parameters, see Table A.1 in Appendix). When no CFS-31 was added into PEDOT:PSS, the coating of the HTL was not possible due to large contact angle and this is attributed to the formation of a non-wettable film (see Fig. 2c). An absence of HTL would largely hamper the charge collection efficiency due to large amount of interfacial recombination that ultimately causes low efficiency. As the CFS-31 concentration increases from 1 v/v% to 3 v/v%, the leakage current (as seen from the *j*-*V* characteristics in Fig. 2b) gradually decreases, indicating the formation of a welldefined PEDOT:PSS film. At a concentration region of 3.5–4.0 v/v%, the device is situated at its most optimal state, giving an efficiency enhancement from 1.9% to 2.8%. At this concentration region, the coated film is at its best quality, allowing a good coverage of HTL on SMDPPEH:PC₆₁BM. Upon increasing the CFS-31 concentration beyond 4%, the device efficiency gradually decreases to 1.5%. We have therefore found that the optimal concentration region for CFS-31 in PEDOT:PSS for SMDPPEH:PC₆₁BM has been narrowed

down to 3.5-4.0 v/v%, as opposed to 4-8 v/v% (as in the case of P3HT:PC₆₁BM [44] and PTB-7:PC₇₁BM [45]). The optimal region is the balance between wettability and the phase segregation of PEDOT and PSS [48]. The function of CFS-31 is to lower the surface energy of PEDOT:PSS, so that it can lie within the wetting envelop of SMDPPEH:PC₆₁BM. From the significant reduction of the contact angle at 4 v/v% of CFS-31 in PEDOT:PSS (Fig. 2c), we postulate that the surface energy of SMDPPEH:PC₆₁BM is larger than compared to P3HT:PC₆₁BM and PTB-7:PC₇₁BM [36]. Hence, a lesser amount of fluorosurfactant would suffice to have PEDOT:PSS lying within its wetting envelop. However, when there is an excess CFS-31 in PEDOT:PSS. there will be hindrance of PEDOT:PSS network by the surfactant molecule, causing a decrease in $V_{\rm oc}$, $j_{\rm sc}$ and fill factor. Hence, in the optimal region of 3.5–4.0 v/v% CFS-31 concentration in PEDOT:PSS, a highest device efficiency of 2.8% was achieved, better than its non-inverted counterparts ($\eta = 2.7\%$, see Table A.2 in Appendix).

3.2. Solvent-vapor-annealing treatment in inverted architecture

It was reported earlier that the solvent-vapor-annealing treatment is beneficial for the diketopyrrolopyrrole (DPP) molecules to form crystallite domains which in turn results in a well interconnected nanomorphology [19,49,50]. Sun et al. have recently reported that a solvent with high vapor pressure and medium solubility for the DPP based donor molecules is ideal for solventvapor-annealing treatments for small molecule systems [49]. This is because the vapor pressure of the solvents can selectively improve the molecular packing structure to form a homogeneous distribution of donor and acceptor. Following this, we have conducted a systematic study of solvent-vapor-annealing treatment with various solvents to SMDPPEH:PC₆₁BM in conventional architecture. We have identified that solvent annealing with chlorobenzene for 7 s gives the most optimized performance of 2.7% (see Fig. A.3 in Appendix). However, when same treatment was carried out in the inverted architecture (with sol-gel TiO_x as electron transport layer), it does not seem beneficial to the device performance (Table 1). All parameters (V_{oc} , j_{sc} and fill factor) decreases, as opposed to the effect observed in conventional



Fig. 2. Device efficiencies for SMDPPEH:PC₆₁BM IOSC at (a) various CFS-31 volume ratio in PEDOT:PSS:CFS-31 with corresponding (b) *j*–*V* characteristics and; (c) wetting properties of 180 μL of PEDOT:PSS:CFS-31 dropped on SMDPPEH:PC₆₁BM film with and without CFS-31 addition. The error bars were obtained from the standard deviation of at least 6 devices.

architecture. In fact, the small molecule based IOSC performs better without solvent-vapor-annealing. Table 1 shows that an efficiency of 2.9% can be obtained, prior to the treatment. When the devices were treated, an observable decrease in the device efficiencies to 1.6% were observed. This effect could be originated from the formation of a non-favorable molecular packing of donor and acceptor phases induced by solvent-vapor-annealing [49,51,52]. In other words, the as-prepared SMDPPEH:PC₆₁BM IOSC, only with proper tuning of CFS-31 concentration, could achieve its most optimal state without any further treatments. This hole transport layer remarkably simplifies the fabrication procedure for small molecule based IOSC.

