Nonfullerene Small Molecules-Enabled High-Performance Organic Photovoltaics for Indoor Energy Harvesting

Chihyung Lee, Ahra Yi, Hyo Jung Kim, Minwoo Nam,* and Doo-Hyun Ko*

Organic photovoltaics (OPVs) have attracted considerable attention as a power source of indoor electronic devices for the Internet of Things (IoT). Herein, high-efficiency and stable nonfullerene OPVs for low-intensity indoor applications are demonstrated while discussing the origin of high photovoltaic performance and the design fundamentals in an indoor environment. Nonfullerene OPVs exhibit higher performance over a wide range of light intensities compared with fullerene OPVs, in spite of relatively lower spectral matching with indoor light sources. To understand this discrepancy, advanced morphological analyses for the bulk-heterojunction (BHJ) photoactive layers are proposed, which demonstrate efficient phase-interpenetrating networks of a polymer donor and a nonfullerene acceptor. These clarify a suppression of trap sites in nonfullerene blends as a key factor to alleviate charge recombination, resulting in high photovoltaic operation under indoor environments. Combined with the morphological benefits for the high performance, the superior stability corroborates high practical usage of nonfullerene OPVs in a variety of application areas.

1. Introduction

Organic photovoltaics (OPVs) are of great interest as promising renewable energy sources based on advantages, such as low cost, mechanical flexibility, and transparency. Tremendous efforts have been devoted to the development of OPV materials, rendering great progress in performance and practical viability of OPV technologies over the last decades. The emergence of the nonfullerene acceptors has brought effective means to overcome challenges in OPVs and a rapid increase in photovoltaic performance. For instance, large intrinsic energy losses ($E_{loss}$) in fullerene-based blends were significantly alleviated in nonfullerene-based systems, showing the improved power conversion efficiencies (PCEs) approaching the commercially acceptable level.$^{[1–4]}$

The unique features of OPVs promise great potential for both indoor and outdoor applications, which complement the traditional silicon photovoltaic technologies. In particular, OPVs can play important roles as efficient off-grid energy sources for tens of billions of the Internet of Things (IoT) devices operating in indoor environments.$^{[5–7]}$ The ambient light sources for indoor applications are around 0.1% of the standard solar emission intensity, so operation in dim light is crucial for indoor performance of OPVs. A combination of mid-bandgap polymers and [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{70}$BM) is widely studied active layer components, which match the indoor light illuminance mostly lying in the visible wavelength region between 400 and 700 nm.$^{[8–10]}$ By contrast, state-of-the-art nonfullerene acceptors have received only minor consideration until recently. This is because their bandgap ($E_g$) values are relatively small to match the indoor light spectrum, whereas such low $E_g$ materials play critical roles in securing the harvest of broadband photons under solar irradiation.$^{[4,11–12]}$

Nonfullerene acceptors, however, afford efficient indoor operation due to the advantages involving low $E_{loss}$, high absorption coefficients, and favorable thermal- and photo-stability. More importantly, nonfullerene acceptors offer great synthetic flexibility and, thus, readily tunable molecular energy levels and absorption spectrum, which can render great contributions to the rapid progress in indoor PCEs.$^{[13–16]}$ A number of studies concerning the indoor operation of nonfullerene OPVs have been reported until recently.$^{[13–16]}$ The state-of-the-art OPVs show the PCEs exceeding 20% in indoor environments, involving PM6:IO-4Cl and PM6:Y6-O OPVs with the PCEs of 26.1% and 31.0%, respectively.$^{[16–19]}$ However, the indoor performance of OPVs still lags behind those of other photovoltaic technologies such as perovskite PVs.$^{[20]}$ To meet the requirements raised by indoor applications, it is necessary to further understand the operating principles and find strategies to improve the low light operation of OPVs involving indoor conditions.
Herein, we demonstrate nonfullerene OPVs as a means to achieve efficient and reliable energy harvesting for low-intensity light and indoor applications. Nonfullerene OPVs showed higher performance over the fullerene OPVs for any irradiative conditions involving an indoor environment, in spite of the drawbacks such as lower spectral overlap with the irradiance spectrum of indoor light sources. This suggests high prospects of newly emerging nonfullerene small molecules in diverse photovoltaic applications. Through the novel morphological approaches, we verified effective nanoscale phase separation in a nonfullerene blend system, featuring homogenous distribution and interpenetration of the phase networks. The morphological characteristics of the nonfullerene blend were advantageous in ameliorating charge recombination and voltage loss \((V_{\text{loss}})\) in OPV applications.\(^{[21]}\) In addition, a superior thermal stability can further consolidate the practical viability of nonfullerene OPVs. This study provides the origins of high performance in nonfullerene OPVs and also provides new design guidelines to develop versatile OPVs in indoor environments, which differ from those used for conventional outdoor OPVs.

