Photoactive layer formation in the dark for high performance of air-processable organic photovoltaics

Akihiro Maeda\textsuperscript{1,2}, Ruiyuan Liu\textsuperscript{1}, Kilho Yu\textsuperscript{1}, Shinya Young Lee\textsuperscript{1}, Kyohei Nakano\textsuperscript{1}, Masahito Takakuwa\textsuperscript{1,2}, Shipei Zhang\textsuperscript{2,3}, Keisuke Tajima\textsuperscript{4}, Kenjiro Fukuda\textsuperscript{1,4,*}, Shinjiro Umezu\textsuperscript{1,2,*} and Takao Someya\textsuperscript{1,2,*}

1 Department of Modern Mechanical Engineering, Waseda University, 3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan
2 Center for Emergent Matter Science, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
3 Thin-Film Device Laboratory, RIKEN, 2-1 Hirosawa, Wako, Saitama 351-0198, Japan
4 Electrical and Electronic Engineering and Information Systems, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

* Authors to whom any correspondence should be addressed.

E-mail: kenjiro.fukuda@riken.jp, umeshin@waseda.jp and takao.someya@riken.jp

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Abstract
Recent progress in organic photovoltaics (OPVs) has led to an increased importance of laboratory-scale fabrication in ambient air using solution processes. However, the effect of the existence of both ambient air and light during the formation of a photoactive layer on the performance of fabricated devices has not been elucidated thus far in detail. Here, we show that photoactive layer formation in completely dark conditions enables air-processable OPVs with a high power conversion efficiency. The degradation in OPV performance caused by the coexistence of air and room light was confirmed by systematically examining atmospheric and room-light irradiation conditions during the formation and drying of the photoactive layer. Moreover, the degradation rate was much faster than that in the case of dried solid photoactive layers exposed to room light in ambient air. The photoactive layer with non-fullerene acceptors showed a much slower degradation rate, owing to room light, than that with fullerene acceptors. Based on these findings, we demonstrate that by eliminating light during formation, slot-die-coated OPVs in ambient air show comparable performance to that of spin-coated OPVs in an inert glovebox.

1. Introduction

The remarkable progress of organic photovoltaics (OPVs) indicates that the field is anticipating a transition from laboratory-scale research and development to industrial-scale manufacturing [1, 2]. The power conversion efficiency (PCE) of single-junction cells is approaching 18% with the development of electron donor and acceptor materials for photoactive layers [3]. Even in the all-coating fabrication process, a PCE of 11.9% has been achieved by fully solution-processed OPVs with improved charge transport layers and coated electrodes [4]. Researchers have attempted to replace the solution process in laboratory-scale spin coating with roll-to-roll compatible coating processes, such as doctor-blade coating [3, 5, 6] and slot-die coating [1, 7]. Recently, a benchmark PCE value of 9.5% was achieved for large-area OPVs with an effective area of 216 cm\textsuperscript{2}, using doctor-blade coated layers in a glovebox [6].

Researchers are now recognizing that it is time to focus on OPV stability [8]. Because there are many complex degradation mechanisms, we need to classify the degradation factors in detail and consider appropriate approaches for each [9–12]. Most studies have focused on the device stability, wherein the fabricated devices were tested under various conditions, such as shelf life in ambient air [13, 14], humidity [14, 15], high temperature [15–17], and light-soaking conditions [16, 18–24]. The recently developed non-fullerene acceptors provide advantages in terms of both PCE and stability compared to fullerene acceptors [25, 26]. Another study revealed that hypo-miscible systems are most kinetically stabilized when both de-mixing and crystallization are suppressed [27].
In addition to the device stability under ambient conditions, air processability is important for the industrialization of OPVs. To maximize the potential of OPVs, roll-to-roll fabrication under ambient air conditions is an important aspect for lowering costs. Although most of the existing photoactive materials require an inert glovebox during formation because of the instability in air, recent material advancements enable good performance through ambient formation processes [5, 7, 14, 28, 29]. Further, studies on the humidity dependency of cell performance show that photoactive layers with certain polymeric acceptors are relatively insensitive to water levels in the air [15, 29]. Additionally, solvent vapor annealing is a good approach for improving the efficiency of the ambient air fabrication process [30].

However, little attention has been paid to the coexistence of ambient air and light during the formation process of photoactive layers. When considering industrial production, the influence of ambient light, rather than strong illumination (such as 1 sun), should be carefully evaluated.

