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Effect of Addition of a Diblock Copolymer on Blend Morphology and Performance of Poly(3-hexylthiophene):Perylene Diimide Solar Cells

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Organic photovoltaic devices are being pursued as a compromise between efficiencies of cost and power conversion. Bulk heterojunction devices that utilize blends of poly(3-hexylthiophene) (P3HT) and the C_{60} derivative PCBM have recently yielded efficiencies between 4 and 5%.[1] Significant effort has been devoted to raising these efficiencies by improving the absorption profile of the blend, usually by substituting P3HT with a low bandgap polymer that absorbs in the red and near IR.[2] An alternative approach is to replace the fullerene component with an electron transporting small molecule that has improved light absorption in the visible range. This is especially attractive since the fullerene content in many devices with the best efficiencies can be as high as 80% by mass.[1b,2a] Derivatives of perylene tetracarboxydiimide (PDI) are good candidates for substitution in place of PCBM, as they are known to form crystalline domains with high electron mobilities when blended with polymers.[3] However, solar cells comprised of blends of PDI and P3HT exhibit low external power conversion efficiencies, generally just below 0.2%.[4] This is possibly attributable to the formation of micrometer-sized PDI crystals upon annealing, resulting in incomplete exciton dissociation. Improvements in efficiency could likely be realized by obtaining nanoscale phase separation, as observed in P3HT/PCBM devices. One approach toward limiting phase separation is to add a compatibilizer to the film. Diblock copolymers have previously been used as compatibilizers for blends of immiscible polymers.[5] In these systems, confinement of block copolymer joints at domain interfaces reduces interfacial tension and suppresses coalesence, limiting domain sizes and improving morphological stability. The utility of this technique in stabilizing P3HT:PCBM blends toward extended

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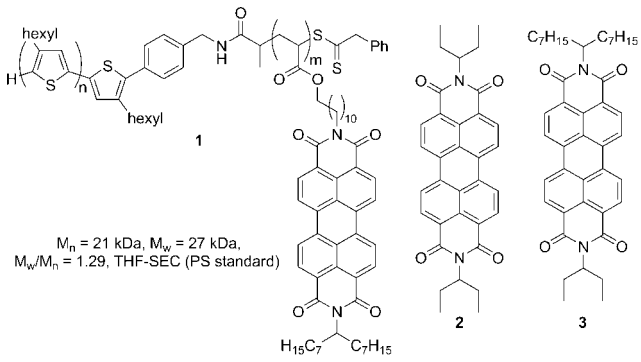

Figure 1. Diblock copolymer used in this study.

thermal annealing has recently been demonstrated.[6] Herein, we report the synthesis of a novel diblock copolymer as a compatibilizer for P3HT:PDI based solar cells. We also demonstrate its usefulness in controlling phase separation of P3HT:PDI blends and improving the efficiency of these solar cells.

A critical component in the execution of this approach is the choice of architecture for the diblock copolymer. Ideally, the individual blocks of the diblock copolymer should have high charge mobilities, ensuring that charge transport in the blend is not impeded by the presence of the compatibilizer. A combination of regioregular P3HT for the thiophene component of the diblock copolymer and a comb polymer first reported by the Thelakkat group for the perylene component was considered an ideal target for our compatibilizer studies.[7] Well-defined diblock copolymers can be synthesized by suitable end functionalization of regioregular P3HT followed by controlled radical polymerization of the perylene component from the chain end. "Reversible addition−fragmentation chain transfer" (RAFT) was chosen for this purpose because of the relatively mild reaction conditions and exceptional control over molecular weight distribution.[8] Using this approach the diblock copolymer shown in Figure 1 was synthesized (see Supporting Information for details).