2. Results and Discussion

Figure 1a shows the energy levels of the donor and acceptor materials used in this study (see the chemical structures and absorption profiles in Figure S1, Supporting Information).\(^{[22–24]}\) Two kinds of blends were prepared using poly\{(2,6-(4,8-bis\{5-(2-ethylhexyl)thiophen-2-yl\}benzo\{1,2-b:4,5-b\}dithiophene\})-alt\{5,5-(1,3-di-2-thienyl-5,7-bis\{2-ethylhexyl\}benzo\{1,2-c:4,5-c\}dithiophene-4,8-dione\}\} (PBDB-T) as a donor in a combination with either PC\(_{70}\)BM or 3,9-bis\{2-methylene\-(3-(1,1-dicyanomethylene)-indanone)\}-5,5,11,11-tetrakis\{5-hexylthienyl\}-dithieno[2,3-d:2',3'-d']-s-indacenof[1,2-b:5,6-b']dithiophene (ITIC-Th) as an acceptor. Figure 1b shows the UV–Vis absorption spectra of both blends relative to the irradiative spectra of indoor light sources such as an light emitting diode (LED) and a fluorescent lamp (FL). PBDB-T:ITIC-Th blend can benefit from broader utilization of the solar spectrum with the extended absorption onset in the near-IR (NIR) regime. The radiative spectra of the ambient artificial lights mainly fall between 400 and 700 nm, unlike that of the standard solar spectrum. Hence, when the OPVs are transferred to indoor environments, the absorption spectrum of PBDB-T:PC\(_{70}\)BM blend matches better with the emission band of the indoor lighting, whereas the redundant absorption beyond 700 nm in the PBDB-T:ITIC-Th blend cannot contribute to the photocurrent.

Figure 1 shows the current density–voltage (\(J–V\)) curves of PBDB-T:PC\(_{70}\)BM and PBDB-T:ITIC-Th OPVs under the 1 sun condition. The broader absorption spectrum of ITIC-Th contributed to the higher short-circuit current density \((J_{\text{SC}})\) in the nonfullerene OPV over the fullerene OPV, and the external quantum efficiency (EQE)-derived \(J_{\text{SC}}\) values agreed with those obtained from the \(J–V\) measurement (Figure 1d). Both the enhanced fill factor (FF) and lower \(V_{\text{loss}}\) played important roles in...
synergistically maximizing the PCE of the nonfullerene OPV compared with the fullerene OPV. The open-circuit voltage ($V_{OC}$) value of 0.86 V for the PBDB-T:ITIC-Th device was greater than 0.82 V for the PBDB-T:PC$_{70}$BM device, even if ITIC-Th has a 0.23 eV smaller $E_g$ compared with PC$_{70}$BM (1.61 vs 1.84 eV). Due to the simultaneous enhancement in every photovoltaic parameter, the OPV based on ITIC-Th showed a higher PCE of 9.31% over 7.42% for the OPV based on PC$_{70}$BM.

The photovoltaic parameters were measured over a wide range of incident light intensities from 100 to 0.1 mW cm$^{-2}$ (Figure 2a,b and Figure S2, Supporting Information). The variation of $J_{SC}$ was nearly independent on incident light intensities ($P$) similarly for both the fullerene and the nonfullerene devices, implying weak bimolecular recombination in the devices, which were evaluated using the $J_{SC} \propto P^{\alpha}$ ($\alpha = 0.95$ vs 0.96). From the natural logarithmic dependence of $V_{OC}$ on the light intensity, the nonfullerene OPV exhibited a moderate slope of $1.11 \text{kT q}^{-1}$ compared with $1.36 \text{kT q}^{-1}$ for the fullerene OPV, where $k$, $T$, and $q$ are the Boltzmann constant, absolute temperature, and elementary charge, respectively. This meant that an ameliorated trap-assisted charge recombination in the nonfullerene OPV contributed mainly to better $V_{OC}$ and higher FF in the nonfullerene OPVs.$^{[26,27]}$ The fitted slope of the $V_{OC}$ variation rose for both devices at weaker light intensities below 1 mW cm$^{-2}$, implying that trap-assisted charge recombination becomes more crucial for low light operation of OPVs. The fitted slope remained relatively moderate ($1.26 \text{kT q}^{-1}$) for the nonfullerene OPV compared with the fullerene OPV ($1.73 \text{kT q}^{-1}$) between 0.1 and 1 mW cm$^{-2}$, which effectively restrained the decay of $V_{OC}$ in the low light levels. Similarly, the nonfullerene OPV exhibited

![Figure 2](image-url)
more stable FF variation when reducing the light intensity below 1 mW cm\(^{-2}\). The PCE, thus, remained relatively high over 10% at weak light intensities for the nonfullerene OPV, unlike the fullerene OPV that displayed a significant PCE loss at the same weak intensities. These results suggest that the nonfullerene OPV with the alleviated trap-assisted charge recombination performed better than the fullerene OPV over a wide range of light intensities, including low light levels at which the trap-assisted charge recombination becomes more significant. This reflects high potential of nonfullerene small molecules in low light applications involving indoor OPVs.