Here, we show that photoactive layer formation in completely dark conditions enables air-processable OPVs while maintaining a high PCE. The formation and drying of the photoactive layer under completely dark conditions in air maintained a PCE comparable to that of the reference OPVs formed in a glovebox. In contrast, continuous room-light illumination in air in the spin-coating process and subsequent drying process leads to rapid degradation of the fabricated OPVs. Both fullerene and non-fullerene acceptors were tested, revealing that non-fullerene bulk-heterojunction (BHI) films exhibit better light stability during the formation process. The non-fullerene OPVs formed and dried in air in the dark achieved an average PCE of 10.88%. Finally, we confirmed that the light-shielding strategy can be utilized for roll-to-roll compatible slot-die coating.

2. Experiments

2.1. Fabrication of organic photovoltaics

Figure 1(a) shows a schematic of the fabricated OPV. A glass with patterned indium tin oxide (ITO; 150 nm; GEOMATEC Co., Ltd) was used as the substrate. Cr/Au electrodes (3.5 nm/100 nm) were prepared as contact pads onto the ITO layer using a thermal evaporator at a pressure below $1 \times 10^{-3}$ Pa. Next, a ZnO precursor was prepared by dissolving zinc acetate dehydrate (329 mg; FUJIFILM) and 2-aminoethanol (94 µl; FUJIFILM) in 2-methoxyethanol (3 ml; FUJIFILM) overnight at room temperature (21 °C–26 °C). The samples were treated with oxygen plasma (300 W, 30 s; PC-300, Samco Inc.), and the ZnO precursor was spin coated at 5000 rpm for 30 s. The ZnO was removed from the Au contacts with an acetone-coated cotton swab, and the samples were annealed at 180 °C for 30 min. Two donor/acceptor blend films were prepared as photoactive layers (figure 1(b)). A fullerene photoactive layer solution was prepared by dissolving poly[(4,8-bis[5-((2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyldiyl-alt-(4-octyl-3-fluorothieno[3,4-b]thiophene)-2-carboxylate-2-6-diy]] (PBDTTT-OFT, 9 mg) and [6,6]-phenyl C$_7$ butyric acid methyl ester (PC$_7$BM, 11 mg; Solenne) in chlorobenzene (970 µl; FUJIFILM) at 100 °C for 2 h. An additive 3,4,5-Trimethoxytoluene (50 µl; TCI) was added to the solution and stirred at 100 °C for 5 min. The solution was spin coated in a glovebox or ambient air (600 rpm, 30 s). Two non-fullerene acceptor photoactive layers were investigated in this study. One was prepared by dissolving PBDTTT-OFT (10 mg) and 2,2′-((2Z,2′Z)-((4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-sindaceno[1,2-b:5,6-b']dithiophene-2,7-diy)bis(4-((2-ethylhexyl)oxy)thiophene-5,2-diyl))bis(methanlylidene))bis(5,6-difuoro-3-oxo-2,3-dihydro-1 H-indene-2,1-diylidene))dimalononitrile (IEICO-4F; 15 mg; 1-Material) in chlorobenzene (970 µl; FUJIFILM) at 70 °C for 2 h. An additive, 1-chloronaphthalene (30 µl; Sigma-Aldrich), was added to the solution and stirred at 70 °C for 5 min. The solution was spin coated in a glovebox or ambient air (1400 rpm, 60 s). The other non-fullerene acceptor photoactive layer was prepared by dissolving poly[(2,6-4,8-bis[5-((2-ethylhexyl)-3-fluoro thiophen-2-yl)benzo[1,2-b:4,5-b'] dithiophene)-alt-(5,5′-(1′,3′-di-2-thiienyl)-5′,7′-bis(2-ethylhexyl) benzol[1′,2′-c,4′,5′-c′]dithiophene-4,8-dione)] (PM6, 7.6 mg; 1-Material) and 2,2′-((2Z,2′Z)-((12,13-bis(2-ethylhexyl) )-3,9-diundecy1-12,13-dihydro-[1,2,5]thiadiazolo [3,4-e]thieno[2′,3′,4′,5′]thieno[2′,3′,4,5]pyrrolo[3,2-g]thieno[2′,3′,4,5]thieno[2,3-b]indole-2,10-diy])bis (methyllylidene) bis(5,6-difuoro-3-oxo-2,3-dihydro-1 H-indene-2,1-diylidene))dimalononitrile (Y6, 9 mg; 1-Material) in a mixed solvent of chloroform (995 µl; FUJIFILM) and 1-chloronaphthalene (5 µl; Sigma-Aldrich). The solution was spin coated in a glovebox or ambient air (3500 rpm, 45 s). Before drying, the formed PM6:Y6 layers were annealed at 110 °C for 5 min under the same environmental conditions as spin coating.

