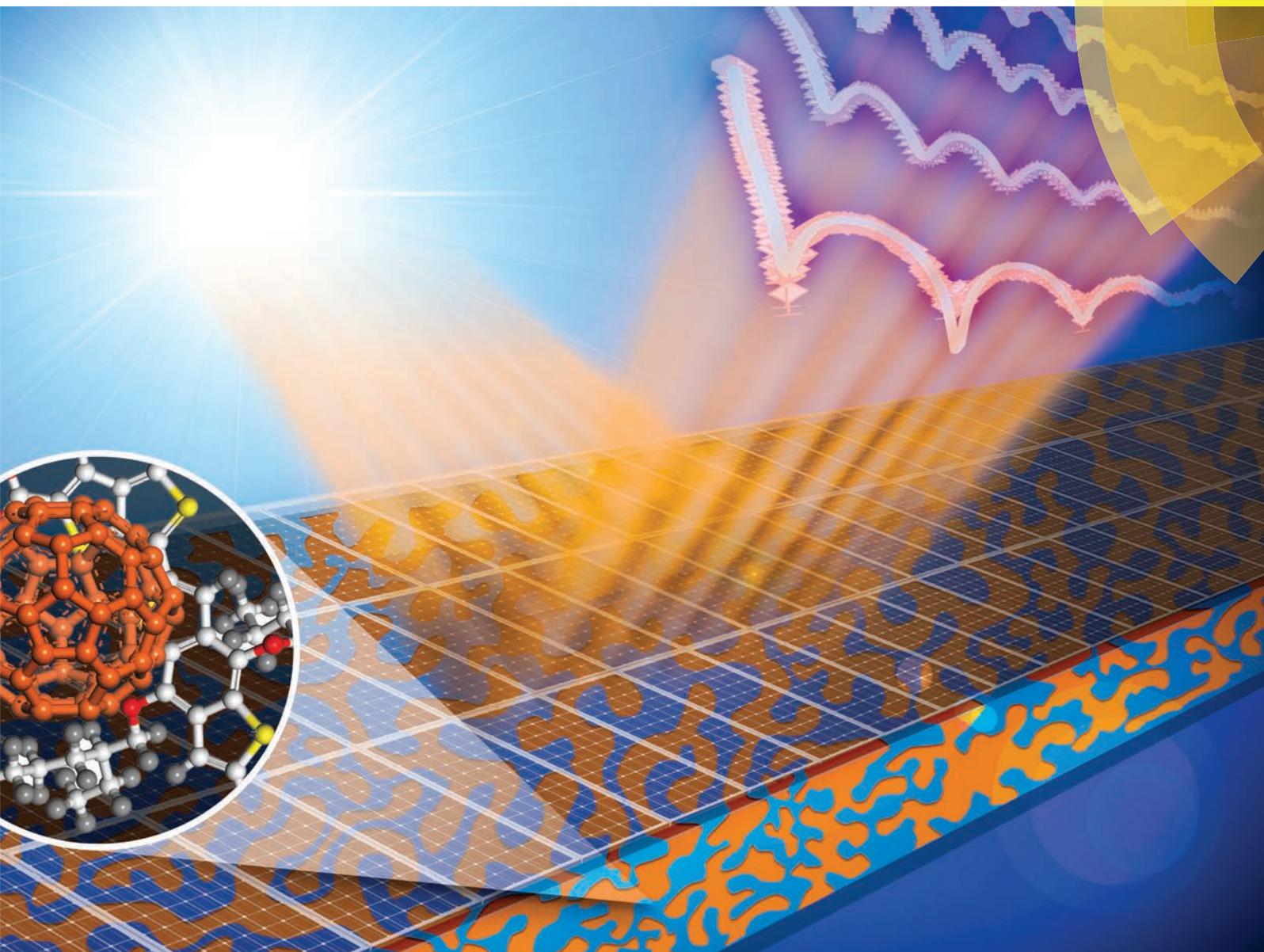


# Nanoscale

[www.rsc.org/nanoscale](http://www.rsc.org/nanoscale)



ISSN 2040-3364



ROYAL SOCIETY  
OF CHEMISTRY

**COMMUNICATION**

Jong K. Keum, Kai Xiao *et al.*

Correlating high power conversion efficiency of PTB7:PC<sub>71</sub>BM inverted organic solar cells with nanoscale structures





Cite this: *Nanoscale*, 2015, 7, 15576

Received 20th May 2015,  
 Accepted 10th July 2015  
 DOI: 10.1039/c5nr03332b  
[www.rsc.org/nanoscale](http://www.rsc.org/nanoscale)

## Correlating high power conversion efficiency of PTB7:PC<sub>71</sub>BM inverted organic solar cells with nanoscale structures†

Sanjib Das,<sup>a</sup> Jong K. Keum,<sup>\*b,c</sup> James F. Browning,<sup>c</sup> Gong Gu,<sup>a</sup> Bin Yang,<sup>b</sup> Ondrej Dyck,<sup>d</sup> Changwoo Do,<sup>c</sup> Wei Chen,<sup>e,f</sup> Jihua Chen,<sup>b</sup> Ilia N. Ivanov,<sup>b</sup> Kunlun Hong,<sup>b</sup> Adam J. Rondinone,<sup>b</sup> Pooran C. Joshi,<sup>g</sup> David B. Geohegan,<sup>b</sup> Gerd Duscher<sup>d</sup> and Kai Xiao<sup>\*b</sup>

Advances in material design and device engineering led to inverted organic solar cells (i-OSCs) with superior power conversion efficiencies (PCEs) compared to their “conventional” counterparts, in addition to the well-known better ambient stability. Here, we report an in-depth morphology study of the i-OSC active and cathode modifying layers, employing a model system with a well-established bulk-heterojunction, PTB7:PC<sub>71</sub>BM as the active layer and poly-[(9,9-bis(3′-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN) as the cathode surface modifying layer. We have also identified the role of a processing additive, 1,8-diiodooctane (DIO), used in the spin-casting of the active layer to increase PCE. Using various characterization techniques, we demonstrate that the high PCEs of i-OSCs are due to the diffusion of electron-accepting PC<sub>71</sub>BM into the PFN layer, resulting in improved electron transport. The diffusion occurs when residual solvent molecules in the spun-cast film act as a plasticizer. Addition of DIO to the casting solution results in more PC<sub>71</sub>BM diffusion and therefore more efficient electron transport. This work provides important insight and guidance to further enhancement of i-OSC performance by materials and interface engineering.