Next, the photovoltaic performance of devices was tested under indoor light sources. Details related to the indoor light sources are provided in the Experimental Section. Figure 2c–f shows the \(J-V\) characteristics of devices under LEDs and FLs (500 and 1000 lux), which represent the illumination conditions for typical indoor applications. The nonfullerene OPV benefited from the simultaneous enhancement in photovoltaic parameters and, consequently, higher power output compared with the fullerene OPV, which was similar to that observed under AM 1.5G illumination. The nonfullerene OPV exhibited a \(V_{OC}\) reduction of 0.19 V at a 500 lux LED in comparison with \(V_{OC}\) obtained under 1 sun illumination, which was smaller than 0.21 V for the fullerene OPV. This corresponded to a much alleviated \(V_{loss}\) of 0.94 V for the nonfullerene OPV compared with 1.23 V for the fullerene OPV for the indoor operation. The reduced \(V_{loss}\) in a synergistic combination with the superior FF contributed greatly to the high PCEs in the nonfullerene OPV under the indoor environments, both of which are the most critical factors to control at weak light intensities. For instance, the nonfullerene OPV achieved the PCEs of 14.96% and 14.18% at 1000 and 500 lux LEDs, respectively, surpassing 11.32% and 10.29% for the fullerene OPV. The nonfullerene OPV exhibited higher \(J_{SC}\) values over the fullerene OPV for the indoor environment, despite the lower spectral overlap with the irradiance spectrum of LEDs. This suggests that, if the device can effectively absorb the incident light, the spectral overlap is not a critical factor in modifying photocurrent and overall efficiency of indoor OPVs. That is, there exists a room for further performance enhancement via rational synthesis of a nonfullerene acceptor, which offers optimum bandgap for efficient indoor light harvesting while securing significantly ameliorated energy loss.\(^{[18]}\)

A different donor:acceptor pair of poly[1-(5-(4,8-bis(5-(2-ethylhexyl)-4-fluoro)phen-2-yl)-6-methylbenzo[1,2-b:4,5-b']dithieno-2,7-yl)](5,7-bis(2-ethylhexyl)-3-(5-methylthiophen-2-yl)-4H,8H-benzo[1,2-c:4,5-c']dithiophene-4,8-dione) (PBDB-TF): 3,9-bis(2-methylene-(3-(1,1-dicyanomethylene)-6,7-difluoro)-indanone)) 5,5,11,11-tetrakis(4-hexylphenyl)dithieno[2,3-d:2',3',4'-d]:3,4-d':3'-d:')-indacen,[1,2-b:5,6-b']dithiophene (IT-4F) was characterized to confirm the superiority of the nonfullerene acceptors (see \(J-V\) characteristics under LEDs in Figure S3, Supporting Information). The \(E_g\) value of 1.53 eV for IT-4F is considered too small to match the indoor irradiance spectrum. In addition, the low band offset due to the low-lying lowest unoccupied molecular orbital (LUMO) of IT-4F could limit \(V_{OC}\) in the PBDB-TF:IT-4F device. Despite these shortcomings, the PBDB-TF:IT-4F OPV exhibited a decent PCE of 19.05% at a 1000 lux LED, surpassing 16.69% for the PBDB-TF:PC\(_{70}\)BM OPV. The superior PCE was attributed to the synergistic advantages of less \(V_{loss}\) (0.87 vs 1.11 V) and superior FF (68.06% vs 64.86%) in the PBDB-TF:IT-4F device compared with its PBDB-TF:PC\(_{70}\)BM counterpart, which was similar to the previous proof of concept devices based on ITIC-Th versus PC\(_{70}\)BM. Notably, the \(V_{OC}\) value of 0.66 V for the PBDB-TF:IT-4F was only 0.07 V lower than 0.73 V for the PBDB-TF:PC\(_{70}\)BM under indoor lighting, whereas the \(E_g\) value of 1.53 eV for IT-4F was only 0.31 eV lower than 1.84 eV for PC\(_{70}\)BM. Interestingly, another state-of-the-art nonfullerene system of PBDB-TF:Y6 exhibited a higher PCE of 23.78% at a 500 lux 3000 K LED, exceeding 22.18% for the PBDB-TF:PC\(_{70}\)BM OPV. The high indoor performance in nonfullerene OPVs, in addition to the successful AM 1.5G operation, suggests high prospects for newly emerging nonfullerene small molecules in a wide range of photovoltaic applications.

Table 1 summarizes the photovoltaic parameters of fullerene versus nonfullerene OPVs under diverse irradiation conditions.

The nanoscale morphology of the bulk-heterojunction (BHJ) films was investigated to gain insight into the origin of the ameliorated trap-assisted charge recombination and \(V_{loss}\) in the nonfullerene blends. To visualize morphological features, we conducted atomic force microscopy (AFM) characterization on both fullerene and nonfullerene blends, as shown in Figure 3a,b. The nanoscale characteristics of the blend morphology were not to be clearly recognized in AFM images, and thus, we created contour profiles on the AFM images of the fullerene and nonfullerene blends to attain the detailed morphological parameters. Figure 3c,d shows the contour maps of the AFM phase images for the blends. Figure 3e,f shows the detailed profile of Figure 3c,d for both donor- and acceptor-rich regions. The contour line indicates the degree of the AFM phase scale divided into eight levels, and the spaces between each contour were filled with nine colors. In the AFM phase of the binary blend, the low and high scales indicate that the rich phases of each polymer donor and small-molecule acceptor are presented by the blue and red colors in the contour image, respectively.\(^{[28]}\)

