

## Research Article

# Investigation on the Effects of Additive on Performance and Photostability of PCDTBT:PC<sub>71</sub>BM Solar Cells

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In this work, the effect of DIM on the PCE and photostability of PCDTBT:PC<sub>71</sub>BM PSCs was investigated. DIM is an effective additive in a BHJ PCDTBT:PC<sub>71</sub>BM solar cell since it fulfills the requirement of a selective PC<sub>71</sub>BM dissolution. PCE of the device based on PCDTBT:PC<sub>71</sub>BM processed with DIM is higher than that of the reference device. In terms of the device stability, the PSCs processed with DIM showed poor stability at longer light exposure time. For the device without DIM especially as the light exposure time was increased, the device stability was better because the PCDTBT could be shielded from air by an aggregated PC<sub>71</sub>BM layer. For the PCDTBT:PC<sub>71</sub>BM device processed with DIM, the results obtained from *J-V* measurement indicates that it has a lower recombination rate. The result from IS measurement shows that for pristine PCDTBT:PC<sub>71</sub>BM devices with 3% DIM, the active layer resistance is lower compared to the device without DIM. However, after irradiating the device for 5 hr, the resistance of the device processed with DIM is higher and it is consistent with decreased PCE of the aged device.

## 1. Introduction

In a polymer solar cell (PSC), morphology of active layers plays a decisive role in determining power conversion efficiency because charge carrier generation, recombination, and transport are all affected by morphology of the active layers formed after spin casting [1–8]. In PSCs, excitons are dissociated into free electrons and holes at the interface between the donor polymer and the acceptor fullerene [9]. To get reasonable PCE, the electrons and holes which are formed from dissociated excitons must be transported and should reach the appropriate extracting electrodes, and this requires bicontinuous paths of donor and acceptor phases. Hence, the optimum morphology of the active layer for PSCs is a trade-off between charge carrier generation and transport to the corresponding electrodes. The problem is that the ideal

morphology of the active layers which strongly depends on the solubility and miscibility of the donor polymer and acceptor fullerenes cannot be formed during spin coating of the active layer. To alleviate the problem and to improve power conversion efficiency (PCE) of PSCs, it is necessary to tune the morphology of the active layers and the following treatments are in use by researchers working in the field. They are thermal annealing, using mixed solvents, and adding suitable additives to host solvent [1, 2, 10–12].

For efficient PSCs, the BHJ donor:acceptor domain length scale of  $\leq 10$  nm with good polymer-fullerene miscibility is highly required. However, literature reports tell us that PC<sub>71</sub>BM aggregate easily forms a large domain size of  $\sim 100$ – $200$  nm diameter [1, 13, 14]. In order to solve the problem of the aggregation of PC<sub>71</sub>BM in polymer:fullerene systems, additives, especially di(R)alkanes with various

functional groups (R), have been added to the BHJ blend solution [15], and they resulted in the significant increase of PCE. In literatures related to PSCs, the use of additives for tuning the morphology of active layers is very common and resulted in improvement of PCEs [1, 16]. It is becoming an attractive method for morphology control.

The solvent additive diiodomethane (DIM) is a commonly used additive, and the use of it has enhanced PCE in PSCs based on different polymers [17]. As observed in our laboratory, the addition of 3% of DIM as processing additives to PCDTBT:PC<sub>71</sub>BM in 1,2-dichlorobenzene (DCB) has improved the power conversion efficiency. PCDTBT is insoluble in DIM while PC<sub>71</sub>BM is soluble. The reason for the better solubility of PC<sub>71</sub>BM in the presence of DIM is that the iodine atom bears a partial negative charge and PC<sub>71</sub>BM is electrodeficient which results in strong interactions with each other [18]. Therefore, when DIM is mixed with the main solvent, it will increase the solubility of PC<sub>71</sub>BM, and this results in optimal mixing of PCDTBT and PC<sub>71</sub>BM and better morphology when the film of PCDTBT:PC<sub>71</sub>BM is formed by spin casting. There is no question that the optimal mixing will give improved PCE compared to a device processed without DIM.

However, little attention is given about the consequence of processing additives on the working lifetime of a real device. Therefore, the main objective of this study is to reveal the effect of additive on the performance and working lifetime of PSC aged by light exposure. In order to identify the effect of DIM on performance and stability of PCDTBT:PC<sub>71</sub>BM-based solar cells, we have fabricated the real device without DIM and 3% DIM and studied the *J-V* characteristics under light irradiation. We also used impedance spectroscopy and UV-visible spectroscopy to find out the effect of DIM on the photostability of the PCDTBT:PC<sub>71</sub>BM-based device.

## 2. Experimental Details

**2.1. Materials and Solutions.** The donor polymer poly[N-9'-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) (average Mw  $2.0 \times 10^4$ - $1.0 \times 10^5$ ) used in this work was obtained from Sigma-Aldrich. The fullerene acceptor [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) >99% purity, mixture of isomers, were obtained from Sigma-Aldrich. All chemicals were used as received. The hole transporting polymer PEDOT:PSS was obtained from Sigma-Aldrich. 1,2-Dichlorobenzene (Riedel-de Haen) was used as host solvent.