3.3. Effect of F-TiO_x electron transport layer on the device performance

To make IOSC device light-soaking free, 80 nm F-TiO_x was incorporated as the ETL. Similar to the studies observed for P3HT and PTB-7 based IOSC [43,45], F-TiO_x ETL does not cause any detrimental effects to the overall device efficiency in SMDPPEH: PC₆₁BM based IOSC when compared to sol–gel TiO_x (Fig. 3a). A significantly improved light-soaking characteristics was also observed, which will be further discussed later. The thickness of ETL is crucial to achieve an optimal state of device resistances and help in suppressing the trap-assisted recombination [53]. Thus, a detailed study on the thickness variation of the ETL was first carried out. After controlling the thickness of F-TiO_x from 50 nm to 100 nm by varying the chemical bath deposition time onto ITO, an optimal thickness of 80 nm was obtained, giving an efficiency of 3.0%, better than its optimized non-inverted counterpart (Table 2 and Fig. 3b). Hence, with the incorporation of F-TiO_x ETL, a more

Table 1

Summary of device parameters to compare SMDPPEH:PC₆₁BM based OSC in conventional (optimized) and inverted architectures with various solvent-vaporannealing (SVA) time with chlorobenzene. The error values were obtained from the maximum standard deviation of at least 6 devices. Detailed optimization procedures of non-inverted device is reported in the Appendix.

Architecture	SVA time [s]	V_{oc} [\pm 5 mV]	j _{sc} [± 0.2 mA/ cm ²]	FF [± 0.7%]	η [± 0.1%]
Non-inverted	7	707	6.7	55.9	2.7
Inverted	0	755	7.9	48.4	2.9
	5	662	7.4	40.8	2.0
	10	564	7.5	38.6	1.6

efficient DPP small molecule based inverted organic solar cell can be obtained.

3.4. Degradation behavior

Apart from the enhancement in device efficiency by the incorporation of PEDOT:PSS:CFS-31 HTL and F-TiO_x ETL, the device stability of SMDPPEH:PC₆₁BM IOSC was also studied in detail. To facilitate the degradation study, three sets of devices consisting of P3HT:PC₆₁BM, PTB-7:PC₇₁BM and SMDPPEH:PC₆₁BM with 80 nm of F-TiO_x ETL were fabricated and characterized under various conditions without encapsulation. The devices with polymer donor materials such as P3HT and PTB-7 were used as control devices. The first set of devices was exposed to air in a controlled dark environment to investigate its air-induced degradation. The second set of devices was exposed to continuous AM1.5G illumination in N₂-filled glove box, which removes the effect of air and moisture to investigate its photo-induced degradation effects. The final set of devices was exposed to AM1.5G illumination in air to study the combination of air-induced and photo-induced degradation behavior. The device efficiencies of SMDPPEH:PC61BM. P3HT:PC₆₁BM and PTB-7:PC₇₁BM used in the degradation studies were 3.0%, 3.4% and 6.6% respectively (see Fig. A.4 and Table A.3 for *i*-V characteristics and device parameters). For the purpose of comparative analysis, all device parameters were normalized at its initial value.

3.4.1. Air-stability

The air-stability of the IOSC devices was investigated by storing the device in dark and ambient condition (25 °C, relative humidity: 45%) while monitoring its efficiency (η) over time, in accordance to International Summit on Organic Photovoltaic Stability (ISOS) D-1 shelf scheme [46]. The device lifetime for IOSC devices with F-TiO_x ETL was reported in Fig. 4 for over 1500 h. P3HT: PC₆₁BM and PTB-7:PC₇₁BM IOSCs were used as control devices. Table 3 also shows the summary of the T_{80} lifetime, quantified by the demarcated line at 80% of initial efficiency in Fig. 4d. SMDPPEH:PC₆₁BM based IOSC is more stable than PTB-7:PC₇₁BM based device, these devices were able to retain 80% of its initial efficiency at 326 h (T₈₀); whereas PTB-7:PC₇₁BM based device can only last for 78 h in the same condition. This result is expected because PTB-7 polymer is more susceptible to the moisture attack from PEDOT:PSS. The high water uptake of PEDOT:PSS when exposed in air is detrimental to the photoactive layer [3]. The hydroxylation of PTB-7 due to the presence of easily cleavable alkoxy (R–C–O) side chains is the source of poor material stability. In contrast, there is no alkoxy side chains attached to the