To investigate how light and ambient air influence the formation and drying of photoactive layers, we performed the spin coating under three conditions: (a) in the nitrogen-filled glovebox with both oxygen and H$_2$O concentrations below 1 ppm and with the glovebox light off but room light on (illuminance of 210–230 lx inside the glovebox), (b) ambient air (21 °C–26 °C, 35%–45% RH) with LED room-light illumination (880–980 lx), and (c) ambient air with no illumination (approximately 0 lx). Following the layer
formation, we stored the samples under three different conditions to dry the film: (a) in the glovebox, (b) uncontrolled ambient air (21 °C–26 °C, 35%–45% RH) with room-light illumination, and (c) in an environmental test chamber (SH-242 bench-top-type temperature and humidity chamber; Espec) with controlled temperature and humidity (25 °C, 30% RH) in ambient air and dark conditions. Unless otherwise stated, the drying time was set to 30 min.

The dried samples were installed in a vacuum evaporator, and a hole-transporting layer of molybdenum oxide (MoO$_X$, 7.5 nm) and an Ag anode (100 nm) were sequentially deposited by thermal evaporation at $<3 \times 10^{-4}$ Pa. Finally, a 1 µm-thick parylene layer was deposited by chemical vapor deposition to form a passivation layer. The effective area of the fabricated cell was 0.04 cm$^2$.

2.2. Photoactive layer formation with slot-die coating
To confirm the roll-to-roll compatibility, we formed a photoactive layer using a slot-die coater (Mini-40, Die-Gate Co., Ltd) under ambient air conditions. The fullerene photoactive layer solution was coated with a 30 µm-width slot at 10 mm s$^{-1}$ and a target wet thickness of 6 µm in ambient air under completely dark conditions. The coated sample was immediately installed in a vacuum chamber, and then MoO$_X$ (7.5 nm) and Ag (100 nm) were sequentially deposited by thermal evaporation. The effective area of the fabricated cell was 0.04 cm$^2$.

2.3. Device characterization
The current density–voltage ($J$–$V$) characteristics of the OPVs were recorded under AM 1.5 G (100 mW cm$^{-2}$, with the intensity calibrated using a silicon reference solar cell) using a SourceMeter (Series 2400; Keithley) under ambient laboratory conditions. External quantum efficiency (EQE) measurements were performed with monochromatic light (SM-250 F; Bunkoukeiki) calibrated with a silicon reference diode. The absorbance of the films was characterized using an ultraviolet–visible–near-infrared (UV–vis–NIR) spectrophotometer (V-780; JASCO Inc.). The surface morphology was imaged using atomic force microscopy (AFM, SPM-9700HT; Shimadzu) in the tapping mode. Ultraviolet photoelectron spectroscopy (UPS) and x-ray photoelectron spectroscopy (XPS) measurements were performed using a photoelectron spectroscopy system (PHI5000 VersaProbe II; ULVAC-PHI Inc.). The light source for UPS was
He I excitation light (21.2 eV). For all UPS measurements, a −5.0 V bias was applied to the samples. The x-ray source for XPS was monochromated Al Kα (1486.6 eV) radiation with an operating power of 50 W (15 kV voltage). The diameter of the analyzed area was 200 µm. The take-off angles were 90° and 45° to the sample substrate for UPS and XPS, respectively. Photoelectron yield spectroscopy (PYS) was conducted using a photoelectron spectrometer (AC2; Riken Keiki Co. Ltd.).