**2.2. Device Fabrication and Characterization.** For ITO cleaning and PEDOT:PSS spin coating, we used our earlier procedure exactly, and the detail of the procedure is given in Endale et al. [19]. Prior to device fabrication, a solution consisting of PCDTBT:PC<sub>71</sub>BM in the blend ratio of 1:4 (*w/w*%) and blend concentration of 22.5 mg/mL in 1,2-dichlorobenzene was stirred for 36 hr. PCDTBT:PC<sub>71</sub>BM solution was spin-casted onto a PEDOT:PSS-coated substrate at 1400 rpm for 54 s. Finally, through a shadow mask 100 nm thick, Al electrodes were vacuum evaporated using

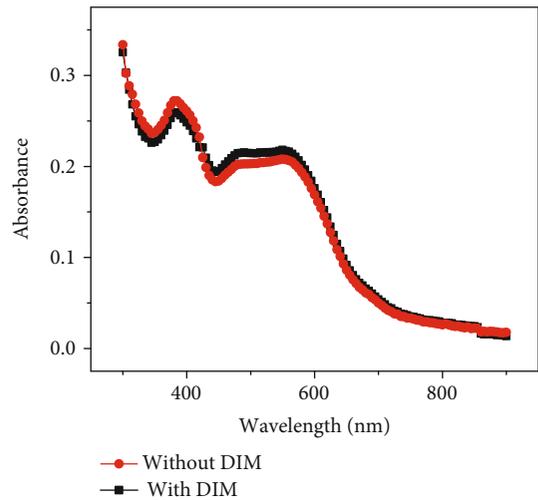


FIGURE 1: UV-visible absorption spectra of PCDTBT:PC<sub>71</sub>BM blend films prepared with and without DIM.

a thermal evaporator (EDWARDS 306) at a pressure of approximately  $4 \times 10^{-6}$  Torr.

To characterize the polymer solar cell, the current-voltage characteristics were measured by using an electrochemical analyzer (Model CHI600A) under white light illumination of  $100 \text{ mW/cm}^2$  from a 150 W xenon lamp of Oriol-type light source (Model 68830). All device preparation and characterization processes were done in open air. For degradation measurements in ambient air, the samples were kept in an open sample holder, exposed to white light illumination of intensity  $100 \text{ mW/cm}^2$ . The photovoltaic cell characteristics PCE,  $J_{sc}$ ,  $V_{oc}$ , and FF were measured at different irradiation time. All devices were not sealed. UV-visible absorption spectra were measured by a UV-Vis Spectrometer Perkin Elmer Lambda 950 UV/VIS/NIR spectrometer from the 300 to 900 nm wavelength range. For UV-visible measurement, blends were spin-coated onto glass substrates using the same conditions as those of the devices.

## 3. Results and Discussion

**3.1. UV-Visible Absorbance Measurement.** Figure 1 shows UV-visible absorbance spectra of PCDTBT:PC<sub>71</sub>BM film with 3% and without DIM. As we can see from Figure 1, there is no much difference between the UV-visible absorbance spectra of PCDTBT:PC<sub>71</sub>BM films with and without DIM. However, we can see a little lower absorption intensity at the high energy region and a little higher absorption intensity at the low energy region for the film processed with DIM.

Figure 2 shows the variation of normalized UV-visible absorbance of BHJ films of PCDTBT:PC<sub>71</sub>BM processed with and without DIM. The observation indicates that with increasing light exposure time, the BHJ films of PCDTBT:PC<sub>71</sub>BM processed with DIM have lower stability or higher rate of degradation compared to the BHJ film without DIM. As a consequence, it is very important to study the effect of DIM on the stability of the PCDTBT:PC<sub>71</sub>BM-based device under light exposure in ambient air. The higher rate of photodegradation of the film of PCDTBT:PC<sub>71</sub>BM

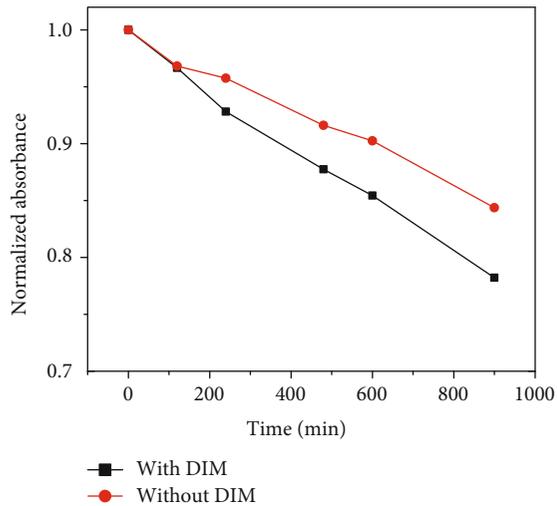


FIGURE 2: Normalized UV-visible absorbance of PCDTBT:PC<sub>71</sub>BM processed with and without DIM as a function of irradiation (100 mW/cm<sup>2</sup> light) time at ambient air.

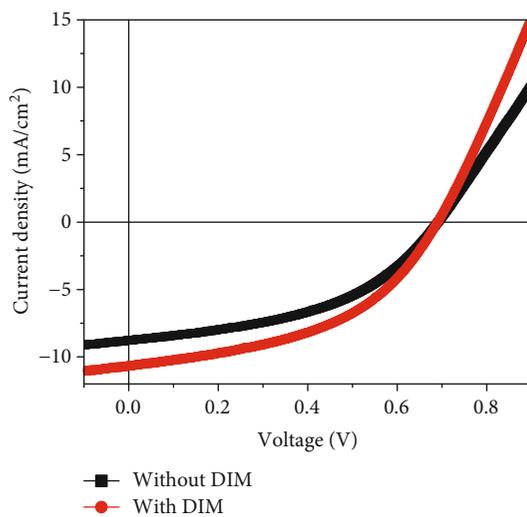


FIGURE 3: Current-voltage characteristics of PCDTBT:PC<sub>71</sub>BM solar cells processed without and with 3% DIM.

with DIM may be explained as follows. Due to solubility of PC<sub>71</sub>BM in DIM, the addition of DIM produces homogeneous morphology between PCDTBT and PC<sub>71</sub>BM. The homogeneous morphology would make more PCDTBT exposed to air, which is more easily degraded by O<sub>2</sub> and H<sub>2</sub>O molecules compared to the BHJ layer without DIM.