Fig. 3. (a) j-V characteristics for SMDPPEH:PC₆₁BM based IOSC with 80 nm of sol-gel TiO_x and F-TiO_x as the electron transport layer; (b) efficiency of IOSC devices with various thicknesses of F-TiO_x.

molecular structure of SMDPPEH (see Fig. 1c). Hence, the material is expected to be more resistant to moisture attack. However, the DPP small molecule is not as stable as compared to P3HT:PC₆₁BM based device (T_{80} =457 h). From the perspective of their chemical structures, the underlying reason is probably due to the presence of longer alkyl side chains (ethyl-hexyl) in SMDPPEH molecular structure. It has been reported that organic materials with longer side chains are generally more unstable compared to materials with shorter ones [54]. Furthermore, Jan et al. have also reported that the DPP based molecule is more stable when there is short or no side chains attached to the molecular backbone [55]. Upon closer look to the device parameters, the source of degradation is dominated by the decrease of $V_{\rm oc}$ (Fig. 4a). Since the presence of side chains is also responsible for the HOMO and LUMO energies of an organic semiconductor [56], the degradation that took place in the long ethyl-hexyl side chain may have altered these energy levels. The alteration of energy alignment would cause a gradual decrease in the $V_{\rm oc}$ after 500 h. This effect was not observed in P3HT based device, which further confirms our argument.

Table 2

Summary of device parameters comparing SMDPPEH:PC₆₁BM based IOSC with 80 nm of sol-gel TiO_x and F- TiO_x ETL at various thickness. The error values indicate the maximum standard deviations over at least 6 devices.

ETL	Thickness [nm]	$V_{ m oc}$ [\pm 5 mV]	j _{sc} [± 0.3 mA/ cm ²]	FF [± 1.0%]	η [± 0.1%]
Sol–gel TiO _x	80	758	7.6	50.6	2.9
F-TiO _x	50	742	8.2	45.3	2.7
	60	755	7.9	48.4	2.9
	70	732	8.3	46.9	2.9
	80	762	7.9	48.6	3.0
	90	745	7.9	48.7	2.9
	100	749	7.0	47.9	2.5

3.4.2. Photochemical stability in N₂ atmosphere

As the light absorption by the chromophores of aromatic compounds can trigger various chemical changes such as photo-Fries rearrangement [6,57] and Norrish reaction [58-60], it is useful to understand the photo-chemical behavior of SMDPPEH molecules in IOSC device. The photo-induced degradation effect of SMDPPEH:PC₆₁BM blend was investigated by exposing the devices under continuous illumination in N₂ filled glove box (oxygen and moisture < 1 ppm), while the *j*-V characteristics was acquired insitu. Fig. 5 shows the photochemical stability of SMDPPEH: PC61BM, P3HT:PC61BM and PTB7:PC71BM IOSC in an N2 atmosphere. The device efficiency gradually increases upon illumination to its maximum value after approximately 1 min. It is interesting to note that the device efficiency of SMDPPEH:PC₆₁BM decreases with illumination. Upon closer examination on the device parameters, it was found that the small molecule degrade in a different manner compared to other materials. Generally, the degradation of organic solar cell is triggered by a change in the short-circuit current density (j_{sc}) [3,61]. However, for SMDPPEH, the decrease in device performance is predominantly triggered by a decrease in open-circuit voltage (V_{oc}) (and with a minute decline in fill factor). The relatively constant j_{sc} throughout the illumination signifies that the donor-acceptor blend has neither charge generation loss nor morphological degradation [61–63]. This initial voltage loss could be originated from the photochemical reaction that causes the formation of trap states in the photoactive layer

Table 3

Summary of T_{80} values for IOSC devices with various photoactive layers.