Organic solar cells (OSCs) have attracted tremendous attention as next-generation photovoltaics due to their potential for generating electricity at a low cost and compatibility with flexible

substrates required for roll-to-roll manufacturing.<sup>1–4</sup> In the past decade, various efforts such as thermal annealing,<sup>5,6</sup> solvent-vapor annealing,<sup>7,8</sup> use of processing additives<sup>9–11</sup> and solvent mixture,<sup>12,13</sup> material design,<sup>14</sup> and interface and band gap engineering<sup>15–17</sup> have been expended to improve the power conversion efficiencies (PCEs) of OSCs.<sup>18</sup>

Compared with the conventional organic solar cells (c-OSCs), where the hygroscopic and corrosive poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate acid) (PEDOT:PSS) hole transport layer and a low work function metal top electrode are detrimental to device lifetime, inverted organic solar cells (i-OSCs) exhibit significantly improved stability under ambient conditions by avoiding these major contributors to device degradation.<sup>19–22</sup> Despite the outstanding long-term device stability, however, early i-OSCs suffered from lower PCE as compared with c-OSCs.<sup>23,24</sup> Moreover, most early i-OSCs used n-type metal oxides such as TiO<sub>x</sub> as the hole blocking layer, requiring high-temperature sintering,<sup>24,25</sup> undesirable for flexible substrates preferred for roll-to-roll manufacturing. Most recently, a thin layer of conjugated polymer, poly [(9,9-bis(3′-(*N,N*-dimethylamino)propyl)-2,7-fluorene)-*alt*-2,7-(9,9-dioctylfluorene)] (PFN) (see Scheme S1, ESI†), was used as a surface modifier for the indium tin oxide (ITO) bottom electrode to drastically reduce the energetic misalignment between ITO and the active layer, resulting in ohmic contact between the two.<sup>26</sup> Beside achieving a record PCE of 9.2% and ambient device stability exceeding 60 days, the room-temperature, solution-processed PFN is favorable for flexible and large-scale roll-to-roll production.<sup>4</sup> These high-performance i-OSCs employed poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-*b*]thiophenediyl]] (PTB7) as the electron donor (ED) and [6,6]-phenyl C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) as the electron acceptor (EA). Further progress by synthesizing a new polymer semiconductor to replace PTB7 has demonstrated a record PCE exceeding 10% for this device architecture.<sup>27</sup>

Despite the above-mentioned progress, the morphological mechanism for the high PCE of these devices remains to be

<sup>a</sup>Department of Electrical Engineering and Computer Science, University of Tennessee, Knoxville, TN 37996, USA

<sup>b</sup>Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA. E-mail: keumjk@ornl.gov, xiaok@ornl.gov

<sup>c</sup>Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

<sup>d</sup>Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996, USA

<sup>e</sup>Materials Science Division, Argonne National Laboratory, Lemont, IL 60439, USA

<sup>f</sup>Institute for Molecular Engineering, The University of Chicago, Chicago, IL 60637, USA

<sup>g</sup>Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5nr03332b

investigated. Specifically, it has so far been unclear how the morphologies of the active layer and the active layer/PFN interface impact i-OSC operation and the associated efficiency. In this work, we focused our efforts on understanding how PFN interacts with PTB7 and PC<sub>71</sub>BM at the interface, affects the active layer morphologies, and enhances the PCEs of the i-OSCs. The lateral and vertical phase morphologies of PFN/PTB7:PC<sub>71</sub>BM were studied by a combination of neutron reflectometry (NR) and cross-section transmission electron microscopy (TEM). Grazing incidence wide-angle X-ray scattering (GIWAXS) was used to study the relative crystallinity and crystal orientation. In addition, small-angle neutron scattering (SANS) was used to study the precursor structures of PTB7 and PC<sub>71</sub>BM in the casting solution, as well as the effect of the solvent additive 1,8-diiodooctane (DIO). The obtained structural information was linked to measured device performance, provide important guidance to the design of more efficient i-OSCs.

Fig. 1a shows the current density *versus* voltage ( $J$ - $V$ ) characteristics for a typical solar cell of each of the following architecture-processing combinations: ITO/PFN (10 nm)/active layer/MoO<sub>3</sub>(8 nm)/Ag i-OSCs with and without a 3 wt% DIO additive in the PTB7:PC<sub>71</sub>BM-in-1,2-dichlorobenzene (DCB) solution for spin-casting the active layer; and ITO/PEDOT:PSS (40 nm)/active layer/Ca (15 nm)/Al c-OSCs with and without a 3 wt%

DIO additive when spin-casting the PTB7:PC<sub>71</sub>BM active layer. Detailed device fabrication is described in the ESI.† The device performance parameters, *i.e.*, short-circuit current density ( $J_{SC}$ ), open circuit voltage ( $V_{OC}$ ), fill factor (FF), and PCE, listed in Table 1 clearly show that i-OSCs with and without DIO exhibit higher PCEs than their c-OSC counterparts and that the DIO additive increases PCEs for both i-OSCs and c-OSCs. The superior performance of the i-OSCs is attributed to efficient charge extraction by the ITO cathode the effective work function of which is drastically modified by PFN.<sup>26,27</sup> Here, PTB7:PC<sub>71</sub>BM i-OSCs fabricated with 3 wt% DIO exhibit PCE as high as 9.3%, much higher than the c-OSCs fabricated using the same solution showing a maximum PCE of 7.2% (Fig. S1†). Also, the i-OSCs retain ~94% of their initial PCEs up to more than 26 days when stored in air while OSCs lose 30% of their initial PCE in just 5 days (Fig. S2†). The higher PCEs of i-OSCs, compared to those of c-OSCs, are due to their higher  $J_{SC}$  values, confirming that this is the result of efficient electron extraction. The external quantum efficiency (EQE) spectra of the same devices in Fig. 1a, recorded under short circuit conditions in air without encapsulations, are shown in Fig. 1b. The integrated  $J_{SC}$  values of i-OSCs, with and without DIO from EQE spectra, are 16.6 and 15.9 mA cm<sup>-2</sup>, respectively, while those of c-OSCs are 14.1