**3.2. Current Density-Voltage Characteristics.** The current density-voltage characteristics ( $J$ - $V$ ) of the PCDTBT:PC<sub>71</sub>BM devices processed with 3% and without DIM are shown in Figure 3. The PCDTBT:PC<sub>71</sub>BM solar cell without DIM (reference cell) showed a PCE of 2.77%,  $J_{sc} = 8.8$  mA/cm<sup>2</sup>, FF = 46%,  $V_{oc} = 691$  mV, and  $R_s = 70$  Ω·cm<sup>2</sup> whereas the PCDTBT:PC<sub>71</sub>BM solar cell processed with 3% DIM showed a PCE of 3.42%,  $J_{sc} = 10.65$  mA/cm<sup>2</sup>, FF = 47%,  $V_{oc} = 690$  mV, and  $R_s = 50$  Ω·cm<sup>2</sup>. For the solar cell proc-

essed with 3% DIM, short-circuit current density has increased by 21% and series resistance has reduced by 34%. As the result shows, the PCDTBT:PC<sub>71</sub>BM solar cell processed with 3% DIM has better PCE with improved short-circuit current density and reduced series resistance.

For the solar cell without DIM, the formation of heavily aggregated PC<sub>71</sub>BM results in lower intercalation into PCDTBT domains, thereby lowering the PCDTBT-PC<sub>71</sub>BM interface area and exciton dissociation. However, when DIM is used, it selectively dissolves PC<sub>71</sub>BM aggregates promoting formation of smaller domains and greater PCDTBT-PC<sub>71</sub>BM interpenetration within the film and optimizing the PCDTBT-PC<sub>71</sub>BM interface and which in turn result in higher exciton splitting. The existence of bicontinuous paths for the transport of holes and electrons facilitates charge carrier transport. The improved dissociation of excitons and good charge collection efficiency lead to better power conversion efficiency.

The increased short-circuit current density for the PCDTBT:PC<sub>71</sub>BM device processed with 3% DIM can be explained as follows. DCB is not the best solvent for PC<sub>71</sub>BM. When PC<sub>71</sub>BM is dissolved in DCB, large PC<sub>71</sub>BM grains are formed [3, 18]. When PSC is fabricated using PC<sub>71</sub>BM as the acceptor, the large PC<sub>71</sub>BM grains could hinder the exciton migration to the donor/acceptor (D/A) interface, thereby limiting the charge separation in the BHJ layer [20]. The addition of solvent processing additive affects the size of fullerene and enhances bicontinuous channel formation within the BHJ composite resulting in higher  $J_{sc}$  [16, 21–24]. When DIM is mixed with the DCB, PC<sub>71</sub>BM grain boundary size is reduced in the BHJ active layer. As PC<sub>71</sub>BM aggregates are diminished, there will be a higher interface area between PCDTBT and PC<sub>71</sub>BM and better bicontinuous channels for charge carrier transport, and this results in higher  $J_{sc}$ . Therefore, the addition of DIM is responsible for higher  $J_{sc}$  relative to the device processed without DIM.

When DIM is added, the reduced value of  $R_s$  indicates that the morphology induced by DIM made charge carrier transport easy in the active layer of PCDTBT:PC<sub>71</sub>BM. Therefore, improved  $J_{sc}$  combined with decreased  $R_s$  mean that the morphology of the active layer processed with 3% DIM permitted more efficient charge carrier generation and transport to the electrodes compared to the device processed without DIM.

**3.3. Effect of DIM on Charge Carrier Generation.** In case of a weak voltage dependence of the photocurrent density and negligible nongeminate recombination at high reverse bias, information about charge carrier generation can be obtained directly from the  $J$ - $V$  curve. The solar cell total current density ( $J$ ) can be expressed as a combination of the dark diode current density ( $J_{dark}$ ) and the photocurrent density ( $J_{ph}$ ) [3, 25]:

$$J = J_{dark} - J_{ph}, \quad (1)$$

$$J(V) = J_{dark}(V) - qLG(I)P_C(I, V), \quad (2)$$

where  $q$  is the elementary charge,  $L$  is the thickness of the active layer,  $G(I)$  is the generation rate of bound electron-hole pairs per unit volume, and  $P_C(I, V)$  is the charge collection probability [3, 26].

From Equations (1) and (2), photocurrent density ( $J_{ph}$ ) of the polymer solar cell is given by the following equation:

$$J_{ph} = qLG(I)P_C(I, V). \quad (3)$$

When sufficiently large reverse bias is applied,  $P_C(I, V) = 1$  since the internal field is large enough to sweep out all the charge carriers to the respective electrodes (nongeminate recombination can be neglected) and Equation (3) becomes

$$J_{sat} = qLG. \quad (4)$$

From Equation (4), the generation rate is given by

$$G = \frac{J_{sat}}{qL}. \quad (5)$$

From the measured saturated current density at  $-1.0V$  ( $J_{sat}$ ), the generation rates for the PCDTBT:PC<sub>71</sub>BM solar cells processed without and with 3% DIM are calculated. For the device processed with 3% DIM,  $G = 1.0 \times 10^{22} \text{ cm}^{-3} \text{ s}^{-1}$ , whereas for the device processed without 3% DIM,  $G = 1.3 \times 10^{21} \text{ cm}^{-3} \text{ s}^{-1}$ . A lower generation rate for devices without 3% DIM is in agreement with a large domain phase separation in PCDTBT:PC<sub>71</sub>BM blend because of lower solubility of PC<sub>71</sub>BM in DCB. When the interface area is lower, excitons undergo geminate recombination because they may not find the interface area for dissociation in their lifetime. Excitons not able to find the interface area undergo geminate recombination. However, when there is a higher interface area, the excitons can get the interface area within their diffusion length and lifetime and get dissociated. The higher generation rate for the device processed with 3% DIM indicates that the effect of DIM is to suppress the formation of the large fullerene clusters, leading to a smaller length scale of the polymer and fullerene phases and an increase of the effective interfacial area for efficient exciton splitting. The results obtained from our measurements are consistent with experimental results reported on the effect of additives by different groups [13, 14, 27].