3. Results and discussion

Figures 2(a)–(c) present the J–V characteristics measured from the representative devices based on fullerene and non-fullerene acceptors under different photoactive layer formation and drying conditions, and table 1 summarizes the corresponding average photovoltaic parameters. The photovoltaic parameters of reference fullerene cells, which were formed and dried in a nitrogen-filled glovebox, exhibit a current density \( (J_{SC}) \) of 16.1 ± 0.3 mA cm\(^{-2} \), an open-circuit voltage \( (V_{OC}) \) of 0.749 ± 0.004 V, and a fill factor \( (FF) \) of 0.740 ± 0.006, resulting in a PCE of 8.92 ± 0.079%. All parameters were significantly lower for cells with a photoactive layer formed and dried in air under room-light illumination. In particular, the average \( J_{SC} \) was 2.1 ± 0.1 mA cm\(^{-2} \). The average PCE was 0.49 ± 0.05%, which corresponds to a maximum power output normalized with the reference cell of that of the reference devices \( (P_{max}/P_{max0}) = 0.055 \). A similar sharp degradation was observed when spin coating was conducted in the glovebox, followed by drying in air under room-light illumination (1.46%, figure S1 and table S1). A surprising decrease in the photovoltaic parameters of reference PM6:Y6 cells, which were formed and dried in the nitrogen-filled glovebox, exhibit a current density \( (J_{SC}) \) of 23.5 ± 0.6 mA cm\(^{-2} \), an open-circuit voltage \( (V_{OC}) \) of 0.674 ± 0.005 V, and FF of 0.708 ± 0.007, resulting in a PCE of 10.88 ± 0.022, which is comparable to that of the reference cells \( (P_{max}/P_{max0}) = 0.997 \). The spin-coating process in the dark in air led to a small improvement in the PCE. The photovoltaic parameters of reference PBDTTT-OFFT:IEICO-4F OPVs having the photoactive layer formed and dried in air under dark conditions exhibit a \( J_{SC} \) of 22.6 ± 0.2 mA cm\(^{-2} \), \( V_{OC} \) of 0.672 ± 0.006 V, and FF of 0.716 ± 0.008, resulting in a PCE of 10.88 ± 0.029%, which is comparable with that of the reference cells \( (P_{max}/P_{max0}) = 0.997 \). The photovoltaic parameters of the reference PM6:Y6 cells, which were formed and dried in the nitrogen-filled glovebox, exhibit a \( J_{SC} \) of 24.4 ± 0.2 mA cm\(^{-2} \), \( V_{OC} \) of 0.805 ± 0.003 V, and FF of 0.704 ± 0.022, resulting in a PCE of 13.84 ± 0.46%. When the photoactive layer was formed and dried in ambient air with room-light illumination, both \( J_{SC} \) and FF decreased by approximately 10% compared to the reference cells, resulting in a PCE of 8.61 ± 0.42% \( (P_{max}/P_{max0} = 0.789) \). By blocking the room-light illumination during the drying of the photoactive layer, all parameters maintained approximately the same values as those of the reference cells, resulting in an average PCE of 10.87 ± 0.27% \( (P_{max}/P_{max0} = 0.996) \). The spin-coating process in the dark in air led to a small improvement in the PCE. The photovoltaic parameters of non-fullerene OPVs having the photoactive layer formed and dried in air under dark conditions exhibit a \( J_{SC} \) of 22.6 ± 0.2 mA cm\(^{-2} \), \( V_{OC} \) of 0.672 ± 0.006 V, and FF of 0.716 ± 0.008, resulting in a PCE of 10.88 ± 0.029%, which is comparable with that of the reference cells \( (P_{max}/P_{max0} = 0.997) \). The photovoltaic parameters of the reference PM6:Y6 cells, which were formed and dried in the nitrogen-filled glovebox, exhibit a \( J_{SC} \) of 24.4 ± 0.2 mA cm\(^{-2} \), \( V_{OC} \) of 0.805 ± 0.003 V, and FF of 0.704 ± 0.022, resulting in a PCE of 13.84 ± 0.46%. When the photoactive layer was formed and dried in ambient air with room-light illumination, both \( J_{SC} \) and FF decreased by approximately 6% and 13%, respectively, compared with the reference cells, resulting in a PCE of 11.07 ± 0.72% \( (P_{max}/P_{max0} = 0.800) \). By blocking room-light illumination during the formation and drying of the photoactive layer, the cells exhibit a \( J_{SC} \) of 23.5 ± 0.3 mA cm\(^{-2} \), \( V_{OC} \) of 0.803 ± 0.004 V, and FF of 0.713 ± 0.014, resulting in a PCE of 13.45 ± 0.46%, which is comparable to that of the reference cells \( (P_{max}/P_{max0} = 0.972) \).

The influence of the room-light illumination during the drying process on the OPV performance was further evaluated (figure S2). The photoactive layers were dried in ambient air with and without room-light illumination for different durations, followed by vacuum drying and anode evaporation. Figure 2(c) shows the PCE obtained as a function of drying time. For both drying with room light and in the dark, a linear approximation with a negative slope to the logarithm of drying time is applicable. The absolute slope of the drying process in the dark was much smaller than that of the drying with room light. This shows that the drying of the photoactive layer in air with room light can be an important degradation factor, and this can be minimized by blocking the light. We also evaluated the continuous operational stability of PBDTTT-OFFT:IEICO-4F OPVs formed in the glovebox and ambient air under dark conditions (figure 2(d)).
Figure 2. Performance of OPVs. Current density–voltage curves of (a) PBDTTT-OFT:PC$_{71}$BM, (b) PBDTTT-OFT:IEICO-4F, and (c) PM6:Y6 BHJ cells formed under different conditions: reference BHJ films formed and dried in the nitrogen-filled glovebox (black circles), BHJ films formed and dried in air with room-light illumination (blue rhombuses), BHJ films formed in air with room light and dried in air in the dark (magenta triangles), and BHJ films formed and dried in air in dark conditions (red squares). The drying time was 30 min for all conditions. (d) The drying time dependency in air for PBDTTT-OFT:IEICO-4F OPVs: BHJ films dried in air in the dark (red squares) and those dried in air with room-light illumination (blue rhombuses). Dashed lines represent fitting results. (e) Operational stability of PBDTTT-OFT:IEICO-4F OPVs in air. Normalized PCEs as a function of MPP tracking test time were plotted: reference OPV with BHJ films formed and dried in the nitrogen-filled glovebox (black circles) and OPV with BHJ films formed and dried in ambient air in the dark (red squares).