Preliminary AFM studies (see Supporting Information) showed the formation of micrometer sized perylene crystals on the surface of thin films cast from $CHCl_3$ solutions of P3HT and PDI **2** (Figure 1), in accordance with the observations of Friend and co-workers. Addition of the diblock copolymer **1** to these mixtures in various amounts had no discernible effect on the blend morphology. Also, the measured power conversion efficiencies at Air Mass 1.5 Global (AM 1.5G), 100 mW/cm^2, were unaltered. We hypothesized that a longer solubilizing group may be required

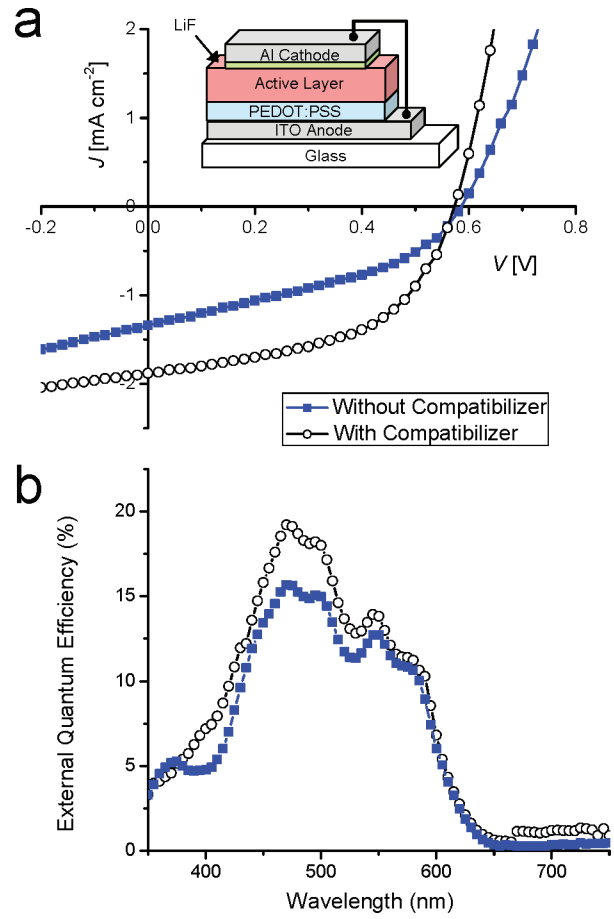

Figure 2. (a) $J-V$ characteristics of solar cells with the configuration shown under 100 mW cm^{-2} AM 1.5G illumination. Both devices utilized an active layer with a 4:1 ratio by mass PDI **3**:P3HT. Solar cells with compatibilizer contained 25% by mass of **1** in the active layer. (b) External quantum efficiency as a functional of wavelength, measured at a 0 V bias, for the devices with and without compatibilizer.

for interaction with the compatibilizer. Toward this end, the dissymmetric PDI **3** was synthesized.

After optimization of various device parameters including annealing conditions, composition of the active layer, and the choice of solvent for spin-casting (see Supporting Information), we were able to obtain devices with a V_{OC} of 0.56 V, J_{SC} of 1.85 mA cm^{-2}, and a fill factor of 0.51 when perylene **3** was used (Figure 2a). All three values are improvements over devices that have been reported earlier. Taken together an efficiency of 0.55 ± 0.03% was obtained, which represents a near threefold improvement in performance over previously reported P3HT:PDI solar cells. In the absence of the compatibilizer, and in otherwise identical conditions, a maximum efficiency of 0.37 ± 0.04% was observed (Figure 2a). These results demonstrate the beneficial effects of both the diblock copolymer and the novel PDI on device performance. To clarify the origin of the improved efficiency, the external quantum efficiencies (EQE) of the devices with and without compatibilizer were also measured (Figure 2b). The device with compatibilizer shows a maximum EQE of 19%, compared to less than 16% for the control. The EQE is improved across a broad spectral range, but the difference is most pronounced at the short wavelength region, where the PDI component absorbs most strongly. This is not simply a result of higher light absorption at those

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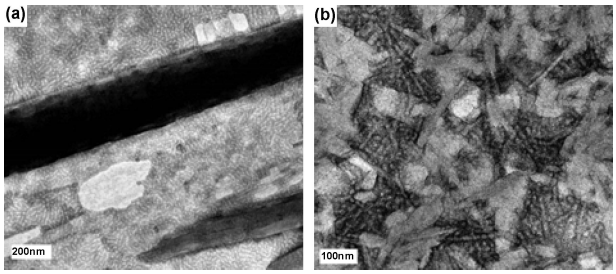

Figure 3. TEM images of two different active layers with a 4:1 ratio by mass PDI **3**:P3HT as used in photovoltaic devices. The blend with compatibilizer in part b contained 25% by mass of **1** in the active layer.

wavelengths, as the thickness and optical absorption spectra of the films with and without compatibilizer are nearly identical (see Supporting Information). This suggests that the improved J_{SC} results from increased dissociation of PDI excitons, perhaps due to smaller domain sizes.