In order to understand the origin of higher performance of the PCDTBT:PC<sub>71</sub>BM solar cell with 3% DIM, we have investigated the recombination mechanisms in the PCDTBT:PC<sub>71</sub>BM solar cell with and without 3% DIM under different illumination intensities. Since exciton quenching of the bulk heterojunction is strongly related to the charge recombination, investigation of the light intensity dependence of the  $J$ - $V$  characteristics helps to probe the dominant recombination mechanism that affects device performance. Therefore, recombination kinetics can be illustrated by the investigation of variations of  $J_{sc}$  as the function of the light intensity. Figure 4 presents the light intensity dependence of  $J_{sc}$  for the PCDTBT:PC<sub>71</sub>BM solar cell processed with and without DIM. Figure 4 reveals that

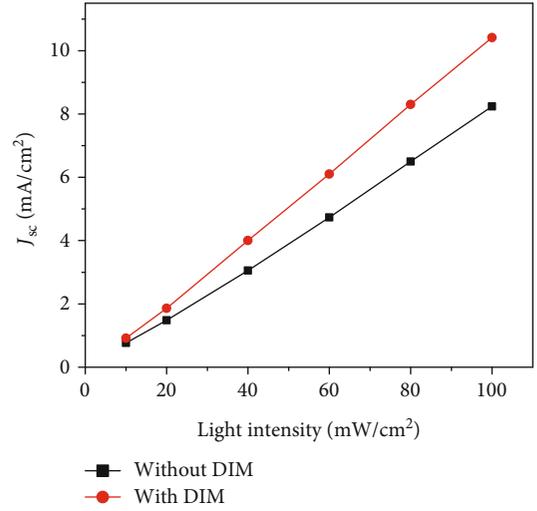


FIGURE 4:  $J_{sc}$  versus light intensity for the PCDTBT:PC<sub>71</sub>BM solar cell processed without and with DIM.

for the PCDTBT:PC<sub>71</sub>BM solar cell without DIM,  $J_{sc}$  has slight nonlinear dependence on light intensity. However, the PCDTBT:PC<sub>71</sub>BM solar cell with DIM shows good linear dependence on light intensity. The dependence of  $J_{sc}$  on light intensity is given by the power law [3, 28]:

$$J_{sc} \propto I^\beta, \quad (6)$$

where  $I$  is the light intensity. In principle, the observance of  $\beta = 1$  indicates that all the charge carriers have been removed prior to recombination (i.e., bimolecular recombination is negligible (maximum carrier sweep out)) [3, 25, 29]. Deviation from  $\beta = 1$  is attributed to nongeminate recombination [24] and space charge effects [30, 31]. For the PCDTBT:PC<sub>71</sub>BM solar cell without DIM,  $\beta = 0.6$  corresponding to the power law fit of Equation (6). However, for the PCDTBT:PC<sub>71</sub>BM solar cell with DIM,  $\beta = 0.8$  is observed. Based on the obtained values of  $\beta$ , it is possible to expect higher nongeminate recombination in the device processed without DIM. For the device processed with DIM,  $\beta$  value more close to unity undoubtedly shows that bimolecular/nongeminate recombination is appreciably suppressed relative to the device without DIM. That is, charge carrier sweep out is the most effective in the device where DIM was used. The obtained results prove that 3% DIM can be used to enhance charge carrier generation and transport which result in improved PCE [32].

**3.4. Effect of DIM on the Stability of PCDTBT:PC<sub>71</sub>BM Solar Cells.** In order to study the effect of DIM on the stability of PCDTBT:PC<sub>71</sub>BM solar cells exposed to continuous illumination of  $100 \text{ mW/cm}^2$  light, solar cells processed with and without DIM were fabricated in open air and their PCEs were compared. The PCDTBT:PC<sub>71</sub>BM solar cells processed without and with 3% DIM were illuminated with  $100 \text{ mW/cm}^2$  light while taking the  $J$ - $V$  measurements, and the  $J$ - $V$  curve is given in Figure 5. Qualitative analysis of Figure 5 implies that for both kinds of devices, PCE,  $J_{sc}$ , FF, and  $V_{oc}$  decreased

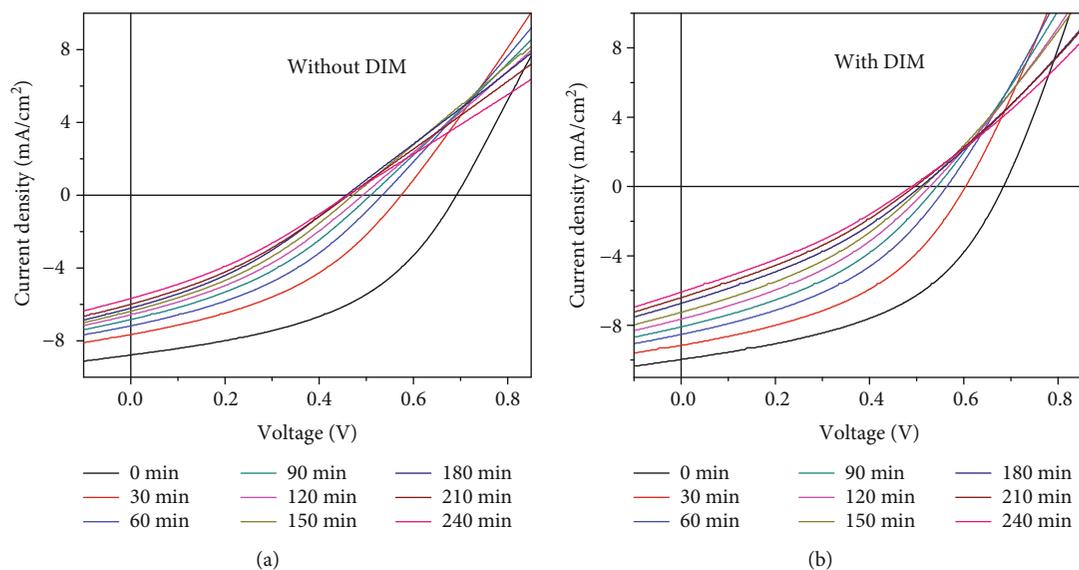


FIGURE 5: The  $J$ - $V$  curves of the PCDTBT:PC<sub>71</sub>BM solar cell processed without (a) and with (b) 3% DIM as a function of light irradiation ( $100 \text{ mW/cm}^2$ ) time at ambient air.

with increasing irradiation time and this can be related with bleaching or/and the degradation of the morphology, the active layer-electrode contact, oxidation of metal electrode, etc. Bleaching of the polymer results in lower absorption of photons. When morphology degrades, it results in an increased rate of exciton and free charge carrier recombination, decreased charge carrier transport to the electrodes, and reduced PCE of the device.