Table 1. Average photovoltaic parameters based on PBDTTT-OFT:PC$_{71}$BM, PBDTTT-OFT:IEICO-4F, and PM6:Y6 processed under different ambient conditions.

| Photoactive layer | Spin-coat condition | Drying condition | $J_{SC}$ (mA cm$^{-2}$) | $V_{OC}$ (V) | FF | PCE (%) |
|-------------------|---------------------|------------------|------------------------|-------------|----|--------|
| PBDTTT-OFT:       | Glovebox            | Glovebox         | 16.1 ± 0.3             | 0.749 ± 0.004 | 0.740 ± 0.006 | 8.92 ± 0.07 |
| PC$_{71}$BM        | Air (Room light)    | Air (Room light) | 21.2 ± 0.1             | 0.481 ± 0.019 | 0.474 ± 0.002 | 4.99 ± 0.05 |
|                   | Air (Room light)    | Air (Dark)       | 15.2 ± 0.2             | 0.712 ± 0.004 | 0.587 ± 0.006 | 6.34 ± 0.13 |
|                   | Air (Dark)          | Air (Dark)       | 15.7 ± 0.3             | 0.705 ± 0.005 | 0.636 ± 0.007 | 7.02 ± 0.19 |
| PBDTTT-OFT:       | Glovebox            | Glovebox         | 22.9 ± 0.2             | 0.674 ± 0.005 | 0.708 ± 0.007 | 10.91 ± 0.23 |
| IEICO-4F          | Air (Room light)    | Air (Room light) | 20.5 ± 0.4             | 0.635 ± 0.006 | 0.642 ± 0.012 | 8.61 ± 0.42 |
|                   | Air (Room light)    | Air (Dark)       | 22.6 ± 0.2             | 0.674 ± 0.005 | 0.713 ± 0.011 | 10.87 ± 0.27 |
|                   | Air (Dark)          | Air (Dark)       | 22.6 ± 0.2             | 0.672 ± 0.006 | 0.716 ± 0.008 | 10.88 ± 0.29 |
| PM6:Y6            | Glovebox            | Glovebox         | 24.4 ± 0.2             | 0.805 ± 0.003 | 0.704 ± 0.022 | 13.84 ± 0.46 |
|                   | Air (Room light)    | Air (Room light) | 23.0 ± 0.4             | 0.785 ± 0.006 | 0.613 ± 0.027 | 11.07 ± 0.72 |
|                   | Air (Dark)          | Air (Dark)       | 23.5 ± 0.3             | 0.803 ± 0.004 | 0.713 ± 0.014 | 13.45 ± 0.46 |

The PCE change obtained from the maximum power point (MPP) tracking shows that the drying condition has a negligible effect on the operation stability.

The EQE spectra of these devices were compared to understand the mechanism of degradation caused by room-light illumination during the drying of the photoactive layer film. The fullerene acceptor cells show a largely decreased EQE within the measured wavelengths ranging from 300 to 1000 nm (figure 3(a)). Based on the EQE curves normalized by the maximum value of each condition, it can be observed that the decrease in EQE is more noticeable for wavelengths ranging from 400 to 600 nm (figure S3(a)). According to the absorption spectra of the active layers, PC$_{71}$BM mainly covers the absorption spectra ranging from 400 to 600 nm (figure S3(c)) [31]. This implies that the exciton diffusion efficiency in the PC$_{71}$BM domain becomes poor for the films dried in air with room light. It can be interpreted that the domain size of PC$_{71}$BM becomes...
larger when the photoactive layer films were dried under room-light illumination; therefore, the excitons cannot reach the donor/acceptor interface. In the case of the PBDTTT-OFT:IEICO-4F acceptor, a minor decrease in EQE for all wavelengths was observed for the cells with the photoactive layer dried in air with room light (figures 3(b) and S3(b)). Conversely, the EQE was almost unchanged when the film was dried under light shielding in air. In addition to the EQE, the absorbance of the active layer was measured. For both PBDTTT-OFT:PC$_{71}$BM and PBDTTT-OFT:IEICO-4F photoactive layers, the drying conditions had a limited influence on the absorption (figures 3(c) and (d)). This implies that the reduction in the EQE is not attributed to the absorption changes of the active layer film.