| Active layer | Light source | \(V_{OC}\) [V] | \(J_{SC}\) [mA cm\(^{-2}\)] or [μA cm\(^{-2}\)] \(^{[a]}\) | FF [%] | PCE [%] |
|--------------|--------------|----------------|----------------------|-------|--------|
| PBDB-T:PC\(_{70}\)BM | 1 sun AM 1.5G | 0.82 | 14.43 | 62.69 | 7.42 |
| | 1000 lux (6000 K) LED | 0.64 | 80.73 | 60.71 | 11.32 |
| | 1000 lux FL | 0.65 | 87.46 | 60.48 | 11.13 |
| PBDB-T:ITIC-Th | 1 sun AM 1.5G | 0.86 | 16.26 | 66.41 | 9.31 |
| | 1000 lux (6000 K) LED | 0.70 | 89.25 | 67.03 | 14.96 |
| | 1000 lux FL | 0.70 | 96.42 | 67.18 | 14.58 |
| PBDB-T:PC\(_{70}\)BM | 1 sun AM 1.5G | 0.91 | 15.96 | 63.79 | 9.26 |
| | 1000 lux (6000 K) LED | 0.73 | 98.46 | 64.86 | 16.69 |
| | 500 lux 3000 K LED | 0.70 | 70.40 | 62.77 | 22.18 |
| PBDB-T:IT-4F | 1 sun AM 1.5G | 0.83 | 19.67 | 67.33 | 10.89 |
| | 1000 lux (6000 K) LED | 0.66 | 118.20 | 68.06 | 19.05 |
| | 500 lux 3000 K LED | 0.81 | 25.06 | 68.89 | 13.90 |

\(^{[a]}\)The \(J_{SC}\) unit is mA cm\(^{-2}\) for 1 sun AM 1.5G and μA cm\(^{-2}\) for indoor light conditions.
In Figure 3e, the fullerene blend exhibited that polymer donor domains were formed as clusters at around 60 nm intervals, and acceptor domains were located in the interface with 40 nm intervals of each other, in which were not penetrated between polymer donor domain clusters. These results implied that the formation of the acceptor-rich domain was suppressed in the fullerene blend, whereas the donor-rich domain was significantly aggregated. On the other hand, the nonfullerene blend in Figure 3f displays that both the donor-rich and acceptor-rich domains are distributed at around 50 and 70 nm within each other. These results indicate that the donor- and acceptor-rich domains were not clustered in the nonfullerene blend, which can allow the donor- and acceptor-rich domains to interpenetrate one another. Consequently, the fullerene blend exhibited nonhomogeneously distributed domains in a cluster form, whereas homogeneously distributed domains in the interpenetrated network form were observed in the nonfullerene blend. The interpenetrated structures in the nonfullerene blend enabled the formation of the uniform and prominent nanoscale phase separation in addition to the homogenous morphology. However, the acceptor-rich phase cannot penetrate in-between donor domains (or vice versa) for the fullerene blend, implying the inefficient donor–acceptor interfacial contacts due to the formation of microscale phase separation. Although the contour imaging approach provided sketchy information on donor or acceptor aggregation in the blends, the quantitative degree of phase distribution for the aggregated polymer donor or acceptor was unattainable. In addition, this approach hardly delivered phase-separation uniformity of the donor or acceptor, which is one of the morphological key factors of forming favorable BHJ in a large area.

Figure 3. AFM surface phase images (2 × 2 μm²) of a) PBDB-T:PC_{70}BM and b) PBDB-T:ITIC-Th blend films, respectively. Contour maps of AFM phase images and detailed profiles for donor-rich (blue) and acceptor-rich (red) regions (0.5 × 0.5 μm²) obtained from c,e) PBDB-T:PC_{70}BM and d,f) PBDB-T:ITIC-Th blend films, respectively. Scale bars in (a,b): 400 nm.
In this regard, a power spectral density (PSD) analysis, which is a series of Fourier transform, was performed on the AFM phase images, as shown in Figure 4a,b. For the 1D PSD as a function of frequency (1D-PSD($f$)) fitting, we followed the computational approach, as described in Figure S4, Supporting Information, and the Experimental Section. The intensity and frequency of the peaks in the 1D-PSD($f$) indicate the degree of repeatability and interval for the distributed phase in the blend morphology, respectively.\[29,30\] Furthermore, the 1D-PSD($f$) peaks in the low- and high-frequency ranges signify the periodically distributed phase in the micro- and nanoscale, respectively. The peaks of the 1D-PSD($f$) in Figure 4a,b can be observed only at the high-frequency ranges, suggesting that the phases in blend morphology are mostly nanoscale size. Therefore, we first contemplated morphology distinction in the nanoscale phase for the fullerene and nonfullerene blends. For calibration, we divided the 1D-PSD($f$) by the square of the frequency ($f^2$) to macroscopically clarify the characteristics of the peaks and reduce the noise signal of AFM characterization. (See Figure 4c,d for the calibrated 1D-PSD($f$) profiles.) Figure 4c,d displays two peaks in both blends in which the phase of each donor and acceptor was distributed with different intervals. The peak intensity in 1D-PSD($f$) is proportional to the degree of phase distribution in blend morphology, and the intervals ($I_{RD}$) of the regularly distributed domains in the blend can be calculated using $2\pi/f_p$, where $f_p$ is the frequency of the peak in