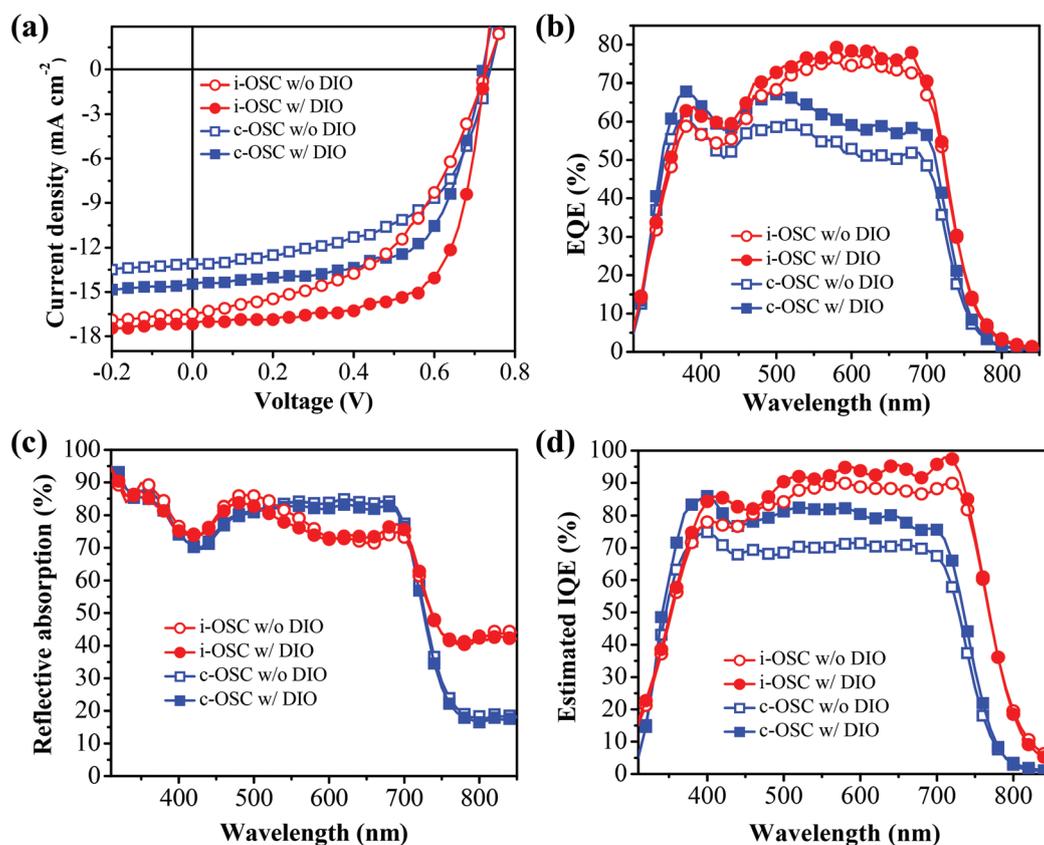


Fig. 1 (a)  $J$ - $V$  curves for devices with different architecture-processing combinations. (b) EQE spectra for the corresponding devices. (c) Reflective absorption spectra *versus* wavelength. (d) Estimated IQE calculated using the results from (b) and (c).

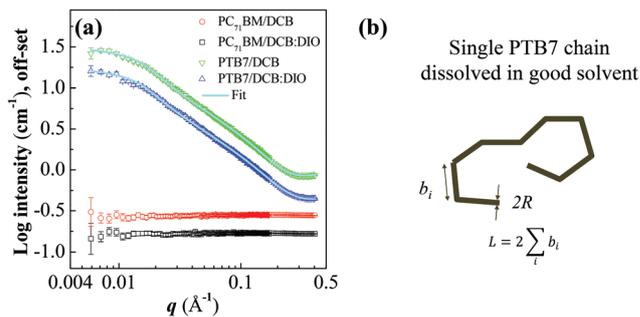
**Table 1** Summary of device performance parameters, *i.e.*,  $J_{SC}$ ,  $V_{OC}$ , FF, and PCE of the OPV devices based on PTB7:PC<sub>71</sub>BM (1:1.5) with or without DIO

Device type	$J_{SC}$ (mA cm <sup>-2</sup> )	$V_{OC}$ (V)	FF (%)	PCE <sub>avg</sub> <sup>a</sup> (%)	PCE <sub>max</sub> (%)
i-OSC w/o DIO	15.3	0.72	47.8	5.3 ± 0.3	5.8
i-OSC w/ DIO	16.9	0.72	67.0	8.2 ± 0.5	9.3
c-OSC w/o DIO	12.9	0.74	52.7	5.0 ± 0.3	5.5
c-OSC w/ DIO	14.4	0.72	62.3	6.5 ± 0.3	7.2

<sup>a</sup> Average PCE for each type was calculated from over 20 devices, measured under AM 1.5 G (100 mW cm<sup>-2</sup>) illumination.

and 12.4 mA cm<sup>-2</sup>, reasonably well-consistent with the  $J_{SC}$  values, measured from  $J$ - $V$  curves in an inert ambient. To estimate the internal quantum efficiency (IQE) spectra, the reflective absorption spectrum for each architecture-processing combination (Fig. 1c) was first measured mimicking the light absorption process in an actual device. Here it should be noted that IQE is defined as the percentage of absorbed photons that are converted into charges and collected at the electrodes at zero bias. The IQE spectra were recorded by following the procedures reported elsewhere.<sup>28,29</sup> Irrespective of the presence of DIO, i-OSCs show higher IQE compared to c-OSCs. The DIO additive increases the IQEs for both the i-OSCs and c-OSCs, and more importantly, the i-OSC using DIO shows an IQE approaching 95% in the 500–700 nm spectral range. In principle, the high IQE originates from highly efficient exciton generation and dissociation, and charge collection.

To understand the origin of the near-unity IQE, we employed a variety of characterization techniques to systematically examine the PTB7:PC<sub>71</sub>BM active film morphology in the i-OSCs as well as processing factors that influence the morphology. It has been shown that the initial precursor structures of electron donor (ED) and acceptor (EA) materials in the casting solution affect the crystallinity and phase morphology of the spun-cast films.<sup>30</sup> Here, we conducted small-angle neutron scattering (SANS) measurements on the PTB7 and PC<sub>71</sub>BM solutions in DCB with and without DIO to investigate the structure of PTB7 (ED) and PC<sub>71</sub>BM (EA) in the solutions, and the effect of DIO. As seen from the SANS curves in Fig. 2, both PC<sub>71</sub>BM solutions in DCB and DCB:DIO merely exhibit flat scattering features, implying complete dissolution. If PC<sub>71</sub>BM forms aggregates or clusters in the solutions, scattering features, showing an asymptotic decay in scattered intensity as a function of the scattering vector  $q$ , must be observed. Here, the scattering vector is defined as  $q = 4\pi \sin \theta / \lambda$ , where  $\lambda$  and  $\theta$  are the wavelength of the incident neutron beam and the half of scattering angle, respectively. The results are consistent with the previous work reported elsewhere by current authors showing complete dissolution of PC<sub>71</sub>BM in DCB and DCB:DIO.<sup>31</sup> We have noticed possibly contradicting results reported by Lou *et al.* based on the small-angle X-ray scattering (SAXS),<sup>32</sup> indicating that the added DIO selectively increases



**Fig. 2** (a) SANS patterns for PTB7/DCB, PTB7/DCB:DIO, PC<sub>71</sub>BM/DCB, and PC<sub>71</sub>BM/DCB:DIO solutions, where the solid lines indicate model fits by a flexible cylinder scattering model with an excluded volume effect. (b) Schematic illustration of a single PTB7 chain dissolved in DCB or DCB:DIO.

