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ARTICLE TYPE

Enhanced Crystalline Morphology of a Ladder-Type Polymer Bulk-Heterojunction Device by Blade-Coating

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A blade-coating process was employed to fabricate bulk-heterojunction (BHJ) polymer solar cells based on a ladder-type polymer (PIDT-PhanQ) with low crystallinity. Compared to the devices processed by conventional spin-coating method, an intriguing morphology with enhanced phase-separation and increased crystallinity was achieved. As a result, power conversion efficiency up to 7.25 % could be achieved from the blade-coated PIDT-PhanQ:PC₇₁BM BHJ film, surpassing the original value obtained by spin-coating (6.29 %). This improved photovoltaic performance is attributed to the improved charge carrier mobilities, which correlates well with the increased crystallinity and organized network of the donor-acceptor phases that produce efficient charge-transporting pathways.

Bulk-heterojunction polymer solar cells (BHJ PSCs) typically consist of a blend of conjugated polymer (electron-donor (D)) and fullerene derivative (electron-acceptor (A)) have attracted significant attention in recent years due to their low-cost, flexibility, and solution processability.¹⁻⁵ The performance of a BHJ PSC has been shown to be strongly dependent upon the interpenetrating networks formed within the BHJ active layer.⁶ The bicontinuous, nanoscale domains comprising the BHJ morphology provide sufficient D-A interfaces for efficient exciton dissociation under illumination while the interconnectivity of the domains of each phase facilitates the hole/electron transport to the collecting electrodes.⁷ The photovoltaic characteristics of certain BHJ films with identical compositions can vary largely by processing with different methods. Thus, the optimization of the active layer morphology is very important for improving device performance.⁸

To date, many high-efficiency, crystalline conjugated polymers have been reported.⁹ However, their photovoltaic performance depends strongly on the processing conditions, such as the use of additives or post-annealing treatments, that have been used to promote molecular ordering and the size scale of the phase-separated BHJ domains so as to optimize charge separation and transport.

We recently have developed a series of indacenodithiophene (IDT)-based ladder-type donor polymers by copolymerizing with different types of acceptors. While the spin-coated devices yielded excellent photovoltaic performance, aforementioned treatments are not very effective due to the low degree of crystallinity in these polymers.¹⁰⁻¹¹ Consequently, we have focused on varying processing conditions prior to complete solvent removal to enhance the performance of these polymers. Here, we report a simple but very effective approach to control the nanoscale phase-separation of BHJ active layers from poly(indacenodithiophene-co-phananthrene-quinoline) (PIDT-PhanQ), and enhance the performance of the PSC derived from it. Consistent with previous studies, the PIDT-PhanQ:[6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) BHJ films processed by a conventional spin-coating method exhibited a power conversion efficiency (PCE) of ~6.30 %.^{10c-e} However, an enhanced PCE up to 7.25 % could be achieved by using blade-coating process to increase the crystallinity of the PIDT-PhanQ. The increased crystallinity is a consequence of the slower solvent evaporation that enables phase-separation of the PIDT-PhanQ, promoting the percolation of the nanoscale domains, creating charge-transporting pathways to enhance device performance.¹²

The chemical structure of PIDT-PhanQ and the corresponding energy level diagram of the components used are shown in **Figure 1**. The device configuration employed in this study consists of ITO/PEDOT:PSS/PIDT-PhanQ:PC₇₁BM/C₆₀-bis/Ag (ITO: indium tin oxide, PEDOT:PSS: poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), C₆₀-bis: fulleropyrrolidinium iodide and Ag (silver)). Detailed information of device fabrication is described in Supplementary Information. Studies were performed on active layers spin-coated in a N₂-filled glove-box and blade-coated in ambient conditions. The photovoltaic performances of the fabricated devices were tested under AM 1.5G illumination at 100 mW cm⁻². The relevant photovoltaic parameters, including open circuit voltage (V_{OC}), fill factor (FF), short circuit current (J_{SC}), and PCE, are summarized in **Table 1**.