The normalized values of PCE are given in Figure 6. As shown in Figure 6, there is a relatively lower rate of decrease of PCE for the device processes with 3% DIM compared to the reference device until irradiation time of 210 min. The results demonstrated that the morphology of the PCDTBT:PC<sub>71</sub>BM film is controlled by the addition of 3% DIM and hence improved the stability of the power conversion efficiency of the devices. Under light irradiation, device performance stability in the PCDTBT:PC<sub>71</sub>BM film treated with DIM is due to the improved solubility and reduction of aggregation of PC<sub>71</sub>BM in the PCDTBT:PC<sub>71</sub>BM BHJ film which facilitated the efficient exciton dissociation and charge transport to the electrode. In the absence of DIM, aggregation of PC<sub>71</sub>BM already formed due to lower solubility of PC<sub>71</sub>BM continuously grows larger and larger and results in a higher rate of geminate and nongeminate recombinations; however, when there is DIM, it hinders aggregation of PC<sub>71</sub>BM at least for some time.

On the other hand, beyond 210 min, for the device processed with 3% DIM, the performance drops on the same fashion with the reference device indicating that the advantage obtained from DIM begins to fade away with time. The reduction of photovoltaic performance is due to inadequate morphology for the efficient dissociation of excitons, charge transportation, and extraction [16]. The obtained result shows that in the long run at ambient condition and continuous irradiation, the PCDTBT:PC<sub>71</sub>BM solar cell processed with 3% DIM has lower environmental stability.

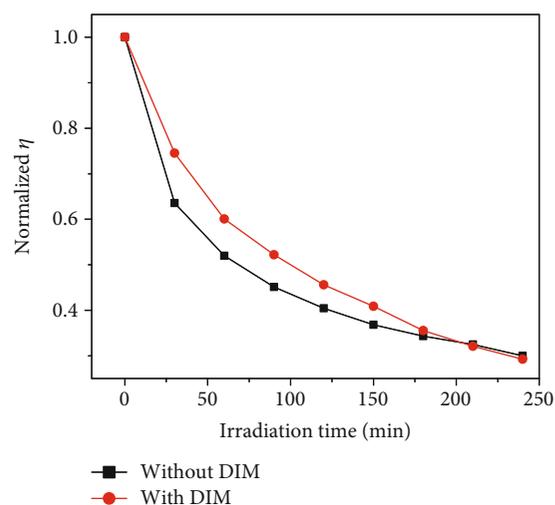


FIGURE 6: Normalized  $\eta$  of the PCDTBT:PC<sub>71</sub>BM solar cell processed without and with 3% DIM as a function of irradiation ( $100 \text{ mW/cm}^2$ ) time at ambient air.

Wang et al. [33] found out that bilayer PSCs show more stable performance than the BHJ PSCs in air condition due to the shielding effect of the PCBM layer. The PTB7 polymer processed with diiodooctane (DIO) showed an increased PTB7 on the film surface because large aggregated PC<sub>71</sub>BM domains dissolved and integrated into PTB7 domains [1]. Because of exposure of the polymer to air, PSCs processed with additives undergo degradation faster than the unprocessed device [34–37]. Based on literature results, it may be the case that the BHJ film of PCDTBT:PC<sub>71</sub>BM processed with DIM shows an increased PCDTBT content on the film surface because large aggregated PC<sub>71</sub>BM domains dissolved and integrated into PCDTBT domains. Consequently, in the long run, the BHJ layer of PCDTBT:PC<sub>71</sub>BM processed with

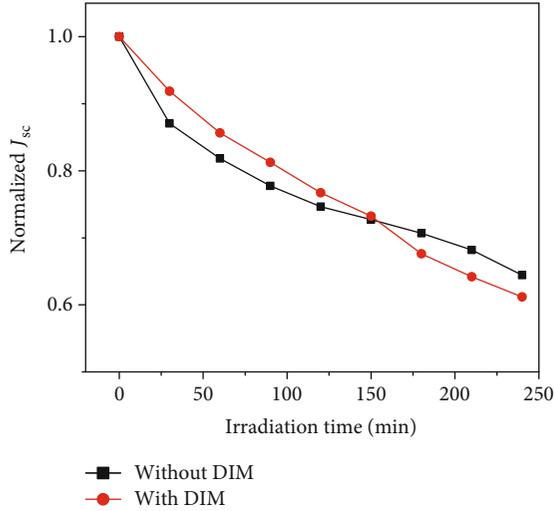


FIGURE 7: Normalized  $J_{sc}$  of the PCDTBT:PC<sub>71</sub>BM solar cell processed without and with 3% DIM as a function of irradiation (100 mW/cm<sup>2</sup>) time at ambient air.

DIM degraded more easily in the air compared to the device without DIM.

The rates of decrease of normalized  $J_{sc}$  for devices with and without DIM are shown in Figure 7. From the time of fabrication until irradiation time of 150 min, the device with DIM had a lower rate of decrease of  $J_{sc}$ ; however, after 150 min, the rate of decay of  $J_{sc}$  had increased in comparison with the device without DIM. The result implies that at ambient condition and continuous irradiation for longer time, the solvent additive DIM contributes for the decrease of  $J_{sc}$  of the solar cell and it has harmful effect on the PCE.