the solubility of PC<sub>71</sub>BM when mixed with the host solvent, chlorobenzene (CB). In the study, it was proposed that the added DIO selectively increases the solubility of PC<sub>71</sub>BM when mixed with CB, resulting in a reduced domain size of PC<sub>71</sub>BM in the spun-cast active layer. In our current and previous studies, however, used solvents, DCB and DCB:DIO are found to dissolve PC<sub>71</sub>BM at the molecular level. The different conclusions might come from the solubility difference between CB and DCB. On the other hand, the SANS patterns of PTB7 solutions in DCB and DCB:DIO appear totally different from those of PC<sub>71</sub>BM solutions. The SANS curves for PTB7 solutions were modeled using a worm-like chain model with an excluded volume effect under the assumption that PTB7 assumes a semi-rigid chain nature in good solvents. Since the SANS curves for both PTB7 solutions in DCB and DCB:DIO are almost identical within the error range, a single set of model parameters was applied to fit both curves. The fit parameters, including contour length ( $L$ ), Kuhn length ( $b_i$ ), and diameter ( $R$ ), are tabulated in Table 2. The  $L$  is about  $\sim 395$  Å, a molecular dimension much larger than that of PC<sub>71</sub>BM. The molecular diameter of PC<sub>71</sub>BM is known to be  $\sim 11$  Å.<sup>32</sup> It is apparent that the different scattering features of PTB7 and PC<sub>71</sub>BM solutions are due to their different molecular sizes and shapes. A schematic diagram showing the possible molecular conformation of PTB7 dissolved in the solvents is shown in Fig. 2b. The identical SANS curves for both PTB7 solutions indicate that the PTB7 chains have an identical swollen or dissolved state regardless of the presence of DIO. Therefore, the SANS results clearly demonstrate that the improved PCEs in both i-OSCs and c-OSCs do not originate from their initial precursor structures in solution.

In order to investigate the effect of the DIO additive on the phase morphology, the PTB7:PC<sub>71</sub>BM films spun-cast from solutions with and without DIO were sectioned using a focused ion beam (FIB), and the exposed cross-sections were imaged by energy-filtered transmission electron microscopy (EF-TEM). Fig. 3 shows the cross-section images of PFN/PTB7:PC<sub>71</sub>BM and PEDOT:PSS/PTB7:PC<sub>71</sub>BM with and without DIO, where the yellow and grey areas indicate PC<sub>71</sub>BM-rich and

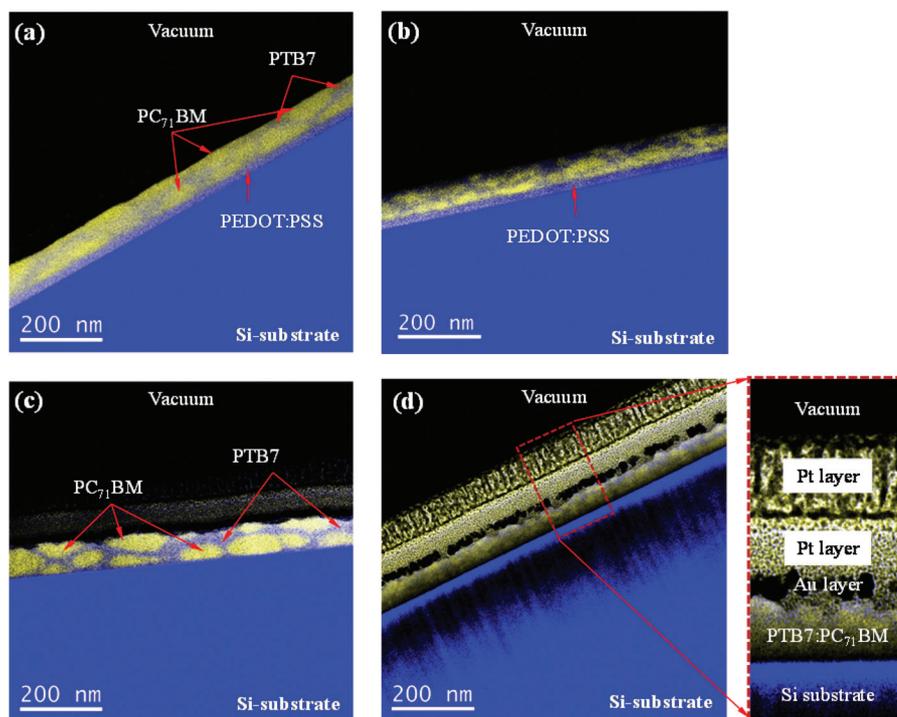
**Table 2** Parameters obtained from the model fits for PTB7 chains dissolved in DCB and DCB:DIO. Since SANS curves for PTB7/DCB and PTB7/DCB:DIO solutions are almost identical to each other with a negligible difference, the same fit parameters were used to fit the curves

	Contour length, $L$ (Å)	Kuhn length, $b_i$ (Å)	Radius, $R$ (Å)	Polydispersity
PTB7 in DCB & DCB:DIO	$395 \pm 5$	$183 \pm 3$	$10.7 \pm 0.3$	$0.089 \pm 0.035$

PTB7-rich regions, respectively. The films exhibit much reduced domain sizes when DIO is used as a processing additive, consistent with the results reported in the literature.<sup>9,33</sup> Nevertheless, in terms of the domain size of PC<sub>71</sub>BM, no clear difference between PFN/PTB7:PC<sub>71</sub>BM and PEDOT:PSS/PTB7:PC<sub>71</sub>BM films with or without DIO was identified, implying no significant effect of the substrate on the sizes of PTB7 and PC<sub>71</sub>BM domains. It is obvious that since the interfacial area between PTB7 and PC<sub>71</sub>BM increases with decreasing domain size, more efficient charge generation is possible as DIO is added to the casting solution resulting in smaller domains. It should be noted that no clear indication of the PFN layer is observed in the TEM images of PFN/PTB7:PC<sub>71</sub>BM regardless of the presence of DIO, while flat interfacial boundaries are clearly identified between PTB7:PC<sub>71</sub>BM and PEDOT:PSS layers in PEDOT:PSS/PTB7:PC<sub>71</sub>BM films both with and without DIO.

It is well known that no diffusion of PC<sub>71</sub>BM into the PEDOT:PSS layer occurs in spin-casting or thermal annealing,<sup>34</sup> which is indeed not preferable, since it would prevent the hole transport to the anode, giving rise to a reduction in PCE. The absence of the PFN layer in the EF-TEM images of the PFN/PTB7:PC<sub>71</sub>BM cross-sections is due to the intermixing between PC<sub>71</sub>BM and PFN, as will be shown in the following section.