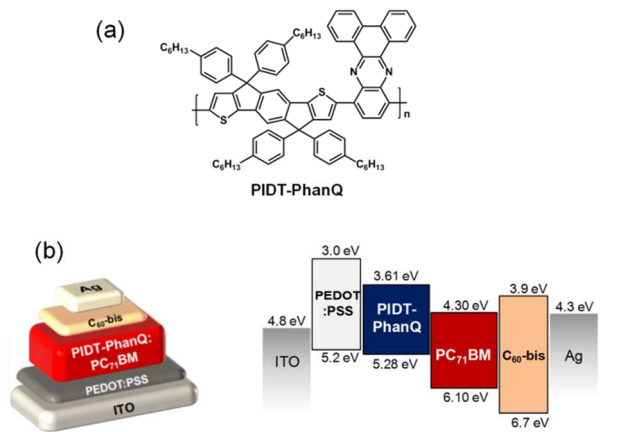


Figure 1. (a) Chemical structure of PIDT-PhanQ, and (b) device structure with the corresponding energy level diagram.

Table 1. Summary of performance of spin- and blade-coated PIDT-PhanQ:PC₇₁BM solar cell devices with different fabrication methods.

Coating method	V_{OC} (V)	J_{SC} (mA cm ⁻²)	FF	PCE (%)
Spin-coating (inert glove-box)	0.87±0.01	10.93±0.10	0.66±0.01	6.25±0.08
Blade-coating (ambient)	0.87±0.01	12.02±0.21	0.68±0.01	7.08±0.10

Interestingly, the PSCs fabricated by different coating methods showed significantly different characteristics as shown in the current density (J)–voltage (V) curves (**Figure 2(a)**). The V_{OC} , FF, J_{SC} , and PCE of spin- and blade-coated PSCs are 0.87 V, 0.66, 10.95 mA cm⁻², 6.29 % and 0.88 V, 0.69, 11.94 mA cm⁻², and 7.25 %, respectively. The blade-coated device showed enhancements in the J_{SC} and FF of 9.04 and 4.55 %, respectively, as the consequence of an improved charge transport in the device.^{9,13} The external quantum efficiency (EQE) spectra, shown in **Figure 2(b)**, also show more efficient photon-to-electron conversion in the blade-coated device in comparison to the spin-coated one.

To understand the underlying reasons for the enhanced photovoltaic performance of the blade-coated device, the morphologies of the BHJ films were characterized by atomic force microscopy (AFM) and transmission electron microscopy (TEM). Shown in **Figure 3(a, b)** are the topographic images of the spin- and blade-coated BHJ films, respectively. Distinct differences are evident. The blade-coated PhanQ:PC₇₁BM BHJ film showed a well-defined nanoscale phase-separated morphology. The root-mean-square (rms) roughness of the blade-coated BHJ film is 1.3 nm, which is comparable to that of the spin-coated film (0.6 nm).

Since the AFM probes only the surface of the film, TEM was used to investigate the morphology in the interior of the film (**Figures 3 (c, d)**). The TEM results are consistent with the AFM results where, for the blade-coated film, a well-defined, nano-phase-separated morphology was evident throughout the film.

Further insight into the origin of the enhanced phase-separation in the blade-coated films was obtained by grazing

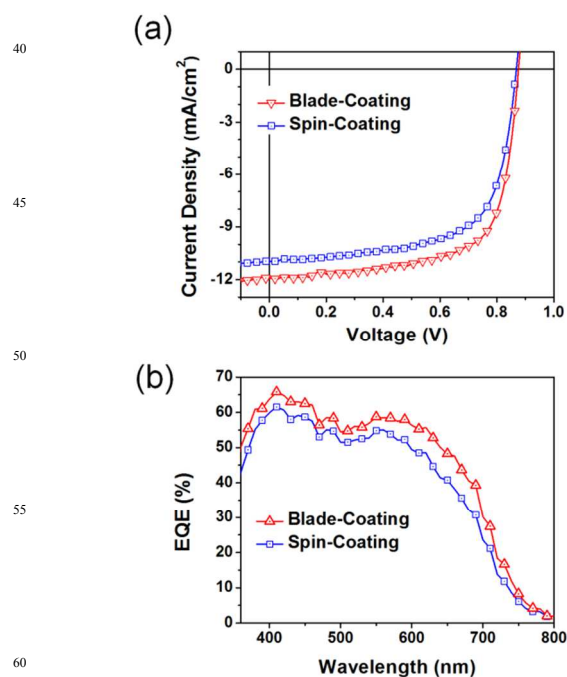


Figure 2. (a) Current density–voltage curves and (b) external quantum efficiency of the spin- (triangles) and the blade-coated (squares) solar cells.