![Figure 4. 1D PSD-frequency spectra of AFM phase images for a) PBDB-T:PC$_{70}$BM and b) PBDB-T:ITIC-Th blend films. 1D calibrated PSD-frequency spectra of AFM phase images for c) PBDB-T:PC$_{70}$BM and d) PBDB-T:ITIC-Th blend films at high-frequency ranges. 1D PSD profiles as a function of the position on AFM phase images for e) PBDB-T:PC$_{70}$BM and f) PBDB-T:ITIC-Th at the high-frequency regimes. The low- and high-frequency ranges are presented in (a,b). The frequency regions of (c,d) are split by the dotted lines to indicate each peak range.](image-url)
1D-PSD(\(f\)). Thus, these peaks can be assigned to the polymer donor or small molecule acceptor from the contour maps of AFM phase images. For instance, Figure 4c displays the peaks at around 0.10 and 0.14 nm\(^{-1}\) (\(I_{\text{RD}}\): 62.8 vs 44.8 nm), and the polymer donor and fullerene acceptor peaks are considered at 0.10 and 0.14 nm\(^{-1}\), each through the results of the rich phase intervals in contour maps. In Figure 3e, the phase distance between neighboring polymer donors is longer than that between adjacent acceptors, and the polymer donors are highly aggregated in the blend. Noticeably, the peak intensity is prominent at 0.10 nm\(^{-1}\) relative to 0.14 nm\(^{-1}\), indicating that the formation of the acceptor phase was suppressed relative to the polymer donor phase in the fullerene blend. However, 1D-PSD(\(f\)) for the nonfullerene blend in Figure 4d exhibits two peaks with the relatively comparable intensities at 0.09 and 0.12 nm\(^{-1}\) (\(I_{\text{RD}}\): 69.8 vs 52.4 nm), which correspond to the acceptor and donor phase signals, via results of domain intervals on contour maps, respectively. These results mean that the nonfullerene blend was built with a homogenous nanoscale phase-separation network by the balanced distribution of donors and acceptors.

The 1D-PSD profiles as a function of the position (\(x\)) at the high-frequency range, which is denoted as 1D-PSD(\(x\)), were further analyzed to macroscopically provide the overall information of the nanoscale phase distribution for both blends. These profiles were calculated using 1D-PSD(\(x\)) = \(\sum\) PSD(f, \(x\)) \(\times\) sin(2\(\pi\)f, \(x\)), where f and x are the frequency and position coordinate, respectively. Here, the position coordinate (\(x\)) is the set of the location numbers for the azimuthally averaged linecut on the AFM phase image, and thus, the 1D-PSD(\(x\)) clearly provides overall information on the phase distribution of 2D blend morphology as a 1D-average linecut form. From the total range (0–2000 nm), we profiled a particular region with a size of 100 nm, which allows clear observation of the nanoscale phase distribution. Figure 4e shows that the morphology in the fullerene blend featured the 1D-PSD(\(x\)) of polymer donor peak (0.10 nm\(^{-1}\)) with a large amplitude relative to the fullerene acceptor peak (0.14 nm\(^{-1}\)) characteristics. On the other hand, the nonfullerene blend in Figure 4f shows a comparable amplitude of 1D-PSD(\(x\)) peaks for both the polymer donor (0.12 nm\(^{-1}\)) and the nonfullerene acceptor (0.09 nm\(^{-1}\)). These results imply that donor and acceptor phases are disproportionally distributed in the fullerene blend mainly due to the polymer donor aggregation, whereas the nonfullerene blend exhibited well-balanced characteristics of both phases, which agree with the results in Figure 4c,d. Moreover, when we plotted the 1D-PSD(\(x\)) even at low-frequency range to obtain the uniformity information for the microscale phase distribution, the nonfullerene blend morphology manifests a relatively uniform microscale phase distribution unlike random phase-distribution features in the fullerene blend (see Figure S5a,b, Supporting Information). In addition, the AFM topography in Figure S6, Supporting Information, exhibits that the nonfullerene blend shows a smooth surface with a lower root mean square (RMS) value of 2.86 nm compared with 3.37 nm for the fullerene blend. This finding conveys that uniform nonfullerene small molecules prevent aggregation of polymer, further strengthening previous analyses through the PSD and contour map characterizations. These confirm that the acceptor material regulated morphological characteristics of blends with a significant influence on the construction and purity of domains. In combinations with uniform distribution of phase-separated regions and smooth surface characteristics, the effective phase separation between the polymer donor and the nonfullerene acceptor is beneficial to build efficient charge interpenetrating networks and prevent the formation of trap sites in nonfullerene OPVs.

To further investigate the microscopic effect of the acceptor, the crystallinity and molecular arrangement of the blends were evaluated via grazing-incidence wide-angle X-ray scattering (GIWAXS) characterization. Figure 5a,b shows the 2D GIWAXS patterns of the blends (see 2D patterns of neat films in Figure S7, Supporting Information). A more prominent (010) \(\pi\)-\(\pi\) stacking peak was observed in the out-of-plane (OOP) direction for the nonfullerene blend. Figure 5c shows the linecut profiles of 2D patterns to compare the effect of the acceptor material on the packing properties of the polymer donor. The coherence lengths of the PBDB-T \(\pi\)-\(\pi\) stacking calculated via the Scherrer equation were 35.0 and 39.6 Å for the fullerene and nonfullerene blends, respectively.[31] The elongated coherence length indicates the improved crystalline structures of PBDB-T in the nonfullerene blend.[32,33] Figure 5d shows the intensity distribution of azimuthal angle profiles of PBDB-T (100) lamella peaks for the fullerene and nonfullerene blends, in which the schematic view of the lamella orientation information is presented in response to the azimuthal angle. This allows a quantitative comparison of the crystal orientation distribution of the polymer in each blend. The intensity area with the azimuthal angle of 90–100° and 170–180° in the intensity distribution profile indicates the fraction of the lamella with edge-on and face-on orientation in each film, respectively.[34,35] The nonfullerene blend showed a higher face-on/edge-on ratio of 0.25 compared with 0.09 for the fullerene blend. These results reflect the improved crystallinity and face-on packing in the nonfullerene blend. Consequently, it can suppress the formation of the trap site and create an efficient charge transport pathway, which is correlated with the reduced \(V_{\text{loss}}\) caused by recombination loss in the nonfullerene devices, showing a similar tendency observed from the AFM characterizations.[36,37]