To investigate the vertical phase morphologies, neutron reflectivity (NR) measurements were performed on PTB7:PC<sub>71</sub>BM films deposited onto PFN-coated substrates. Fig. 4a shows the experimental and fitted NR curves for PFN/PTB7:PC<sub>71</sub>BM films, which were prepared by spin-casting PTB7:PC<sub>71</sub>BM solutions with and without DIO on top of PFN films. As a reference, experimental and fit NR curves for an ~8 nm thick pristine PFN film are also included in Fig. 4a. Fitting to the experimental NR curves were performed using Parratt formalism,<sup>35</sup> from which the obtained neutron scattering length density (SLD) distributions and the composition distributions of PC<sub>71</sub>BM ( $V_{PC_{71}BM}$ ), calculated from the SLD distributions, are depicted in Fig. 4b and c, respectively.  $V_{PC_{71}BM}$  of each layer was calculated using eqn (S1) and (S2), shown in the ESI.† As seen in Fig. 4b, the PFN film consists of two layers with different SLDs, *i.e.*,  $\rho_{PFN} = 0.83 \times 10^{-6}$  and  $1.14 \times 10^{-6} \text{ \AA}^{-2}$ . This could be due to the phase separation of copolymeric PFN, where the higher SLD could be due to the enrichment of poly[[9,9-bis(3'-(*N,N*-dimethylamino)propyl)-2,7-fluorene]] with a short side chain, and the lower SLD to that of poly[2,7-(9,9-dioctylfluorene)] with its long alkyl side chain. The SLDs of



**Fig. 3** Cross-section TEM images of PEDOT:PSS/PTB7:PC<sub>71</sub>BM films (a) without and (b) with 3 wt% DIO; and PFN/PTB7:PC<sub>71</sub>BM films (c) without and (d) with 3 wt% DIO.

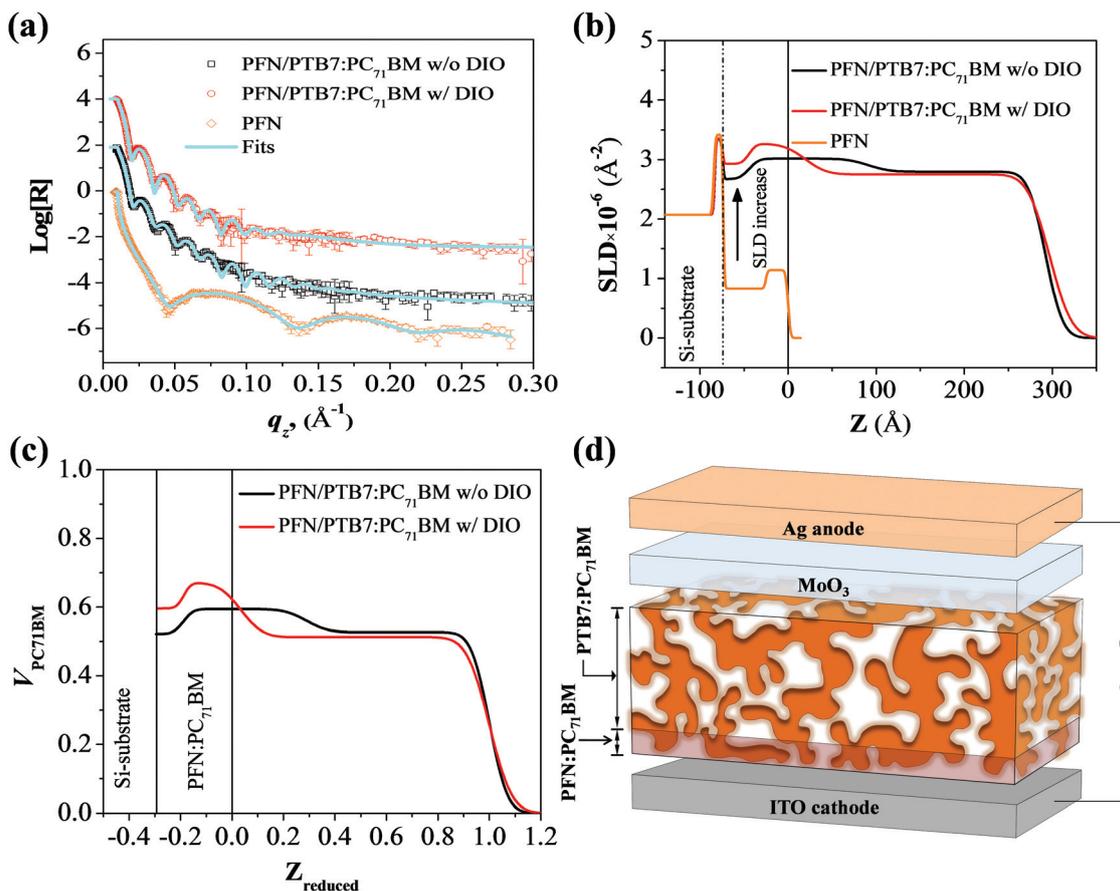


Fig. 4 (a) Experimental and modeled NR curves for PFN/PTB7:PC<sub>71</sub>BM films with and without DIO. (b) The SLD profiles used to fit the NR curves shown in (a). (c) Volume fraction profiles of PC<sub>71</sub>BM vs. reduced distance from the substrate, calculated from the SLD profiles shown in (b). (d) Schematic illustration showing how PC<sub>71</sub>BM diffuses into the PFN layer.

PFN layers increase drastically after spin-casting PTB7:PC<sub>71</sub>BM. In the film spun-cast without DIO, the SLDs of PFN layers increase from  $\rho_{\text{PFN}} = 0.83 \times 10^{-6}$  and  $1.14 \times 10^{-6} \text{ \AA}^{-2}$  to  $2.67 \times 10^{-6}$  and  $3.02 \times 10^{-6} \text{ \AA}^{-2}$ , respectively. With DIO, the PFN SLDs increase even more to  $2.93 \times 10^{-6}$  and  $3.26 \times 10^{-6} \text{ \AA}^{-2}$ . Since the increased SLDs of PFN after spin-casting are higher than those of PTB7 ( $\rho_{\text{PTB7}} = 1.26 \times 10^{-6} \text{ \AA}^{-2}$ ) and PFN ( $\rho_{\text{PFN}} = 0.83 \times 10^{-6}$  and  $1.14 \times 10^{-6} \text{ \AA}^{-2}$ ), the increases in SLDs can only be attributed to the diffusion of high-SLD PC<sub>71</sub>BM. The SLD of PC<sub>71</sub>BM is  $\rho_{\text{PC}_{71}\text{BM}} = 4.34 \times 10^{-6} \text{ \AA}^{-2}$  as shown in Fig. S3 and 4.† The calculated  $V_{\text{PC}_{71}\text{BM}}$ , with the PFN layer underneath, using eqn (S2),† are 0.52 and 0.59 in PFN/PTB7:PC<sub>71</sub>BM without using DIO, and are 0.60 and 0.67 with DIO. The diffusion of PC<sub>71</sub>BM into the PFN layer occurs when the residual solvent molecules (DCB or DCB:DIO) that remain in the films act as plasticizers and make PC<sub>71</sub>BM molecules mobile. Based on the TEM cross-section images (Fig. 3) and NR results (Fig. 4), a schematic illustration of the i-OSC active layer morphology is depicted in Fig. 4d. Here, the diffusion of PC<sub>71</sub>BM into PFN layers has a very important implication on the device efficiency, since it can alter the process of electron transport. That is, the diffusion of PC<sub>71</sub>BM into PFN layers and the phase-separated domain formation of PC<sub>71</sub>BM can

produce much more interfacial contacts between PC<sub>71</sub>BM and PFN. Also, the increased PC<sub>71</sub>BM diffusion induced by the added DIO facilitates even more interfacial contacts between PC<sub>71</sub>BM and PFN, resulting in a more efficient electron transport to the cathode and electron collection.