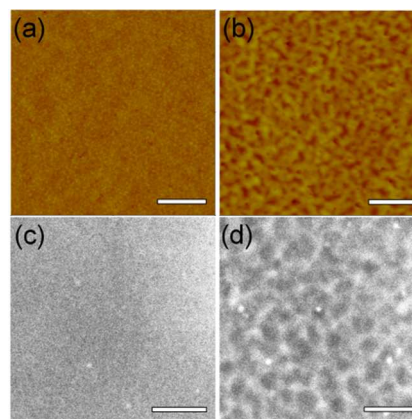


Figure 3. Atomic force microscopy images of (a) spin-coated and (b) blade-coated films, and transmission electron microscopy images of (c) spin-coated and (d) blade-coated films (scale bar: 1 μ m (a, b) and 400 nm (c, d)).

incidence X-ray diffraction (GIXD). Shown in **Figures 4a and 4b** are the 2D GIXD profiles for the spin-coated and blade-coated films. A qualitative examination of these profiles shows that the blade-coated films are more ordered than the spin-coated films and the ring of scattering arising from PC₇₁BM is sharper and more intense. Line profile of the spin-coated film shows only a diffuse halo arising from the liquid-like packing of the PC₇₁BM at $q_{xy}=1.34 \text{ \AA}^{-1}$, while in the plane of the film a weak (100) reflection from the separation distance between adjacent PIDT-PhanQ chain is observed. However, the blade-coated film exhibits a well-defined (100) reflection at 0.40 \AA^{-1} and a (200) reflection at 0.66 \AA^{-1} , corresponding to a d -spacing of 15.70 \AA . In addition, a well-defined shoulder at 1.95 \AA^{-1} , corresponding to the π - π stacking between PIDT-PhanQ chains is seen. There is no strong

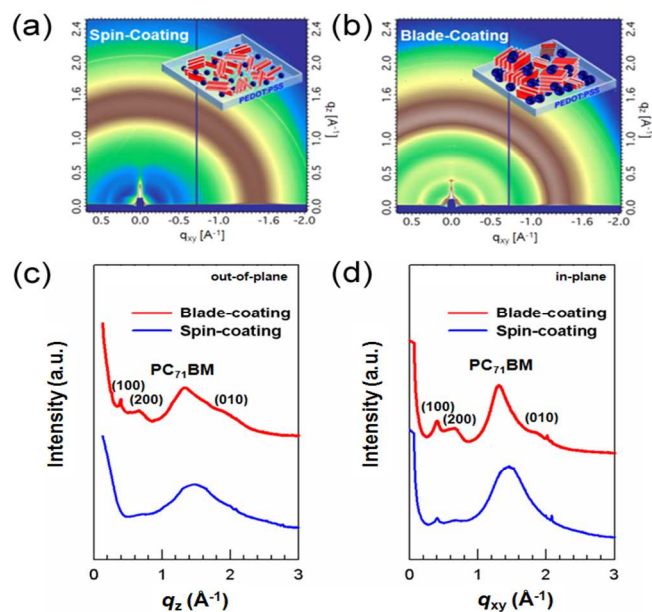


Figure 4. 2D-GIXD pattern images of (a) spin-coated and (b) blade-coated films (insets: schematic illustration of orientation of PIDT-PhanQ and PC71BM crystallites). (c) Out-of-plane and (d) in-plane GIXD spectra of spin-coated and blade-coated PIDT-PhanQ:PC71BM bulk-heterojunction films.

azimuthal dependence to these reflections, indicating a random orientation of PIDT-PhanQ crystallites. Moreover, diffraction of PC71BM corresponding to d -spacing of 4.68 Å was found to be sharper and more intense for the blade-coated film, suggesting a better defined phase-separated morphology and more densely packed PC71BM in the blade-coated BJJ film.¹⁴

From the combined AFM, SEM and GIXD measurements, it can be concluded that the blade-coated PIDT-PhanQ:PC71BM BJJ film exhibits better-ordered PIDT-PhanQ and PC71BM domains, while the spin-coated film has a poorly defined phase-separated morphology with much less order and crystallinity. The increased crystallinity and better defined phase-separated morphology of the blade-coated film will promote the formation of percolated pathways that will enhance charge separation, hole/electron transport to the electrodes and device performance.