Figure 8 shows measurements of the dark current, solar cell current, dark current minus solar cell current, and dark current minus reverse saturation current of the PCDTBT:PC<sub>71</sub>BM solar cell processed with 3% DIM and illuminated with solar illumination intensity of 40 mW/cm<sup>2</sup> in ambient air. In Figure 8, the dark current minus reverse saturation current ( $J_{sat}$ ) curve is the estimate of the response that the solar cell would have in the absence of any recombination. In Figure 8, the curve of dark current minus reverse saturation current shows that recombination mainly reduces the fill factor and open-circuit voltage of the solar cell.

Figure 9 shows that the FF of both devices processed with and without DIM decreased continuously upon light irradiation. Based on Figure 8, charge carrier recombination is the cause for lower FF measured after light exposure. As Figure 9 shows, until irradiation time of 150 min, the solar cell processed with 3% DIM had a relatively lower rate of reduction in FF compared to the solar cell processes without DIM. However, after irradiation time of 150 min, the solar cell processed with 3% DIM showed continuous increase in the rate of reduction of FF compared to the device without DIM. Again, similar to the case of  $J_{sc}$ , in the long run, the additive DIM has negative effect on the FF of the PCDTBT:PC<sub>71</sub>BM solar cell exposed to light at ambient condition.

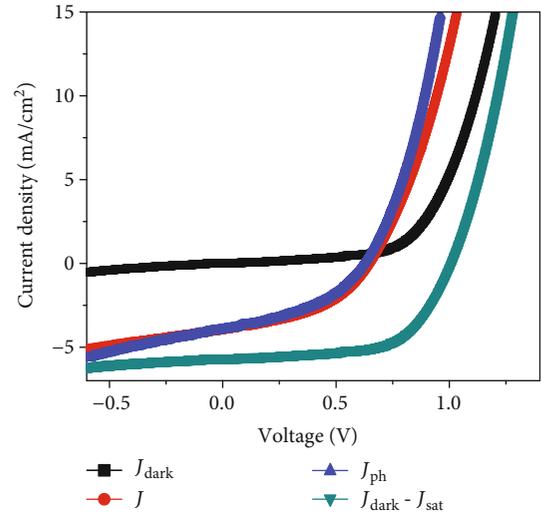


FIGURE 8: Measurements of the dark current, solar cell current, dark current minus solar cell current, and dark current minus reverse saturation current of the PCDTBT:PC<sub>71</sub>BM solar cell processed with 3% DIM and illuminated with solar illumination intensity of 40 mW/cm<sup>2</sup> in ambient air.

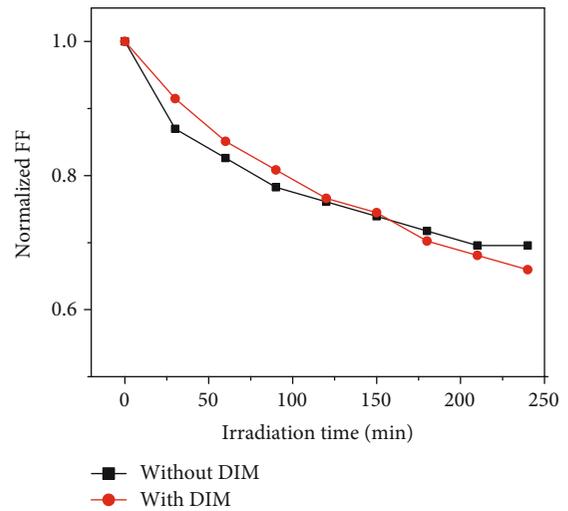


FIGURE 9: Normalized FF of the PCDTBT:PC<sub>71</sub>BM solar cell processed without and with 3% DIM as a function of irradiation (100 mW/cm<sup>2</sup>) time at ambient air.

The rate in reduction of  $V_{oc}$  of the PCDTBT:PC<sub>71</sub>BM solar cell processed without and with 3% DIM as a function of irradiation (100 mW/cm<sup>2</sup>) time at ambient air is given in Figure 10. The results indicate that the devices processed with DIM has a lower rate of reduction compared to the reference device in the study time. However, close examination of the result in Figure 10 (especially the last three values) indicates that after longer exposure time, the device processed with DIM may not have stable  $V_{oc}$  and will give a reduced value.

Figure 11 shows the variation of normalized series resistance for the PCDTBT:PC<sub>71</sub>BM solar cell processed without and with 3% DIM as a function of irradiation (100 mW/cm<sup>2</sup>) time at ambient air. The obtained values reveal that with

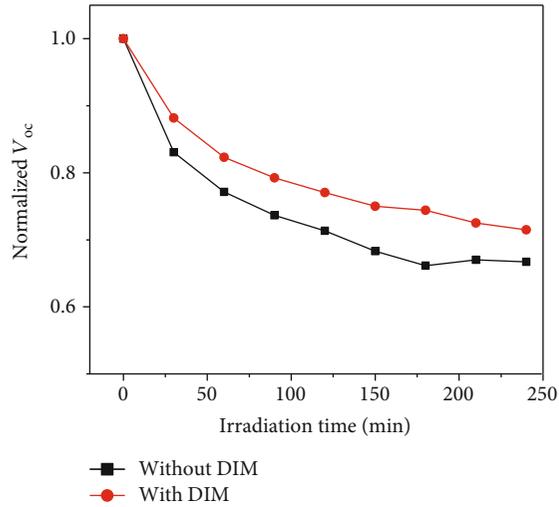


FIGURE 10: Normalized  $V_{oc}$  of the PCDTBT:PC<sub>71</sub>BM solar cell processed without and with 3% DIM as a function of irradiation ( $100 \text{ mW/cm}^2$ ) time at ambient air.