In order to confirm the aforementioned hypothesis, PTB7:PC<sub>71</sub>BM solutions in DCB with and without DIO were spun-cast onto bare quartz substrates and dried completely, followed by PFN spin-casting. The measured and fitted NR curves for PTB7:PC<sub>71</sub>BM/PFN films spun-cast with and without DIO are depicted in Fig. 5a, from which the acquired SLD and  $V_{\text{PC}_{71}\text{BM}}$  distributions are shown in Fig. 5b and c, respectively. As can be seen in Fig. 5b, the SLDs of PFN layers in both PTB7:PC<sub>71</sub>BM/PFN films remain unchanged compared to that of pristine PFN films. Also, the SLDs of PTB7:PC<sub>71</sub>BM layers in PTB7:PC<sub>71</sub>BM/PFN films with and without DIO are identical to those of PTB7:PC<sub>71</sub>BM-only films (Fig. S3†). The results reveal that the diffusion of PC<sub>71</sub>BM does not occur in PTB7:PC<sub>71</sub>BM/PFN films, since no DCB or DCB:DIO remains in the film. The film probably contains residual methanol after spin-casting PFN solution (in methanol), however, methanol is a non-solvent for PC<sub>71</sub>BM, and hence it cannot act as a plasticizer for PC<sub>71</sub>BM diffusion.

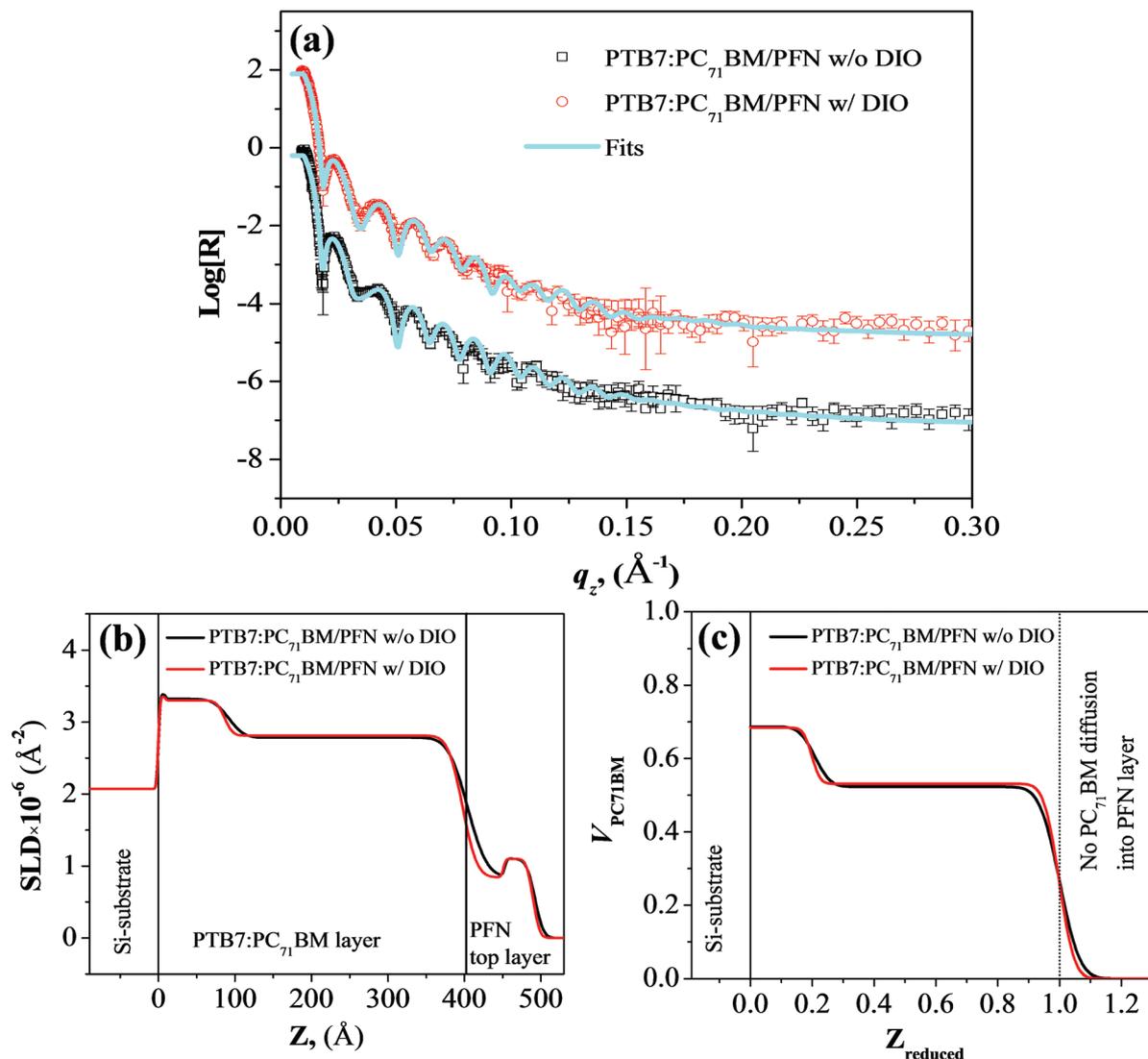


Fig. 5 (a) Experimental and modeled NR curves for PTB7:PC<sub>71</sub>BM/PFN films with and without DIO. (b) The SLD profiles used to fit the NR curves shown in (a). (c) Volume fraction profiles of PC<sub>71</sub>BM vs. reduced distance from the substrate, calculated from the SLD profiles shown in (b).