Photoactive layer	<i>T</i> ₈₀ ^a					
	Air only (hour)	Light in N ₂ (min)	Light in air (min)			
P3HT:PC ₆₁ BM PTB-7:PC-1:BM	457 78	247 84	97 3			
SMDPPEH:PC ₆₁ BM	326	429 ^b	110 ^b			

^a Time taken for device to degrade to 80% of its initial value.

^b Extrapolated from fitted function at $\eta_{\text{norm.}} = 0.8$.



Fig. 4. Normalized (a) V_{oc} ; (b) j_{sc} ; (c) fill factor and (d) efficiency for inverted SMDPPEH:PC₆₁BM (\bullet), P3HT:PC₆₁BM (\bullet) and PTB7:PC₇₁BM (\blacktriangle) under exposure to ambient condition in dark. The dotted horizontal line in (d) marks the lifetime (T_{s0}) of each device. The lines in (d) represent the fitted degradation profile according to experimental data. The error bars are the standard deviation obtained from at least 6 devices, which were calculated based on the initial value of the device parameters.



Fig. 5. Normalized (a) open circuit voltage; (b) short circuit current density; (c) fill factor and (d) efficiency for inverted SMDPPEH:PC₆₁BM (\bullet), P3HT:PC₆₁BM (\bullet) and PTB7: PC₇₁BM (\blacktriangle) under illumination in N₂ filled environment. The dotted horizontal line in (d) marks the lifetime (T_{80}) of each device. The black line in (d) represents the fitted degradation profile according to experimental data. The error bars are the standard deviation obtained from at least 6 devices, which were calculated based on the initial value of the device parameters.



Fig. 6. Normalized (a) open circuit voltage; (b) short circuit current density; (c) fill factor and (d) efficiency for inverted SMDPPEH:PC₆₁BM (\bullet), P3HT:PC₆₁BM (\bullet) and PTB7: PC₇₁BM (\blacktriangle) under illumination in air. The dotted horizontal line in (d) marks the lifetime (T_{80}) of each device. The black line in (d) represents the fitted degradation profile according to experimental data. The error bars are the standard deviation obtained from at least 6 devices, which were calculated based on the initial value of the device parameters.

[64]. We believe that similar effect may have taken place in the SMDPPEH molecules as it was being illuminated. As a result, the small molecule was found to be the most stable under illumination in N₂ environment among all the photoactive materials used in this study. From Table 3 and Fig. 5d, the estimated T_{80} lifetimes of SMDPPEH:PC₆₁BM, P3HT:PC₆₁BM and PTB-7:PC₇₁BM were 437 min, 245 min and 84 min respectively.

3.4.3. Photochemical stability in air

When freshly prepared IOSC devices were subjected to degradation under light in air, the device performance is generally expected to reduce more rapidly than the isolated testing because it is a combination of both air-induced and light-induced degradation process [45]. However, the SMDPPEH:PC₆₁BM based IOSC is not only stable, but its device efficiency also increases after an initial exposure (see Fig. 6). The device efficiency, as observed in Fig. 6d, increases when the device was illuminated in the first 20 min. This phenomenon was not observed in P3HT:PC₆₁BM and PTB-7:PC₇₁BM based device, where a continual decrease of performance took place. The increased efficiency was triggered by an increase in V_{oc} and j_{sc} after the exposure to light in air. Hörmann et al. have previously reported that in SMOSC, the morphology of donor and acceptor materials is a more dominant factor for change in device V_{oc} compared to its effective energy gap [65]. The mutual orientation of donor and acceptor molecules can largely influence the $V_{\rm oc}$ of the device due to orientation-dependent electronic coupling at the donor-acceptor interface. Vandewal et al. have also reported that by proper control of interfacial area between donor and acceptor in a SMOSC, the device V_{oc} can be affected by the change in the corresponding charge carrier lifetime [66]. Therefore, we also associate the increase in Voc of SMDPPEH:PC61BM device to morphological influence induced by light in air. The change in j_{sc} can be associated to the chemical [67,68] and morphological [61,63,69] changes in the photoactive layer, as reported elsewhere. However, the absorption spectra show no changes in the chromophore of the small molecule before and after degradation (Fig. 7a), thus ruling out the factor of influence of j_{sc} due to the chemical change in photoactive layer. Hence, we postulate that the initial increase in device j_{sc} is caused by the change in small molecule morphology due to illumination in air. The photoinduced alteration of morphology and vertical phase separation may become favorable to the inverted architecture. Therefore, we



Fig. 7. (a) UV-vis absorption spectra of freshly prepared and degraded device; (b) Raman spectra for fresh and degraded (illuminated in air for 2 h) SMDPPEH: $PC_{61}BM$ films in air.

believe that the DPP based small molecules IOSC undergo photochemical induced morphological changes that results in a favorable configuration for efficient charge transport properties.