The charge-transporting properties were examined by measuring the space charge limited current (SCLC) charge carrier mobilities in the BJJ layers to confirm the effect of phase-separation and increased crystallinity.¹⁵ Hole-only (ITO/PEDOT:PSS/PIDT-PhanQ:PC71BM/MoO₃/Ag) and electron-only (ITO/ZnO/PIDT-PhanQ:PC71BM/Ca/Al) devices were fabricated by spin- and blade-coating and their corresponding J - V curves are shown in **Figure 5**. The BJJ film processed by blade-coating showed higher hole ($8.6 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and electron ($3.0 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) mobility values than those of the spin-coated film where hole and electron mobility values of 3.3×10^{-3} and $1.9 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively, were measured. Due to the enhanced crystalline ordering of the blade-coated films, continuous charge carrier pathways are readily

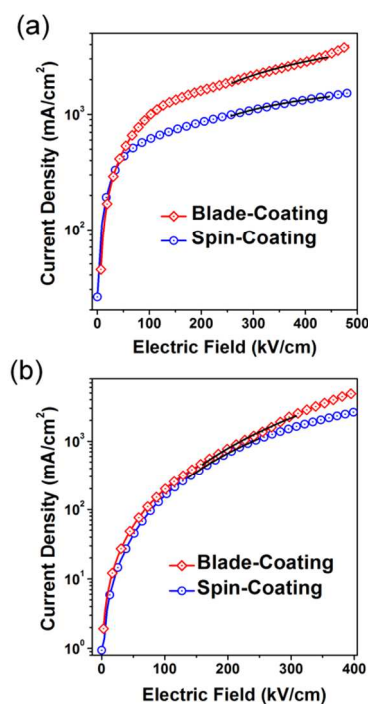


Figure 5. Current density–electric field curves of (a) hole-only and (b) electron-only devices based on PIDT-PhanQ:PC71BM films processed by spin-coating (circles) and blade-coating (diamonds) (black solid lines are fitted curves using a space charge limited current model).

facilitated in BJJ film, correspondingly resulting in the improved charge carrier transport as well as the enhanced device performance in the blade-coated devices.

Conclusions

In conclusion, we have demonstrated a simple but effective route to promote the nanoscale phase-separation and crystallization in BJJ made of PIDT-PhanQ:PC71BM. The enhanced crystallinity in the BJJ film can be attributed to the reduced rate of solvent evaporation during blade-coating that enables the PIDT-PhanQ:PC71BM to phase-separate into interconnected nanoscopic domains with more order. Consequently, devices with improved charge-transporting properties and PCEs up to 7.25 % could be achieved without post-treatment, surpassing ~6.30 % PCE characteristic of spin-coated devices. These results indicate that photovoltaic properties of polymer-based BJJ films can be effectively improved by engineering the morphology as it is produced from solution. The results shown here also demonstrate that blade-coating can be a very beneficial route for the future development of high-performance roll-to-roll printed solar cells.

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Notes and references

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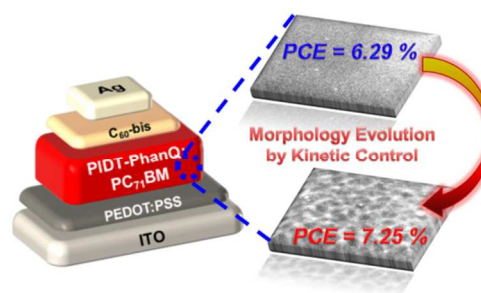
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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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- Bulk-heterojunction film based on PIDT-PhanQ and PC₇₁BM exhibits exceptional nanoscale phase-separation with increased domain crystallinity by blade-coating, resulting in significantly enhanced photovoltaic performance as compared to the device processed by conventional spin-coating.