Two-dimensional (2D) grazing-incidence wide-angle X-ray scattering (GIWAXS) was used to obtain insights into the global orientation, molecular packing, and crystallinity of PTB7, as well as the aggregation of PC<sub>71</sub>BM. A 2D GIWAXS pattern for PFN/PTB7 is first shown in Fig. 6a. Here,  $q_y$  is the in-plane scattering vector given by  $q_y = 2\pi/\lambda_x[\sin(\psi)\cos(\alpha_f)]$ , where  $\lambda_x$ ,  $\psi$ , and  $\alpha_f$  are the wavelength, in-plane exit angle, and out-of-plane exit angle, respectively. In the 2D GIWAXS pattern, the in-plane reflection arcs discerned at  $q_y = 0.283 \pm 0.008 \text{ \AA}^{-1}$  ( $d$ -spacing = 22.2  $\text{\AA}$ ) are due to the (100) planes of PTB7 crystals. A broad out-of-plane reflection arc was also observed at  $q_z = 1.56 \pm 0.05 \text{ \AA}^{-1}$  ( $d$ -spacing = 4.1  $\text{\AA}$ ), which is indexed by (010) reflection. The broad in-plane (100) and out-of-plane (010) reflection indicates that the planes of PTB7 aromatic backbones are roughly aligned parallel to the surface plane of the substrate with the alkyl side chains directed toward the in-plane direction. This orientation is the so-called ‘face-on’

orientation of PTB7 crystals. While the face-on orientation of PTB7 crystals is desired for high PCE, it is not the case in the blend films as addressed in the 2D GIWAXS patterns depicted in Fig. 6b and c. In the 2D patterns of the blend films, the observed (100) reflection rings imply random orientation of PTB7 crystals. The broad reflection halos centered at  $q \approx 1.37 \text{ \AA}^{-1}$  ( $d$ -spacing = 4.7  $\text{\AA}$ ), on the other hand, are attributed to the short range ordering of randomly oriented PC<sub>71</sub>BM crystals, *i.e.*, (311) reflection. The random orientation of PTB7 and PC<sub>71</sub>BM crystals could possibly implicate that the growth process of oriented PTB7 and PC<sub>71</sub>BM crystals is impeded by each other during the film formation process. One of the most notable features (Fig. 6d) is that the in-plane GIWAXS slices for PFN/PTB7:PC<sub>71</sub>BM films cast with and without DIO almost overlap with each other, indicating the same degree of crystallinity. Our results are in agreement with previous reports.<sup>33,36</sup> More importantly, the result indicates that the improved PCEs

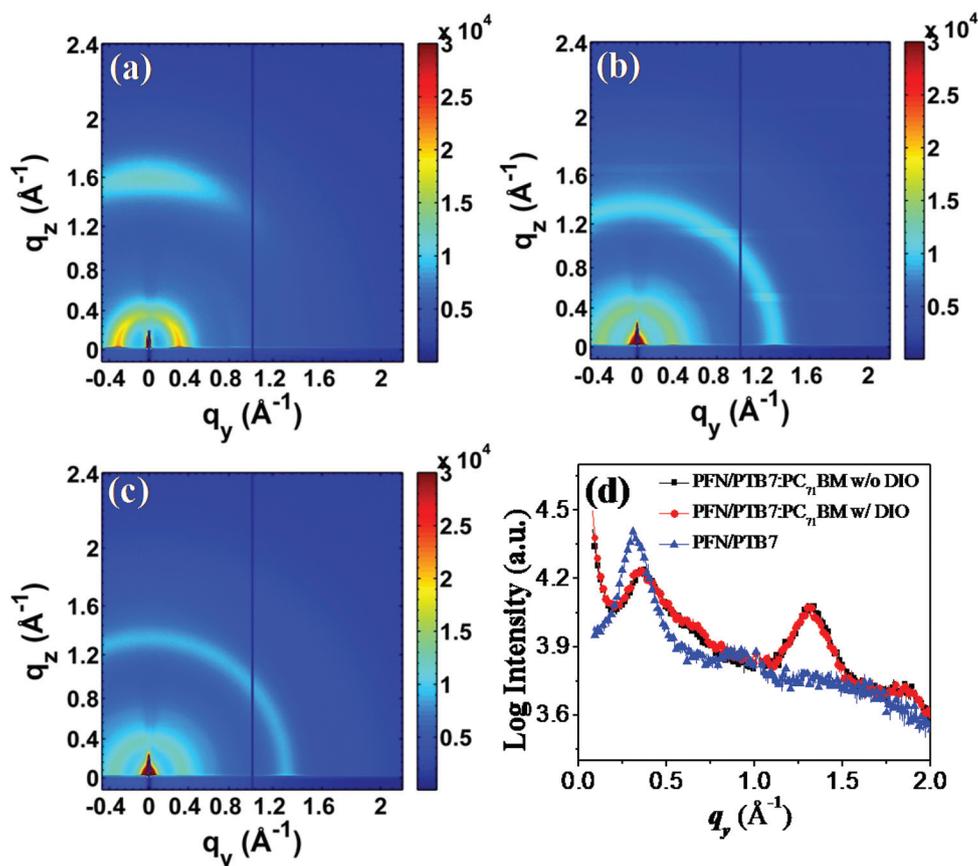


Fig. 6 2D GIWAXS patterns of (a) PFN/PTB7, (b) PFN/PTB7:PC<sub>71</sub>BM without DIO, and (c) PFN/PTB7:PC<sub>71</sub>BM with DIO films. (d) In-plane GIWAXS profiles extracted from the respective 2D GIWAXS patterns.

resulted from the DIO additive in neither the i-OSCs nor the c-OSCs based on PTB7:PC<sub>71</sub>BM active layers are related to crystallinity and orientation morphology.

In summary, the nanoscale structural aspects of high PCE of PTB7:PC<sub>71</sub>BM i-OSCs using PFN as the ITO modifier were investigated. SANS results of PTB7 and PC<sub>71</sub>BM solutions indicate that both PTB7 and PC<sub>71</sub>BM remain in completely dissolved states in both pristine DCB and DCB:DIO; no effect of DIO on the solution morphologies was identified. In the spun-cast films, however, DIO was found to play a vital role in the morphological evolution occurring during the film formation process after spin-casting. In both i-OSCs and c-OSCs, the DIO added to the casting solutions induces the formation of much smaller PTB7 and PC<sub>71</sub>BM domains, which was revealed by cross-section TEM. The formation of smaller PC<sub>71</sub>BM domains forms the basis for more efficient exciton transport to the PTB7/PC<sub>71</sub>BM interface and more effective charge separation at the interface. In i-OSCs, PC<sub>71</sub>BM was found to diffuse into the PFN layer as the casting solutions are spun-cast on top of the PFN layer, where more PC<sub>71</sub>BM diffusion occurs when DIO is added to the casting solutions. The increased PC<sub>71</sub>BM diffusion into the PFN layer increases the interfacial contact between PC<sub>71</sub>BM and PFN, and hence improves electron transport and collection at the cathode, increasing the PCE.

## Acknowledgements

This research was conducted at the Center for Nanophase Materials Sciences (CNMS) and Spallation Neutron Source (SNS), which are sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, U.S. Department of Energy. Work by Wei Chen was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division. This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

## References

- 1 M. Kaltenbrunner, M. S. White, E. D. Głowacki, T. Sekitani, T. Someya, N. S. Sariciftci and S. Bauer, *Nat. Commun.*, 2012, **3**, 770.
- 2 Z. Liu, J. Li and F. Yan, *Adv. Mater.*, 2013, **25**, 4296–4301.
- 3 S. I. Na, S. S. Kim, J. Jo and D. Y. Kim, *Adv. Mater.*, 2008, **20**, 4061–4067.