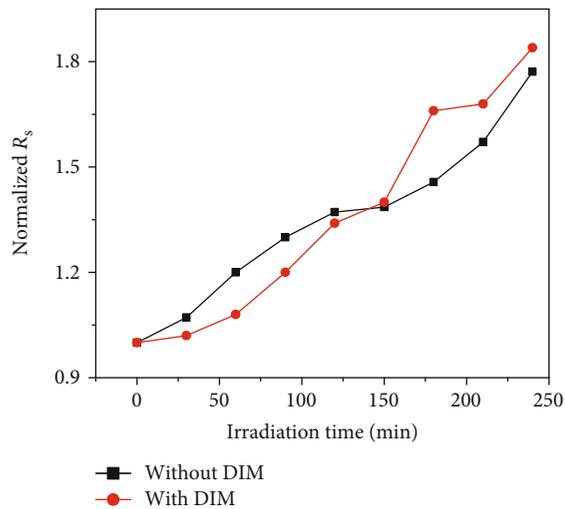


FIGURE 11: Normalized  $R_s$  of the PCDTBT:PC<sub>71</sub>BM solar cell processed without and with 3% DIM as a function of irradiation time at ambient air.

irradiation time, the series resistance of the device with DIM is continuously increasing. The increased  $R_s$  is consistent with the reduction of  $J_{sc}$  after aging the device with light irradiation. The increased  $R_s$  is also the cause for the lower FF of the device processed with DIM.

**3.5. Impedance Analysis.** In PSC, electrical property of the BHJ blend film is dictated by the morphology characteristics. Therefore, making connection between film morphology and electrical properties is very indispensable. Impedance spectroscopy (IS) allows the possibility of making a reasonable cause-effect relation between the morphology of the BHJ and the performance of PCDTBT:PC<sub>71</sub>BM solar cells at different times of irradiation.

As literature shows, IS has been widely used in determining the electric characteristics through simple equivalent

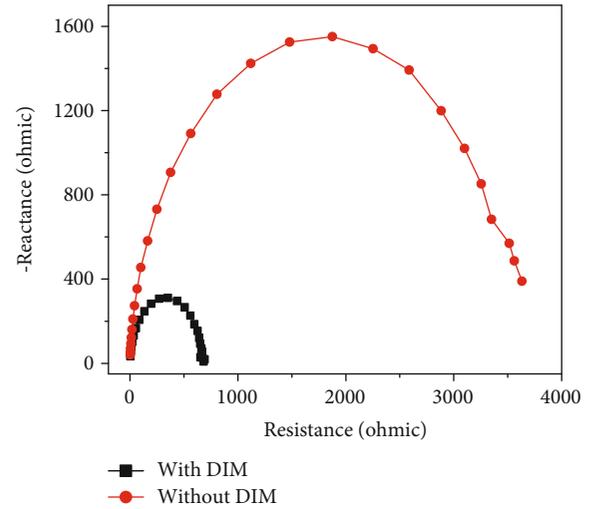


FIGURE 12: Cole-Cole plots of the PCDTBT:PC<sub>71</sub>BM solar cells processed with and without 3% DIM.

lent circuit models in PSCs [38]. The interfaces of the PCDTBT:PC<sub>71</sub>BM solar cells can be considered as simple elements such as resistances and capacitances in circuit models. With the representation of the interfaces and BHJ film as resistances and capacitances, the electrical properties of the PCDTBT:PC<sub>71</sub>BM BHJ layer can be connected to current density-voltage ( $J$ - $V$ ) characteristics of the devices. In PCDTBT:PC<sub>71</sub>BM solar cells, the interface between the PCDTBT and PC<sub>71</sub>BM in the BHJ can directly relate to the morphology of the BHJ, and the morphology of the BHJ directly affects performance of the device. To analyze the relationship between the morphology and the device performance of the solar cell based on PCDTBT:PC<sub>71</sub>BM and with and without 3% DIM under different aging times, we used the IS method.

Let us assume that in the PCDTBT:PC<sub>71</sub>BM solar cell,  $R_{12}$  corresponds to the resistance of the PCDTBT:PC<sub>71</sub>BM active layer and the interface between PEDOT:PSS/PCDTBT:PC<sub>71</sub>BM and PCDTBT:PC<sub>71</sub>BM/Al.  $R_{\infty}$  corresponds to the resistance of the electrodes and wires connected for measurement. Since both PSCs have the same device structure, only the BHJ PCDTBT:PC<sub>71</sub>BM blend is processed under different conditions. Thus,  $R_{\infty}$  inside all the cells can be assumed to be the same. However,  $R_{12}$  can give us information about the resistance which is affected by solvent additives, DIM.

Figure 12 shows the IS results of PCDTBT:PC<sub>71</sub>BM solar cells processed with and without 3% DIM. In Figure 12, the radius of the Cole-Cole plot is higher for the device processed without DIM, and this implies that the resistance of the whole device is higher compared to the device processed with 3% DIM. The pristine PCDTBT:PC<sub>71</sub>BM solar cells processed without 3% DIM show  $R_{12}$  of  $3725 \Omega$ . On the other hand, PCDTBT:PC<sub>71</sub>BM solar cells processed with 3% DIM have much reduced  $R_{12}$  of  $682 \Omega$ . The much lower value of  $R_{12}$  of PCDTBT:PC<sub>71</sub>BM solar cells processed with 3% DIM implies that the thin film morphology of the PCDTBT:PC<sub>71</sub>BM blend was much improved through the

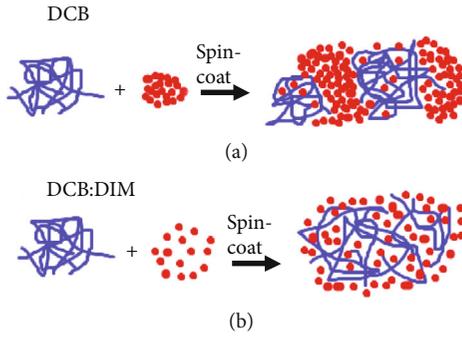


FIGURE 13: Schematic of PCDTBT and PC<sub>71</sub>BM aggregation in (a) DCB and (b) DCB:DIM and the resulting film morphology.

higher interfacial area between PCDTBT and PC<sub>71</sub>BM due to addition of DIM.