The achievement of high stability while pursuing optimized performance is a key issue for the practical viability of OPVs. Under 1 sun conditions, both photo-induced degradation and molecular/morphological mutation in organic materials are important to limit the stability of OPVs due to the strong irradiation and heat under solar light.[38,39] The main origin of the decay is different in indoor conditions, as the environmental conditions become mild. As an example, the initial PCEs were almost unchanged at weak irradiation for an extended timescale (Figure S8, Supporting Information), which reflects that photodegradation could be nearly negligible for indoor operation of OPVs. On the contrary, the devices showed distinct decay tendency when morphological changes occur in the active layer. Figure 6 shows the variations in performance for the two OPV devices as a function of annealing duration at 45 °C (a temperature higher than ranges of common indoor environments), which was applied to accelerate morphological mutations in the BHJ layer. The nonfullerene OPV showed much better stability over a long time with a moderate PCE reduction from 14.96% to 14.23% (95.1% retention) after a month at 45 °C, whereas a considerable PCE loss from 11.32% to 9.61% (84.9%
Figure 5. GIWAXS 2D patterns of the a) PBDB-T:PC$_{70}$BM and b) PBDB-T:ITIC-Th blend films. c) Linecut profiles of the GIWAXS patterns for OOP and in-plane (IP) directions. d) Azimuthal intensity profile of the PBDB-T (100) scatter for the blends.

Figure 6. Time-dependent variations in photovoltaic performance for fullerene and nonfullerene OPVs: a) $V_{OC}$, b) $J_{SC}$, c) FF, and d) PCE. The parameters were obtained with repeated cycles of thermal annealing at 45 °C in dark conditions and testing under 1000 lux LED irradiation at room temperature. Each point indicates a mean value obtained from five devices.
retention) was observed for the fullerene OPV. The better morphological stability in the nonfullerene acceptors is attributed to their anisotropic molecular structures and rigid backbones compared with fullerenes. The decent device stability in addition to the unconditional high performance is beneficial to practical usage of the nonfullerene acceptors in a variety of commercial fields. In addition, the experimental results suggest that the stability of indoor OPVs largely relies on the morphological changes in the BHJ active layer, and, thus, provide a new criterion to evaluate the stability of OPVs in indoor environments, which differs from that used for outdoor OPVs. Note that this is a proof-of-concept study to elucidate benefits of nonfullerene acceptors over PC70BM, and there exists a room for further performance enhancement by optimizing energy levels and absorption spectrum of nonfullerene acceptors, which can be readily tunable through molecular design. An in-depth study focusing on the development of high-performance indoor OPVs based on advanced nonfullerene acceptor systems has currently been underway.

3. Conclusion

In summary, nonfullerene OPVs promise efficient light energy harvesting for both indoor and outdoor circumstances. To find origins of the superior photovoltaic operation, advanced morphological analyses were devised to the nonfullerene blends involving contour imaging approach and PSD. The favorable morphological features with improved molecular crystallinity and effective phase separation were assigned as key factors for the suppressed charge recombination and $V_{Loss}$, which inspired more efficient operation of nonfullerene OPVs as compared with fullerene OPVs over a wide range of incident light intensities. The nonfullerene OPVs were highly stable under real operational conditions, which is beneficial to practical applications of nonfullerene OPVs in a variety of realistic fields. The state-of-the-art nonfullerene acceptors are mostly designed for effective 1 sun operation, and thus, further optimization is required, focusing on the low-intensity artificial light circumstance. With the great synthetic flexibility, designing new nonfullerene small molecules to secure both a high $V_{OC}$ and effective indoor light absorption will give a noticeable rise in indoor PCEs over the currently dominant photovoltaic technologies.

4. Experimental Section

OPV Device Fabrication: The nonfullerene blend was prepared by dissolving PBDB-T:ITIC-Th (1:1 by wt%) in chlorobenzene, whereas PBDB-T:PC70BM (1:1 by wt%) in chlorobenzene:1,8-diodooctane (97/3 vol/vol) solvent was used as the fullerene blend solution. A ZnO electron transport layer was deposited on a cleaned indium tin oxide (ITO) substrate and thermally annealed at 300 °C for 10 min. The blend solution was spin-coated onto the ZnO layer in a glove box filled with Ar. A top electrode comprising MoO$_3$ (8 nm) and Ag (100 nm) was thermally evaporated through a shadow mask under vacuum (~10$^{-7}$ Torr). The fabrication process was completed by sealing the devices using encapsulation glass and UV-curable epoxy. The active area of devices was 4 mm$^2$.