After the performance increase in the first 20 min, the device continues to degrade due to chemical changes that occur in the material. Raman spectroscopic analysis can be used to understand its chemical degradation behavior [70]. As a result, Raman spectrum for the fresh and degraded (>2 h) SMDPPEH:PC₆₁BM films were acquired. Fig. 7b shows that after SMDPPEH is exposed to light in air, the Raman intensities of the DPP conjugated C=Cmode around 1420–1440 cm⁻¹ decreases [71]. Furthermore, the intensities of C=C antisymmetric stretching (\sim 1515 cm⁻¹) and symmetric stretching (\sim 1460 cm⁻¹) modes of thiophene [72] also decreases after the exposure. This phenomenon suggests the degradation of the small molecule occurs at these sites, causing a continual decline in its device efficiency. Unlike PTB-7 [45], there is no hypsochromic shift in the chromophore of the small molecules; this observation generally indicates the superior stability of the chemical structure in air and light. This observation is attributed mainly due to the absence of harmful side chains such as alkoxy groups. Overall, SMDPPEH has a similar lifetime compared to P3HT:PC₆₁BM device, as seen in Table 3. Overall, the degradation studies have shown that DPP based small molecules are stable in IOSC, suggesting its potential to be used on further developments of high-efficiency material.

3.5. Light-soaking characteristics

To test the capability of $F-TiO_x$ to be used in a wide range of photoactive layers in organic solar cells to reduce the light-soaking time, the light-soaking characteristics of SMDPPEH:PC₆₁BM based IOSC device with sol-gel TiO_x and F- TiO_x as ETL were investigated, together comparing with P3HT:PC₆₁BM and PTB-7:PC₇₁BM based IOSC devices. The results in Fig. 8 show that, regardless of the photoactive layer used, the IOSCs with F-TiO_x as ETL have a significant decrease in light-soaking time from at least 320 s down to 60 s (see Table 4). This reduction in light-soaking time can be translated to a reduction of at least 30 minutes when the devices are taken to be light-soaked in outdoor environment. (see Fig. A.5 in Appendix for detailed estimation steps). Therefore, this result is of significance to its practicality. We have therefore shown that the F-TiO_x ETL can be used as a universal material to fabricate a lightsoaking free IOSC device; it can be used in a wide range of polymeric and small molecule materials such as P3HT, PTB-7 low bandgap polymer and SMDPPEH small molecules as donor materials.



Fig. 8. Light-soaking characteristics of P3HT:PC₆₁BM, PTB-7:PC₇₁BM and SMDPPEH:PC₆₁BM IOSC using (a) sol–gel TiO_x and (b) F-TiO_x as electron transport layer. The solid lines are the fitted data with logistic function (see Section 6.5 in Appendix for details).

Table 4

Summary of light-soaking time (τ_{soak}) of P3HT:PC₆₁BM, PTB-7:PC₇₁BM and SMDPPEH:PC₆₁BM IOSC using (a) sol–gel TiO_x and (b) F-TiO_x as electron transport layer.

Photoactive layer	$\tau_{\rm soak}^{a}$ [S]			
	Sol-gel TiO _x	F-TiO		
P3HT:PC ₆₁ BM	434	34		
PTB-7:PC71BM	326	56		
SMDPPEH:PC61BM	491	57		

^a Light-soaking time: time required to reach 95% of maximum efficiency.