For both PBDTTT-OFT:PC$_{71}$BM and PBDTTT-OFT:IEICO-4F photoactive layers, the drying conditions have limited influence on the absorption. For fullerene photoactive layers, the possible degradation of the materials was investigated using XPS and UPS (figure S4). The C 1s, O 1s, F 1s, and S 2p spectra were identical between the samples of glovebox/glovebox and air (room light)/air (room light), indicating that light irradiation did not induce oxidation or partial decomposition of molecules. We evaluated the density of states (DOS) of the polymer in the BHJ film using UPS and PYS. The results are shown in figure S5. The secondary electron cut-off energies of these samples were almost identical (figure S5(a)); no surface dipoles were induced by the degradation. The DOS near the highest occupied molecular orbital (HOMO) of these samples was also the same (figure S5(b)), indicating that degradation did not cause unexpected charge
doping of the polymer. The gap states were evaluated using PYS following a previous method \[32\]. The HOMO edges of these samples had a Gaussian shape, and no obvious gap states were observed (figure S5(c)). These photoelectron spectroscopies strongly suggest that there was no material degradation by light irradiation.

We also compared the performance of OPVs obtained from photoactive layer solutions prepared under different environmental conditions. The presence of air and room light during the preparation of the photoactive layer solution had a negligible effect on the photovoltaic performance (figure S6). The influence of humidity in the drying process on the device performance was also studied, in which the photoactive layer was dried in air under dark conditions for 30 min at a constant temperature of 25 °C and relative humidities of 30%, 60%, and 90% RH. The OPV performance was almost unchanged for the three humidity conditions (figure S7). However, this insensitivity to humidity is inconsistent with the results from a previous study \[15\], in which both FF and \(V_{OC}\) degraded when the photoactive layer with PCBM was formed under high humidity conditions. Our results differ probably because the previous study did not consider the effect of room light.

Surface imaging using AFM for both the height and phase modes revealed that fullerene cells show topological differences under different formation/drying conditions. The air formation and drying led to a small increase in the dark region in the height image, and the grain boundaries became blurred (figures 4(a) and (b)). More notably, the phase images showed that the width of the mesh-like network covering each domain increased when the active layer was formed in ambient air with room light. The brighter region in the phase mode exhibits softer and/or higher adsorption surfaces; therefore, the mesh-like network implies an aggregated polymer region. It is reasonable to consider that the donor or acceptor aggregates during the drying process in ambient air with room light. By contrast, the PBDTTT-OFT:IEICO-4F photoactive layers did not exhibit clear differences in the AFM images (figures 4(c) and (d)).

A series of experimental results suggested that the coexistence of air and room light during the transformation of the photoactive layer from a liquid to a solid film leads to the phase separation of the donor polymer and acceptor. Aggregation of fullerene acceptors is known to occur especially in photoactive layers with additives to enhance the solubility \[33\]. Furthermore, the degradation of the fabricated fullerene OPVs was accelerated by ultraviolet light illumination \[27, 34\]. Conversely, IEICO-4F is a highly hypo-miscible system with poly[4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b;4,5-b']dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluorothieno[3,4-b] thiophene-)-2-carboxylate-2,6-diyl)] (PTB7-Th or PBDTTT-EFT). Such a system can suppress both de-mixing and crystallization, leading to the long-term stability of OPVs. The donor polymer PBDTTT-OFT used in this study has a similar chemical structure and a superior thermal stability to PTB7-Th \[35\], insensitivity to the drying conditions can be achieved. According to the comparison parameters summarized in table 1, the \(V_{OC}\) of fullerene OPVs shows a larger change under different active layer formation conditions than non-fullerene cells. The lowest unoccupied molecular orbital
of fullerene acceptors is sensitive to their aggregation conditions in solid states \cite{36}. The change in $V_{OC}$ under different drying conditions also supports the morphological changes in the active layers.

Finally, the slot-die coating process was applied to the fullerene photoactive layer films (figure 5). The coating process was conducted in ambient air under dark conditions, and the obtained film was immediately dried in a vacuum chamber. The obtained photovoltaic parameters are $J_{SC}$ of 16.3 ± 0.2 mA cm$^{-2}$, $V_{OC}$ of 0.745 V, and FF of 0.722, resulting in a PCE of 8.75 ± 0.3%, which is almost comparable to that of reference cells having a spin-coated photoactive layer formed in the glovebox (table S4). This confirms that the roll-to-roll compatible fabrication process in ambient air can be fully utilized to achieve comparable performance to that of the controlled formation and drying of photoactive layer films.