OPV Characterization: The $J$–$V$ characteristics of the OPVs were obtained using a source meter (Keithley 2400, Tektronix) under solar and indoor irradiation conditions. The solar light was provided by a solar cell $I$–$V$ parameter test system (K3000 LED 100, McScience), which was adjusted using a sun spectroradiometer (S2441, Soma Optics). The total integrated power in the whole spectral region was 140 and 280 $\mu W \text{cm}^{-2}$ for 500 and 1000 lux LEDs and 155 and 310 $\mu W \text{cm}^{-2}$ for 500 and 1000 lux FLs, respectively. For the thermal durability test, the $J$–$V$ characteristics were obtained with the repeated cycles of thermal annealing at 45 °C in dark conditions and device testing under LED irradiation at room temperature. To rule out effects from other factors such as oxygen and moisture, the devices with full encapsulation were used in the characterization process. The EQE spectra of devices were monitored using a spectral solar cell QE test system (K3100, McScience). GIWAXS measurements were conducted at the 5A beamline of the Pohang Accelerator Laboratory, Republic of Korea. The grazing angle was controlled to be 0.13°.

Morphology Analysis: The surface topography and phase images of blend films were measured using a tapping mode and noncontact mode AFM, respectively (XE-150, Park Systems). The contour imaging of the phase images was obtained using the Origin 9.0 program, in which the phase images were divided evenly into eight levels of the phase scale, and nine colors were set between contours using the “Contour/Color Fill” in the program. The PSD profiles of the 2D AFM topography ($N_x - N_y$, 1024 – 1024 pixels) were calculated using Python 3.7 (NumPy, SciPy) codes. The 2D fast Fourier transform (FFT) function was used for AFM phase to generate a 2D power spectrum pattern $P(f_x, f_y)$ on the frequency coordinate, in which frequencies $(f_x, f_y)$ take a discrete range from $1/L$ to $N_x/2L$ or to $N_y/2L$, respectively. Then, the image size parameters such as the full size of the AFM 2D array ($L_x - L_y$, 2000 – 2000 nm) and size per pixel ($l_x - l_y$, 1.935 – 1.935 nm) were calibrated by adding coefficients to the squared $P(f_x, f_y)$, which is called a 2D-PSD and can be described as $Z(f_x, f_y) = \frac{1}{l_x l_y} \left| P(f_x, f_y) \right|^2$. The 1D-PSD($f$) was obtained by azimuthal average according to the radius at zero frequency in the 2D-PSD pattern. A summary of fitting work flow is provided in Figure S4, Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This research was supported by the Energy Technology Development Program of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant (Grant No. 20193002010370) funded by the Korean government, and by the Technology Development Program to Solve Climate Changes of the National Research Foundation of Korea, which was funded by the Ministry of Science, ICT, and Future Planning (NRF-2016M1A2A2940912). The research was also supported by the Basic Science Research Program of the National Research Foundation of Korea (NRF-2020R1A2C2005844).

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.
Keywords

indoor energy harvesting, morphology, nonfullerene acceptors, organic photovoltaics, recombination

Received: February 1, 2021
Revised: April 16, 2021
Published online:

[1] J. Zhang, H. S. Tan, X. Guo, A. Facchetti, H. Yan, Nat. Energy 2018, 3, 720.
[2] J. Hou, O. Inganäs, R. H. Friend, F. Gao, Nat. Mater. 2018, 17, 119.
[3] C. Yan, S. Barlow, Z. Wang, H. Yan, A. K.-Y. Jen, S. R. Marder, X. Zhan, Nat. Rev. Mater. 2018, 3, 18003.
[4] Y. Cui, H. Yao, J. Zhang, K. Xian, T. Zhang, L. Hong, Y. Wang, Y. Xu, K. Ma, C. An, C. He, Z. Wei, F. Gao, J. Hou, Adv. Funct. Mater. 2020, 32, 1908205.
[5] M. Mainville, M. Leclerc, ACS Energy Lett. 2020, 5, 1186.
[6] F.-C. Chen, Adv. Opt. Mater. 2019, 7, 1800662.
[7] M. Nam, H. Y. Noh, J. Cho, Y. Park, S.-C. Shin, J.-A. Kim, J. Kim, H. H. Lee, J. W. Shim, D.-H. Ko, Adv. Funct. Mater. 2019, 29, 1900154.
[8] H. Yin, J. K. W. Ho, S. H. Cheung, R. J. Yan, K. L. Chiu, X. Hao, S. K. So, J. Mater. Chem. A 2018, 6, 8579.
[9] S.-C. Shin, C. W. Koh, P. Vincent, J. S. Goo, J.-H. Bae, J.-J. Lee, C. Shin, H. Kim, H. Y. Woo, J. W. Shim, Nano Energy 2019, 58, 466.
[10] Y.-J. You, C. E. Song, Q. V. Hoang, Y. Kang, J. S. Goo, D.-H. Ko, J.-J. Lee, W. S. Shin, J. W. Shim, Adv. Funct. Mater. 2019, 29, 1901171.
[11] J. Yuan, Y. Zhang, L. Zhou, G. Zhang, H.-L. Yip, T.-K. Lau, X. Lu, C. Zhu, H. Peng, P. A. Johnson, M. Leclerc, Y. Cao, J. Ulanski, Y. Li, Y. Zou, Joule 2019, 3, 1140.
[12] H. Yao, Y. Cui, R. Yu, B. Gao, H. Zhang, J. Hou, Angew. Chem., Int. Ed. 2017, 56, 3045.
[13] H. S. Ryu, S. Y. Park, T. H. Lee, J. Y. Kim, H. Y. Woo, Nanoscale 2020, 12, 5792.
[14] Y. Cui, L. Hong, J. Hou, ACS Appl. Mater. Interfaces 2020, 12, 38815.
[15] Y. Cui, H. Yao, T. Zhang, L. Hong, B. Gao, K. Xian, J. Qin, J. Hou, Adv. Energy Mater. 2019, 31, 1904512.
[16] Z. Ding, R. Zhao, Y. Yu, J. Liu, J. Mater. Chem. A 2019, 7, 26533.
[17] M. Nam, J.-H. Kang, J. Shin, J. Na, Y. Park, J. Cho, B. Kim, H. H. Lee, R. Chang, D.-H. Ko, Adv. Energy Mater. 2019, 9, 1901856.
[18] Y. Cui, Y. Wang, J. Bergqvist, H. Yao, Y. Xu, B. Gao, C. Yang, S. Zhang, O. Inganäs, F. Gao, J. Hou, Nat. Energy 2019, 4, 768.
[19] L.-K. Ma, Y. Chen, P. C. Y. Chow, G. Zhang, J. Huang, C. Ma, J. Zhang, H. Yin, A. M. H. Cheung, K. S. Wong, S. K. So, H. Yan, Joule 2020, 4, 1486.
[20] R. Cheng, C.-C. Chung, H. Zhang, F. Liu, W.-T. Wang, Z. Zhou, S. Wang, A. B. Djurišić, S.-P. Feng, Adv. Energy Mater. 2019, 9, 1901980.
[21] Q. Yue, W. Liu, X. Zhu, J. Am. Chem. Soc. 2020, 142, 11613.
[22] W. Zhao, S. Li, H. Yao, S. Zhang, Y. Zhang, B. Yang, J. Hou, J. Am. Chem. Soc. 2017, 139, 7148.
[23] Y. He, G. Zhao, B. Peng, Y. Li, Adv. Funct. Mater. 2010, 20, 3383.
[24] Y. Lin, F. Zhao, Q. He, L. Huo, Y. Wu, T. C. Parker, W. Ma, Y. Sun, C. Zhang, D. Zhu, A. J. Heeger, S. R. Marder, X. Zhan, J. Am. Chem. Soc. 2016, 138, 4955.
[25] L. J. A. Koster, M. Kemerink, M. M. Wienk, K. Maturová, R. A. J. Janssen, Adv. Mater. 2011, 23, 1670.
[26] S. R. Cowan, A. Roy, A. J. Heeger, Phys. Rev. B 2010, 82, 245207.
[27] M. M. Mandoc, W. Veumann, L. A. J. Koster, B. de Boer, P. W. M. Blom, Adv. Funct. Mater. 2007, 17, 2167.
[28] V. Jovanov, N. Yumnam, A. Muller, M. Gruber, V. Wagner, J. Phys. Chem. C 2017, 121, 9173.
[29] F. M. Mwema, E. T. Akinlabi, O. P. Oladijo, in Photoenergy and Thin Film Materials (Eds: X.-Y. Yang), Wiley-Scrivener, Wuhan, China 2019, Ch. 9.
[30] Y. Gong, S. T. Misture, P. Gao, N. P. Mellott, J. Phys. Chem. C 2016, 120, 22358.
[31] D.-M. Smilgies, J. Appl. Crystallogr. 2009, 42, 1030.
[32] G. Zhang, K. Zhang, Q. Yin, X.-F. Jiang, Z. Wang, J. Xin, W. Ma, H. Yan, F. Huang, Y. Cao, J. Am. Chem. Soc. 2017, 139, 2387.
[33] J. M. Szarko, J. Guo, Y. Liang, B. Lee, B. S. Rolczynski, J. Strzalka, T. Xu, S. Loser, T. J. Marks, L. Yu, L. X. Chen, Adv. Mater. 2010, 22, 5468.
[34] G.-P. Kini, Q. V. Hoang, C. E. Song, S. K. Lee, W. S. Shin, W. So, M. A. Uddin, H. Y. Woo, J. C. Lee, Polym. Chem. 2017, 8, 3622.
[35] H. Chen, D. Hu, Q. Yang, J. Gao, J. Fu, K. Yang, H. He, S. Chen, Z. Kan, T. Duan, C. Yang, J. Ouyang, Z. Xiao, K. Sun, S. Lu, Joule 2019, 3, 3034.
[36] T. Heumuller, W. R. Mateker, I. T. S. Quintana, K. Vendewal, J. A. Bartelt, T. M. Burke, T. Ameri, C. J. Brabec, M. D. McGehee, Energy Environ. Sci. 2014, 7, 2974.
[37] G. Zhang, X.-K. Chen, J. Xiao, P. C. Y. Chow, M. Ren, G. Kuppan, X. Jiao, C. C. Chen, X. Du, R. Xia, Z. Chen, J. Yuan, Y. Zhang, S. Zhang, Y. Liu, Y. Zou, H. Yan, K. S. Wong, V. Coropceanu, N. Li, C. J. Brabec, J.-L. Bredas, H.-L. Yip, Y. Cao, Nat. Commun. 2020, 11, 3943.
[38] M. Nam, M. Cha, H. H. Lee, K. Hur, K.-T. Lee, J. Yoo, I. K. Han, S. J. Kwon, D.-H. Ko, Nat. Commun. 2017, 8, 14068.
[39] M. Nam, J. Yoo, Y. Park, H. Y. Noh, Y. Park, J. Cho, J.-A. Kim, J. Kim, H. H. Lee, R. Chang, D.-H. Ko, J. Mater. Chem. A 2019, 7, 9698.