4. Conclusions

Solution-processed small molecule based inverted organic solar cells based on SMDPPEH:PC₆₁BM was fabricated for the first time in this work. Firstly, systematic studies in incorporating modified transport layers: PEDOT:PSS:CFS-31 and fluorinated TiO_x (F-TiO_x) into the new material system were carried out. Using these transport layers, we have fabricated an inverted SMDPPEH:PC₆₁BM device with an enhanced device efficiency of 3%, higher compared to non-inverted counterparts (2.7%). Secondly, an exclusive and detailed investigation on the device lifetime was carried out and it was found that SMDPPEH has a comparable material stability to P3HT, suggesting a potential to develop DPP based materials further for implementation of high-efficiency OSC devices. Lastly, we have also shown that the F-TiO_x electron transport layer can be used universally to fabricate a light-soaking free IOSC with a wide range of photoactive material including polymer, low band-gap polymer and small molecule systems.

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Appendix A. Appendix

A.1. Optimization of PEDOT:PSS:CFS-31 annealing conditions and formulation in inverted organic solar cells

Fig. A.1a shows the summary of device efficiency when subjected to different PEDOT:PSS:CFS-31 annealing temperatures ranging from 25 °C to 120 °C for 5 min in a N₂ environment. Without thermal annealing (25 °C), the moisture content in the PEDOT: PSS still remains on the film, leaving the photoactive layer vulnerable to the moisture attack [73], resulting in a low device efficiency of 0.01%. As the annealing temperature was increased from 40 °C to 80 °C, the device efficiency also gradually increases from 0.5% to 1.3% as the moisture content is reduced. At 100 °C, the small molecule based IOSC gives the most optimal efficiency of 1.6%. This temperature was also previously found to be optimal for SMDPPEH:PC₆₁BM OSC as it induces crystallization in the blended films that helps in improving its device performance [74]. When the films were annealed above 100 °C, which is close to its glasstransition temperature (126 °C), an abrupt deterioration in the device efficiency (0.8%) was observed. Absorption spectra for



Fig. A.1. Device efficiencies for SMDPPEH:PC₆₁BM IOSC at various (a) PEDOT:PSS annealing temperature; (b) UV–vis absorption spectra of freshly prepared SMDPPEH:PC₆₁BM IOSC at various annealing temperatures for 10 min; (c) PEDOT: PSS annealing time. The error bars were obtained from the standard deviation of at least 6 devices.

SMDPPEH:PC₆₁BM films annealed at 80 °C, 100 °C and 120 °C are shown in Fig. A.1b. The absorption band around 710 nm represents the highly ordered and strong intermolecular interaction of oligothiophene-DPP system [75]. A hypsochromic shift from 711 nm to 704 nm was clearly observed when the film was annealed at 120 °C, signifying a change in the chemical structure in the molecule, disrupting the intermolecular interaction. Hence, 100 °C was chosen as the optimal annealing temperature for PEDOT:PSS:CFS-31 in SMDPPEH:PC₆₁BM based IOSC.

Further improvement on the IOSC device performance was anticipated by varying the annealing time. It is noteworthy that the annealing time of a photoactive layer and PEDOT:PSS:CFS-31 is also crucial, not only to the degree of crystallization of the small molecule, but also to the degree of moisture removal from the PEDOT:PSS:CFS-31 film [76]. On one hand, if the small molecules were not allowed enough time to crystallize, the charge transport property will not reach its full potential. On the other hand, if the moisture removal process in PEDOT:PSS:CFS-31 was not given sufficient time, deterioration of the material would still happen

Table A.1

Summary of device parameters for SMDPPEH:PC₆₁BM based IOSC prepared using various CFS-31 concentration ratio in PEDOT:PSS. The error values indicate the maximum standard deviations over at least 6 devices. The optimal region for efficient IOSC device is situated at 3.5–4.0 v/v% region.

CFS-31 concentra- tion [v/v%]	$V_{\rm oc}$ [\pm 10 mV]	j _{sc} [± 0.3 mA/ cm²]	FF [± 1.7%]	η [± 0.2%]
0	33	1.1	22.9	0.0084
1	701	5.9	37.8	1.6
2	760	6.6	48.1	2.4
3	769	6.9	49.7	2.6
3.5	754	7.8	48.0	2.8
4	750	7.4	50.4	2.8
5.5	730	6.9	48.6	2.5
7	693	6.7	37.2	1.7



Fig. A.2. Experimental setup for the solvent-vapor-annealing of devices in this work.

and result in a sub-standard device efficiency. To achieve optimal device efficiency, the annealing duration was varied from 1 minute to 20 minutes at a constant temperature of 100 °C. As the annealing duration increases, a maximum device efficiency of 1.9% can indeed be achieved after 10 min (Fig. A.1c). Hence, PEDOT:PSS: CFS-31 annealing treatment of 100 °C for 10 min was used as the optimized condition for fabricating SMDPPEH:PC₆₁BM IOSC in subsequent studies. Despite the well-optimized annealing condition, the device efficiency was still lower than the commonly reported values (2.8%) [77,78].