To demonstrate this, the polymer blends were imaged by transmission electron microscopy (TEM). Representative images of films cast under conditions identical to the best devices, followed by staining with RuO_4 vapor, are shown in Figure 3. The darker domains are attributable to P3HT, the more oxidatively sensitive component of the blend. Films cast without compatibilizer (Figure 3a) show large domains of P3HT and PDI, indicative of unfavorable phase separation on the micrometer length scale. In films with compatibilizer (Figure 3b) such phase separation is largely suppressed and smaller domains are observed.[5] The nanometer scale phase separation should provide a high interfacial surface area for exciton dissociation, contributing to the improved J_{SC} and EQE.

If the smaller phase separation observed by TEM is in fact leading to improved harvesting of PDI excitons, the photoluminescence (PL) spectra of the blend films should show increased quenching upon addition of compatibilizer. Figure 4 shows PL spectra of polymer films cast on glass slides under conditions identical to those used in solar cell fabrication. The emission observed is attributed to fluorescence from the PDI component. No emission from P3HT could be observed, implying that the P3HT domains in both blends may contain PDI impurities, as has been previously suggested.[4a] Addition of the compatibilizer does result in reduced PL, consistent with the posited explanation for the improved J_{SC} and EQE in the solar cells. However, not all the PL is quenched, indicating that additional improvement should be possible with further optimization of the compatibilizer structure and device processing conditions.

The TEM images and PL spectra likely explain the increased J_{SC} in the solar cells. However, the compatibilizer also improves the device fill factor, leading to improved overall efficiency. The reasons for this are not clear at this time and warrant further study. In addition to the compatibilizer **1**, the new dissymmetric perylene **3** also plays an important role in improving the performance, as revealed by an efficiency of 0.37% in devices without compatibilizer.

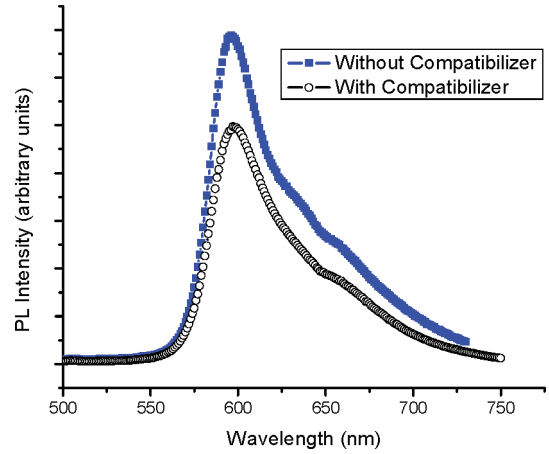

Figure 4. Photoluminescence (PL) of blend films on glass. Both films contain a 4:1 ratio by mass PDI **3**:P3HT, with or without 25% by mass compatibilizer. Films were excited at 468 nm. PL is normalized by dividing by the film absorbance, after subtracting the contribution to the absorbance from P3HT.

We have shown that only one long solubilizing group is required for interaction with the compatibilizer. Variations in the nature of the substituent on the imide can modulate the slip stacking of adjacent perylene molecules in crystals and broaden their absorption profile.[9] On the basis of this, dissymmetric perylenes with different substituents on the imide nitrogen are currently being synthesized for device applications.

In conclusion, we have synthesized a novel diblock copolymer, which helps in controlling the large scale phase separation within blends of P3HT and PDI. Device performance is enhanced in the presence of the compatibilizer with optimized devices showing an efficiency of 0.55%. Additionally, TEM suggests that the components of the blend form smaller domains and PL spectra show partial quenching of the PDI emission. Further studies aimed at improving P3HT/PDI blend solar cells are in progress. Additionally, the diblock copolymer itself is potentially a fully functional photovoltaic material. Studies aimed at using it as the sole active layer material are currently in progress.

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Supporting Information Available: Experimental details, compound synthesis and characterization, AFM images, and UV/vis absorbance spectra (PDF). This material is available free of charge via Internet at http://pubs.acs.org.

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