4. Conclusion

In this study, we systematically investigated how the coexistence of air and room light during the formation of the photoactive layer affects the OPV performance. Compared to the fabricated devices that have completely dried photoactive layer films, performance deterioration in response to weak room light is much more rapid during the liquid–solid phase change. Weak room-light illumination, which has received less attention in performance studies, is an important degradation parameter during the drying of photoactive layer films. Based on these findings, we demonstrated that air-processed OPVs achieve comparable performance to that of OPVs formed in a nitrogen-filled glovebox by eliminating light during the process. The strong effects of both ambient air and weak light illumination during formation/drying are confirmed for both fullerene and non-fullerene BHJ films, and it was also confirmed that the air stability of the BHJ film is another important parameter for decreasing the degradation speed during the formation/drying process of photoactive layers. This suggests that other BHJ films can also be formed in ambient air under dark conditions if they are not extremely unstable in ambient air. By combining this technology with an air-stable photoactive layer and other materials, roll-to-roll manufacturing in ambient air can be fully applied for the fabrication of large-area and high-efficiency OPVs.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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ORCID iDs

Kenjiro Fukuda  https://orcid.org/0000-0001-8015-5819
References

[1] Meng X et al 2019 A general approach for lab-to-manufacturing translation on flexible organic solar cells Adv. Mater. 31 1903649
[2] Guo J and Min J 2019 A cost analysis of fully solution-processed PTO-free organic solar cells Adv. Energy Mater. 9 1802521
[3] Cui Y et al 2020 Single-junction organic photovoltaic cells with approaching 18% efficiency Adv. Mater. 32 19080205
[4] Sun L et al 2020 Flexible all-solution-processed organic solar cells with high-performance nonfullerene active layers Adv. Mater. 32 1907840
[5] Dong S, Zhang K, Xie B, Xiao J, Yip H L, Yan H, Huang F and Cao Y 2019 High-performance large-area organic solar cells enabled by sequential bilayer processing via nonhalogenated solvents Adv. Energy Mater. 9 1802832
[6] Tsai C Y et al 2020 Large area organic photovoltaic modules fabricated on a 30 cm by 20 cm substrate with a power conversion efficiency of 9.5% Sol. Energy Mater. Sol. Cells 218 110762
[7] Chang Y M, Liao C Y, Lee C C, Lin S Y, Teng N W and Tan P H S 2019 All solution and ambient processable organic photovoltaic modules fabricated by slot-die coating and achieved a certified 7.56% power conversion efficiency Sol. Energy Mater. Sol. Cells 202 110064
[8] Burlingame Q, Ball M and Loo Y L 2020 It’s time to focus on organic solar cell stability Nat. Energy 5 947–9
[9] Wang K, Li Y and Li Y 2020 Challenges to the stability of active layer materials in organic solar cells Macromol. Rapid Commun. 41 1900437
[10] Wang Y, Lee J, Hou X, Labanti C, Yan J, Mazzolini E, Parhar A, Nelson J, Kim J and Li Z 2021 Recent progress and challenges toward highly stable nonfullerene acceptor-based organic solar cells Adv. Energy Mater. 11 2003002
[11] Duan L and Uddin A 2020 Progress in flexible stability of organic solar cells Adv. Sci. 7 1903259
[12] Speller E M et al 2019 From fullerene acceptors to non-fullerene acceptors: prospects and challenges in the stability of organic solar cells J. Mater. Chem. A 7 23361–77
[13] Liu Z, Li J and Yan F 2013 Package-free flexible organic solar cells Adv. Funct. Mater. 23 1251209
[14] Zheng Z, He E, Lu Y, Yin Y, Pang X, Guo F, Gao S, Zhao L and Zhang Y 2021 Benzo[1,2-b:4,5-b’]-difuran polymer-based non-fullerene organic solar cells: the roles of non-fullerene acceptors and molybdenum oxide on their ambient stabilities and processabilities ACS Appl. Mater. Interfaces 13 15458–58
[15] Xu Y, Yuan J, Zhou S, Seifrid M, Ying L, Li B, Huang F, Bazan G C and Ma W 2019 Ambient processable and stable all-organic polymer solar cells Adv. Funct. Mater. 29 1808074