Table A.1 shows the optimization of CFS-31 concentration ratio in PEDOT:PSS from 0 v/v% to 7.0 v/v%. An optimal region was found

Table A.2

Summary of device parameters of SMDPPEH:PC₆₁BM based IOSC with various solvents at different solvent-vapor-annealing (SVA) durations.

Solvent	SVA time [s]	V _{oc} [± 8 mV]	j _{sc} [± 1.4 mA/ cm²]	FF [± 4.5%]	η [± 0.4%]	η _{max} [%]
No SVA	0	578	6.5	35.8	1.4	1.6
CB	5	682	6.7	48.7	2.2	2.8
	7	707	6.7	55.9	2.7	2.8
	10	675	5.4	45.3	1.7	1.9
	15	588	4.6	35.1	0.9	1.0
	20	627	2.4	33.4	0.5	0.7
	30	627	1.8	35.6	0.4	0.5
THF	10	480	4.3	31.1	0.7	1.3
	20	376	1.0	29.3	0.1	0.2
	30	475	0.9	29.9	0.1	0.2
CHCl ₃	10	578	3.1	36.9	0.7	0.7
	20	471	3.5	32.2	0.5	0.7
	30	465	3.6	32.1	0.5	0.6



Fig. A.3. j-V characteristics for conventional SMDPPEH:PC₆₁BM OSC (after solvent-vapor-annealing treatment) by (a) chlorobenzene (CB); (b) tetrahydrofuran (THF); (c) chloroform (CHCl₃) and (d) summary of device efficiencies when the respective solvents.

to be situated in the range of 3.5-4.0 v/v%, which gives an efficiency of 2.8%.

A.2. Solvent-vapor annealing treatment for the photoactive layer in conventional architecture

We have designed the experiment for solvent-vapor-annealing treatment as follows: three commonly used solvents, chlorobenzene (CB), tetrahydrofuran (THF) and chloroform (CHCl₃)

Table A.3

Summary of device parameters comparing SMDPPEH:PC₆₁BM, P3HT:PC₆₁BM and PTB-7:PC₇₁BM based IOSC with 80 nm of F-TiO_x ETL. The error values indicate the maximum standard deviations over at least 10 devices.

Photoactive layer	V _{oc} [mV]	j _{sc} [mA/cm ²]	FF [%]	η [%]	η _{max} [%]
SMDPPEH:PC ₆₁ BM P3HT:PC ₆₁ BM PTB-7:PC ₇₁ BM	$\begin{array}{c} 762 \pm 1 \\ 621 \pm 3 \\ 759 \pm 3 \end{array}$	$\begin{array}{c} 7.9 \pm 0.1 \\ 8.6 \pm 0.2 \\ 15.3 \pm 0.3 \end{array}$	$\begin{array}{c} 48.6 \pm 0.3 \\ 62.0 \pm 1.7 \\ 56.7 \pm 1.4 \end{array}$	$\begin{array}{c} 2.9 \pm 0.1 \\ 3.3 \pm 0.1 \\ 6.6 \pm 0.1 \end{array}$	3.0 3.4 6.6



Fig. A.4. j-V characteristics of SMDPPEH:PC₆₁BM, P3HT:PC₆₁BM and PTB-7:PC₇₁BM based IOSC with 80 nm of F-TiO_x ETL used in the degradation studies.