- 4 B. Zhao, Z. He, X. Cheng, D. Qin, M. Yun, M. Wang, X. Huang, J. Wu, H. Wu and Y. Cao, *J. Mater. Chem. C*, 2014, **2**, 5077–5082.
- 5 G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery and Y. Yang, *Nat. Mater.*, 2005, **4**, 864–868.
- 6 W. Ma, C. Yang, X. Gong, K. Lee and A. J. Heeger, *Adv. Funct. Mater.*, 2005, **15**, 1617–1622.
- 7 T. A. Bull, L. S. Pingree, S. A. Jenekhe, D. S. Ginger and C. K. Luscombe, *ACS Nano*, 2009, **3**, 627–636.
- 8 J. D. Zimmerman, X. Xiao, C. K. Renshaw, S. Wang, V. V. Diev, M. E. Thompson and S. R. Forrest, *Nano Lett.*, 2012, **12**, 4366–4371.
- 9 Y. Liang, Z. Xu, J. Xia, S. T. Tsai, Y. Wu, G. Li, C. Ray and L. Yu, *Adv. Mater.*, 2010, **22**, E135–E138.
- 10 F. Etzold, I. A. Howard, N. Forler, A. Melnyk, D. Andrienko, M. R. Hansen and F. Laquai, *Energy Environ. Sci.*, 2015, **8**, 1511–1522.
- 11 S. V. Kesava, Z. Fei, A. D. Rimshaw, C. Wang, A. Hexemer, J. B. Asbury, M. Heeney and E. D. Gomez, *Adv. Energy Mater.*, 2014, **4**, 1400116.
- 12 F. Zhang, K. G. Jespersen, C. Bjoerstroem, M. Svensson, M. R. Andersson, V. Sundström, K. Magnusson, E. Moons, A. Yartsev and O. Inganäs, *Adv. Funct. Mater.*, 2006, **16**, 667–674.
- 13 L. Ye, S. Zhang, W. Ma, B. Fan, X. Guo, Y. Huang, H. Ade and J. Hou, *Adv. Mater.*, 2012, **24**, 6335–6341.
- 14 Y. Liu, J. Zhao, Z. Li, C. Mu, W. Ma, H. Hu, K. Jiang, H. Lin, H. Ade and H. Yan, *Nat. Commun.*, 2014, **5**.
- 15 A. T. Yiu, P. M. Beaujuge, O. P. Lee, C. H. Woo, M. F. Toney and J. M. Fréchet, *J. Am. Chem. Soc.*, 2012, **134**, 2180–2185.
- 16 H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu and G. Li, *Nat. Photonics*, 2009, **3**, 649–653.
- 17 K.-H. Tu, S.-S. Li, W.-C. Li, D.-Y. Wang, J.-R. Yang and C.-W. Chen, *Energy Environ. Sci.*, 2011, **4**, 3521–3526.
- 18 M. A. Green, K. Emery, Y. Hishikawa, W. Warta and E. D. Dunlop, *Prog. Photovoltaics: Res. Appl.*, 2015, **23**, 1–9.
- 19 Z. Xu, L. M. Chen, G. Yang, C. H. Huang, J. Hou, Y. Wu, G. Li, C. S. Hsu and Y. Yang, *Adv. Funct. Mater.*, 2009, **19**, 1227–1234.
- 20 C.-H. Hsieh, Y.-J. Cheng, P.-J. Li, C.-H. Chen, M. Dubosc, R.-M. Liang and C.-S. Hsu, *J. Am. Chem. Soc.*, 2010, **132**, 4887–4893.
- 21 M. T. Dang, L. Hirsch and G. Wantz, *Adv. Mater.*, 2011, **23**, 3597–3602.
- 22 S. K. Hau, H.-L. Yip, N. S. Baek, J. Zou, K. O'Malley and A. K.-Y. Jen, *Appl. Phys. Lett.*, 2008, **92**, 253301.
- 23 C. Waldauf, M. Morana, P. Denk, P. Schilinsky, K. Coakley, S. Choulis and C. Brabec, *Appl. Phys. Lett.*, 2006, **89**, 233517.
- 24 S. K. Hau, H.-L. Yip, O. Acton, N. S. Baek, H. Ma and A. K.-Y. Jen, *J. Mater. Chem.*, 2008, **18**, 5113–5119.
- 25 C. Tao, S. Ruan, X. Zhang, G. Xie, L. Shen, X. Kong, W. Dong, C. Liu and W. Chen, *Appl. Phys. Lett.*, 2008, **93**, 193307.
- 26 Z. He, C. Zhong, S. Su, M. Xu, H. Wu and Y. Cao, *Nat. Photonics*, 2012, **6**, 591–595.
- 27 Z. He, B. Xiao, F. Liu, H. Wu, Y. Yang, S. Xiao, C. Wang, T. P. Russell and Y. Cao, *Nat. Photonics*, 2015, **9**, 174–179.
- 28 B. Yang, Y. Yuan and J. Huang, *J. Phys. Chem. C*, 2014, **118**, 5196–5202.
- 29 O. E. Semonin, J. M. Luther, S. Choi, H.-Y. Chen, J. Gao, A. J. Nozik and M. C. Beard, *Science*, 2011, **334**, 1530–1533.
- 30 J. K. Keum, K. Xiao, I. N. Ivanov, K. Hong, J. F. Browning, G. S. Smith, M. Shao, K. C. Littrell, A. J. Rondinone, E. A. Payzant, J. Chen and D. K. Hensley, *CrystEngComm*, 2013, **15**, 1114–1124.
- 31 M. Shao, J. K. Keum, R. Kumar, J. Chen, J. F. Browning, S. Das, W. Chen, J. Hou, C. Do, K. C. Littrell, A. Rondinone, D. B. Geohegan, B. G. Sumpter and K. Xiao, *Adv. Funct. Mater.*, 2014, **24**, 6647–6657.
- 32 S. J. Lou, J. M. Szarko, T. Xu, L. Yu, T. J. Marks and L. X. Chen, *J. Am. Chem. Soc.*, 2011, **133**, 20661–20663.
- 33 M. R. Hammond, R. J. Kline, A. A. Herzing, L. J. Richter, D. S. Germack, H.-W. Ro, C. L. Soles, D. A. Fischer, T. Xu, L. Yu, M. F. Toney and D. M. DeLongchamp, *ACS Nano*, 2011, **5**, 8248–8257.
- 34 H. Lu, B. Akgun and T. P. Russell, *Adv. Energy Mater.*, 2011, **1**, 870–878.
- 35 L. G. Parratt, *Phys. Rev.*, 1954, **95**, 359.
- 36 B. A. Collins, Z. Li, J. R. Tumbleston, E. Gann, C. R. McNeill and H. Ade, *Adv. Energy Mater.*, 2013, **3**, 65–74.