[16] He Y, Heumüller T, Liu W, Feng G, Classen A, Du X, Liu C, Li W, Li N and Brabec C J 2021 Evidencing excellent thermal- and photostability for single-component organic solar cells with inherently built-in microstructure Adv. Energy Mater. 9 1900409
[17] Yang W et al 2020 Simultaneous enhanced efficiency and thermal stability in organic solar cells from a polymer acceptor additive Nat. Commun. 11 1218
[18] An Q, Zhang F, Gao W, Sun Q, Zhang M, Yang C and Zhang J 2018 High-efficiency and air stable fullerene-free ternary organic solar cells Nano Energy 45 177–83
[19] Xu, X, Xiao J, Zhang G, Wei L, Jiao X, Yip H L and Cao Y 2020 Interface-enhanced organic solar cells with extrapolated T80 lifetimes of over 20 years Sci. Bull. 65 208–16
[20] Wes A, Kumar R, Butcher J F, Lami V, Paulus F, Bakulin A A and Yanynzof Y 2020 Energy transfer to a stable donor suppresses degradation in organic solar cells Adv. Funct. Mater. 30 1907432
[21] Han Y et al 2021 An efficiency of 16.46% and a T 80 lifetime of over 4000 h for the PM6:Y6 inverted organic solar cells enabled by surface acid treatment of the zinc oxide electron transporting layer ACS Appl. Mater. Interfaces 13 17869–81
[22] Liu T, Burlingame Q C, Sorli J C, Ball M L, Cheng G, Yao N and Loo Y 2021 The effects of chromophore halogenation on the stability of UV-absorbing organic solar cells Adv. Energy Mater. 11 2100225
[23] Hu L, Jiang Y, Sun L, Xie C, Qin F, Wang W and Zhou Y 2021 Significant enhancement of illumination stability of nonfullerene organic solar cells via an aqueous polyethyleneimine modification J. Phys. Chem. Lett. 12 2067–14
[24] Burlingame Q, Huang X, Liu X, Jeong C, Coburn C and Forrest S R 2019 Intrinsically stable organic solar cells under high-intensity illumination Nature 573 394–7
[25] Baran D et al 2017 Reducing the efficiency-stability-cost gap of organic photovoltaics with highly efficient and stable small molecule acceptor ternary solar cells Nat. Mater. 16 363–9
[26] Gasparini N, Wadsworth A, Moser M, Baran D, McCulloch I and Brabec C J 2018 The physics of small molecule acceptors for efficient and stable bulk heterojunction solar cells Adv. Energy Mater. 8 1703298
[27] Ghasemi M et al 2021 A molecular interaction–diffusion framework for predicting organic solar cell stability Nat. Mater. 20 523–32
[28] Li P, Mainville M, Zhang Y, Leclerc M, Sun B, Izquierdo R and Ma D 2019 Air-processed, stable organic solar cells with high power conversion efficiency of 7.41% Small 15 1804671
[29] Guo Y, Li Y, Awartani O, Zhao J, Han H, Ade H, Zhao D and Yan H 2016 A vinylene-bridged perylene-diimide-based polymeric acceptor enabling efficient all-polymer solar cells processed under ambient conditions Adv. Mater. 28 8483–9
[30] Fan X et al 2020 Vacuum-free, all-solution, and all-air processed organic photovoltaics with 11% improved efficiency and stable small molecule acceptor ternary solar cells Sol. RRL 4 1900543
[31] Huang W, Jiang Z, Fukuda K, Jiao X, McNell C R, Yokota T and Someya T 2020 Efficient and mechanically robust ultraflexible organic solar cells based on mixed acceptors Joule 4 128–41
[32] Nakano K, Kaji Y and Tajima K 2021 Highly sensitive evaluation of density of states in molecular semiconductors by photoelectron yield spectroscopy in air ACS Appl. Mater. Interfaces 13 28574–82
[33] Pearson A J, Hopkinson P E, Goudere E, Domanski K, Abdul-Jalebi M and Greenham N C 2016 Critical light instability in CB/DIO processed PBDTTTEFT:PC71BM organic photovoltaic devices Org. Electron. 30 225–36
[34] Liu Q, Touzert J, Liu F, Mantilla-Perez P, Bajo M M, Russell T P and Martorell J 2017 Circumventing UV light induced nanomorphology disorder to achieve long lifetime PB7:Th pCBM-based solar cells Adv. Energy Mater. 7 1701201
[35] Xu X et al 2018 Thermally stable, highly efficient, ultraflexible organic photovoltaics Proc. Natl Acad. Sci. 115 4589–94
[36] Zhong Y, Irawa S, Hashimoto K, Tajima K, Koganzewa T and Yoshida H 2015 Crystallization-induced energy level change of [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) film: impact of electronic polarization energy J. Phys. Chem. C 119 23–28