were selected and the SMDPPEH:PC₆₁BM blend films were exposed to various time durations up to 30 s with a setup shown in Fig. A.2. Fig. A.3 shows the j-V characteristics of the device with each solvent at different time durations up to 30 s (Fig. A.3a-c) and the summary of the efficiencies obtained (Fig. A.3d). It is worth noting here that, lower boiling point solvents which provide significant efficiency enhancement in small molecules [79] and polymer [80] based OSC do not seem to work in the case of SMDPPEH:PC₆₁BM OSC. When treated with THF and CHCl₃, the device efficiency decreases significantly even after 10 s compared to the device without solvent-vapor-annealing treatment (Table A.2). Unlike the other two solvents, when the device is treated by chlorobenzene vapor (a higher boiling point solvent), its efficiency increases after 10 s. Upon further investigation, a high efficiency of 2.7% can be achieved in 7 s. The device efficiency value (2.7%) has matched with the typical values for non-inverted SMOSC of 2.8% [77,78]. This optimized processing condition will be used for fabricating SMDPPEH:PC₆₁BM based inverted organic solar cells.

Table A.4

Estimation of light-soaking time reduction in outdoor condition based on lightsoaking experiments done in indoor environment.

Photoactive laver	τ _{soak} [S]		τ_{soak} reduction in indoor [s]	τ_{soak} reduction in outdoor [mins]	
Sol-gel F-TiO _x TiO _x					
P3HT:PC ₆₁ BM PTB-7:PC ₇₁ BM	434 326	34 56	400 270 424	47 33 46	
PC ₆₁ BM	491	57	434	40	



Fig. A.5. (a) Typical solar irradiance at function of time for a sunny day at Singapore; (b) Indoor light soaking calculation with an assumption of 8 min of light-soaking time; (c) Outdoor light-soaking calculation by equating the energy density (area under the curve highlighted in yellow) obtained from (b) and calculate the corresponding light-soaking time required.

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Table A.5Fitting parameters of various TiO_x in inverted organic solar cells based on Eq. A.1.

Electron transport layer	Active layer	A ₀	<i>A</i> ₁	τ_0	p	τ_{soak}
Sol-gel TiO _x	P3HT:PC ₆₁ BM	0	1	87.7	1.8	434
F-110 _x Sol_gel TiO	DTR_7.DCRM	0	1	10.4	2.5	34
F-TiO _x	T TD-7.1 C71DW	0	1	21.3	3.1	56
Sol-gel TiO _x	SMDPPEH:PC ₆₁ BM	0	1	143.5	2.4	491
F-TiO _x		0	1	28.5	4.3	57

A.3. Typical device j–V characteristics used in degradation studies

For the degradation studies, SMDPPEH:PC₆₁BM, P3HT:PC₆₁BM and PTB-7:PC₇₁BM based IOSC were fabricated. The typical device performances are summarized in the Table A.3. Fig. A.4 shows the corresponding j–V characteristics of each type of inverted device. These devices were fabricated and used to study the device airstability, photochemical stability in N₂ atmosphere and photochemical stability in air Fig. A.5.

A.4. Significance of light-soaking time reduction in outdoor applications

Assumptions:

- (1) 100% conversion of photon to electron in solar cells.
- (2) Intensity is proportional to the number of photons, and proportional to the light soaking time. [i.e. Intensity ∞ photon density ∞ electron density ∞ time].
- (3) Identical irradiance wavelength spectrum between indoor and outdoor
- (4) Same device area is used.

If a device requires 8 min (480 s) of light-soaking treatment under indoor illumination, it would require at least, if not more than, 1 h 10 min of light-soaking in outdoor applications. Note that this treatment has to be done *every morning* throughout the entire lifetime of the device. Following the estimation method, the reduction of light-soaking time in the outdoor is calculated and summarized in Table A.4. It can be shown that, a mere reduction of 5 min could result in a reduction of 33 minwhen the devices were used in outdoor applications.

A.5. Fitting function for calculation of light soaking time

The light soaking time (τ_{soak}) was determined by fitting the experimental data in Fig. 8 with a logistic function shown in Eq. (A.1). The fitting was done using Origin Pro 9.0. The fitted parameters were tabulated in Table A.5. τ_{soak} was then obtained by defining $\eta_{\text{norm.}}(\tau_{\text{soak}}) = 0.95$ and mapped back to the experimental data of Fig. 8.

$$\eta(t) = \frac{A_0 - A_1}{1 + (t/\tau_0)^p} + A_1 \tag{A.1}$$

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