The smaller value of  $R_{12}$  for the device treated with DIM indicates a slower charge recombination and a smaller dark current [39, 40]. The smallest  $R_{12}$  value in DIM-treated devices implies that the DIM allows more effective suppression of the recombination of charge carriers in the cells and lower charge transport resistance. The result obtained from IS is consistent with the recombination results previously obtained.

From literatures, we know that mixing additive with polymer:PC<sub>71</sub>BM blend can lead to more favorable morphology of the polymer:PC<sub>71</sub>BM BHJ due to decreasing the size of PC<sub>71</sub>BM and increasing the interface area between the polymer chains and PC<sub>71</sub>BM molecules [18, 41]. The result from the Cole-Cole plot in Figure 12 shows that the resistance decreased after mixing 3% DIM with PCDTBT:PC<sub>71</sub>BM blend. Without DIM, the PC<sub>71</sub>BM aggregates are large and hinder PC<sub>71</sub>BM intercalation into the PCDTBT network during film formation, so large segregated domains with the lower interface area form (Figure 13) and increased the resistance. On the contrary, as shown in Figure 13, when DIM is added, the PC<sub>71</sub>BM aggregates dissolve and the higher interface area between PCDTBT chain and PC<sub>71</sub>BM molecules will be formed, and as a result, the resistance decreases. Based on the general effect of additives and the result of resistance measurement, the sound logical inference is that in addition of DIM the interface area between PCDTBT chains and PC<sub>71</sub>BM molecules should be increased so that the resistance decreases.

Figure 14 is the Cole-Cole plots of the PCDTBT:PC<sub>71</sub>BM solar cells processed with and without 3% DIM of pristine and 5 hr irradiated device. In Figure 14 for both devices, the radius of the Cole-Cole plot increased after irradiating the device for 5 hr at ambient air, which implies that the resistance of the whole device has increased. The cause for increase of  $R_{12}$  after light irradiation is the decrease of the interface area between the PCDTBT and PC<sub>71</sub>BM. As the interface area decreases in PCDTBT:PC<sub>71</sub>BM due to PC<sub>71</sub>BM aggregate formation, the separation of exciton and penetration of carriers in the BHJ layer reduced.

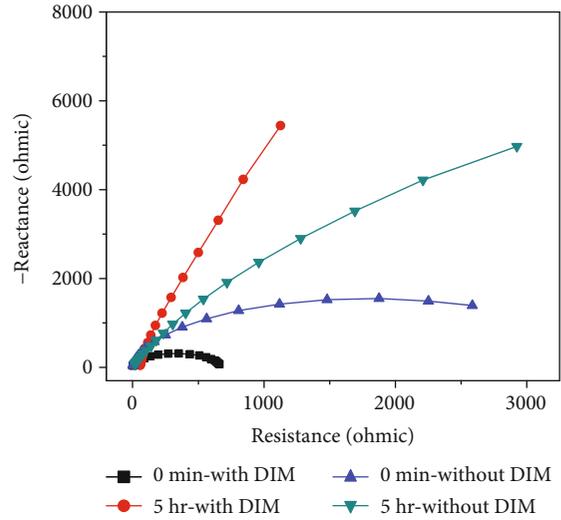


FIGURE 14: Cole-Cole plots of the PCDTBT:PC<sub>71</sub>BM solar cells processed with and without 3% DIM of pristine and 5 hr irradiated device.

#### 4. Conclusions

In this work, the effect of DIM on the PCE and stability of PSCs made of PCDTBT:PC<sub>71</sub>BM was investigated. DIM is an effective additive in the BHJ PCDTBT:PC<sub>71</sub>BM solar cell since it fulfills the requirement of a selective PC<sub>71</sub>BM dissolution. PCE of the device based on PCDTBT:PC<sub>71</sub>BM processed with DIM is higher than the reference device without DIM. The device without DIM has lower short-circuit current density. The reason is that without DIM, the PC<sub>71</sub>BM aggregates are large which hinder PC<sub>71</sub>BM intercalation into the PCDTBT network during film formation, and this creates large, segregated domains of PCDTBT and PC<sub>71</sub>BM. As a result of the reduced interface area, there will be lower exciton dissociation at the interface. However, on DIM addition, the PC<sub>71</sub>BM aggregates dissolve, and this facilitates integration of the PC<sub>71</sub>BM molecules into the PCDTBT system resulting in a greater PCDTBT:PC<sub>71</sub>BM interface area and smaller domains. Because of the higher interface area, there will be a higher rate of exciton dissociation, and this results in higher short-circuit current density.

In terms of the device stability, PSCs processed with DIM showed poor stability at longer light exposure time. For the device without DIM especially as the light exposure time was increased, the device stability was better. The obtained result tells us that using the solvent additive DIM in the PCDTBT:PC<sub>71</sub>BM solar cells not only affects PCE of the device but also affects its working lifetime. Hence, while using DIM to enhance PCE of PCDTBT:PC<sub>71</sub>BM solar cells, it is good to consider the stability of the device. For the PCDTBT:PC<sub>71</sub>BM device processed with DIM, the results obtained from  $J-V$  measurement indicate that it has a lower recombination rate. The result from IS measurement shows that for pristine PCDTBT:PC<sub>71</sub>BM devices with 3% DIM, the active layer resistance is lower compared to the device without DIM. However, after irradiating the device for

5 hr, the resistance of the device processed with DIM is higher, and it is consistent with decreased PCE of the aged device.

### Data Availability

All types of data used to support the findings of this study are available from the corresponding author upon request.

### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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