

Near-infrared Dye Sensitization in Bulk Heterojunction Polymer Solar Cells

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Polymer solar cells with a low-bandgap dye molecule are demonstrated by employing ternary blends of poly(3-hexylthiophene) (P3HT), fullerene derivative (PCBM), and silicon phthalocyanine derivative (SiPc) under different annealing conditions. The solvent annealing induces selective allocation of SiPc molecules at amorphous P3HT domains that would be formed at the interface between P3HT and PCBM crystalline domains, and furthermore effectively suppresses diffusion and aggregation of low molecular weight components which degrade the performance of the thermally annealed devices. As a result, the solvent-annealed ternary blend solar cells exhibited an enhanced power conversion efficiency of 4.5%.

Introduction

Bulk heterojunction (BHJ) solar cells based on polymer/fullerene blends have attracted much attention because they have potential advantages in terms of lightweight, flexibility, low cost, large-area, simple processing and high-throughput productivity (1-4). Currently, the most prominent materials in BHJ polymer solar cells are a binary blend of regioregular poly(3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene (PCBM), which exhibit power conversion efficiencies (PCEs) around 4–5% (5-7), and the photovoltaic conversion kinetics has been investigated in detail by transient absorption spectroscopy (8). However, P3HT can absorb only a quarter of the total photons in the solar light (9). Consequently, a variety of low band-gap polymers with strong absorption bands in the near-infrared region have been developed to harvest a broad range of the solar light (9-12). On the other hand, dye sensitization has been recently reported as an alternative approach to improving the light-harvesting efficiency in BHJ polymer solar cells by several groups including us (13-18). However, PCE of such devices still remains modest at around 3%. Herein we demonstrate highly efficient BHJ ternary blend solar cells with a PCE of 4.5%.

In ternary blend solar cells, dye molecules are simply blended as the third component to harvest solar photons at longer wavelengths that the original donor and acceptor materials cannot collect. This is a simple and versatile method and therefore various dye molecules are applicable. In most cases, however, the dye addition rarely improves but rather degrades the device performance (19, 20). Dye aggregation is one of the major obstacles to the efficient light harvesting in ternary blends. We have previously demonstrated that an appropriate selection of dyes with bulky groups can effectively suppress the formation of dye aggregates and consequently improve the light-harvesting

efficiency (14). Considering the large photocurrent due to dye molecules, we speculated that the majority of dye molecules are located at the donor/acceptor interface. Such a selective allocation of dye molecules is also the key to the improvement but the mechanism is still open for question. In this study, we estimate the local concentration of dye molecules at the interface of P3HT/PCBM, and discuss the driving force for such a selective allocation of dye molecules.

Experimental Section

Ternary blend solar cells with P3HT/PCBM/SiPc were fabricated as follows. Indium–tin–oxide (ITO)-coated glass substrates (10 Ω per square) were washed by ultrasonication in toluene, acetone, and ethanol for 15 min, dried with N_2 , and then cleaned with a UV– O_3 cleaner for 30 min. A thin layer (ca. 40 nm) of poly(3,4-ethylenedioxythiophene) with poly(4-styrenesulfonate) (PEDOT:PSS, H.C.Starck, PH500) was spin-coated onto the cleaned ITO-coated substrates at a spin rate of 3000 rpm and the layer was dried at 140 $^{\circ}C$ for 10 min in air. For the device fabricated by thermal annealing, a blend layer of P3HT/PCBM/SiPc (ca. 200 nm) was spin-coated from a chlorobenzene solution on the PEDOT:PSS film at 1200 rpm for 60 s and the film was annealed at 150 $^{\circ}C$ for 30 min in a N_2 -filled glove box. For the device fabricated by solvent annealing, a blend layer of P3HT/PCBM/SiPc (ca. 200 nm) was spin-coated from an *o*-dichlorobenzene solution on the PEDOT:PSS film at 600 rpm for 60 s. Then, the wet film was dried in covered glass petri dishes for 60 min. Finally, the Ca/Al electrode (20/80 nm) was thermally deposited on top of the active layer at 2.5×10^{-4} Pa. The blend solution was prepared as follows: P3HT (Aldrich, $M_w = 87,000$) and PCBM (Frontier Carbon) were dissolved in chlorobenzene (20 and 16 $mg\ mL^{-1}$) or *o*-dichlorobenzene (20 and 20 $mg\ mL^{-1}$), the solution was stirred at 40 $^{\circ}C$ overnight, and then SiPc (Aldrich) was dissolved in the solution at room temperature. Note that the dye concentration was optimized in the range from 1.5 to 9.1 wt% in the ternary blend films. For comparison, P3HT/PCBM control devices without dyes were also prepared separately under the same condition to give the same active layer thickness. For absorption spectra measurements, P3HT, PCBM, and PS (Scientific Polymer Products, $M_w = 22,000$) films doped with SiPc were prepared by spin-coating on glass substrates previously cleaned as described above from chlorobenzene solutions: P3HT, PCBM, and PS were separately dissolved in chlorobenzene at a concentration of 15 $mg\ mL^{-1}$ respectively and then SiPc was dissolved in the solution (1.5–100 wt% in the final films).

Absorption spectra were measured with a spectrophotometer (Hitachi, U-3500). The film thickness was evaluated with an atomic force microscope (Shimadzu, SPM-9500J) in the contact mode at room temperature. The J – V characteristics were measured with a DC voltage and current source/monitor (Advantest, R6243) in the dark and under the illumination with AM1.5G simulated solar light with 100 $mW\ cm^{-2}$. The light intensity was corrected with a calibrated silicon photodiode reference cell (Bunkoh-Keiki, BS-520). The photocurrent action spectra were measured with a digital electrometer (Advantest, R8252) under monochromatic light illumination from a 500-W xenon lamp (Thermo Oriel, Model 66921) with optical cut filters and a monochromator (Thermo Oriel, UV–visible Conerstone). The active area of the device was 0.07 cm^2 . The illumination was carried out from the ITO side under N_2 atmosphere. At least 5 devices were fabricated to ensure the reproducibility of the J – V characteristics.

Results and Discussion

Figure 1a shows the device configuration and chemical structures employed in ternary blend polymer solar cells. We employed P3HT as a donor material, PCBM as an acceptor material, and silicon phthalocyanine bis(trihexylsilyl oxide) (SiPc) as a light-harvesting dye that has an absorption band at longer wavelengths than P3HT. The active layer was annealed under two different conditions: thermal annealing at 150 °C and solvent annealing under *o*-dichlorobenzene vapor.

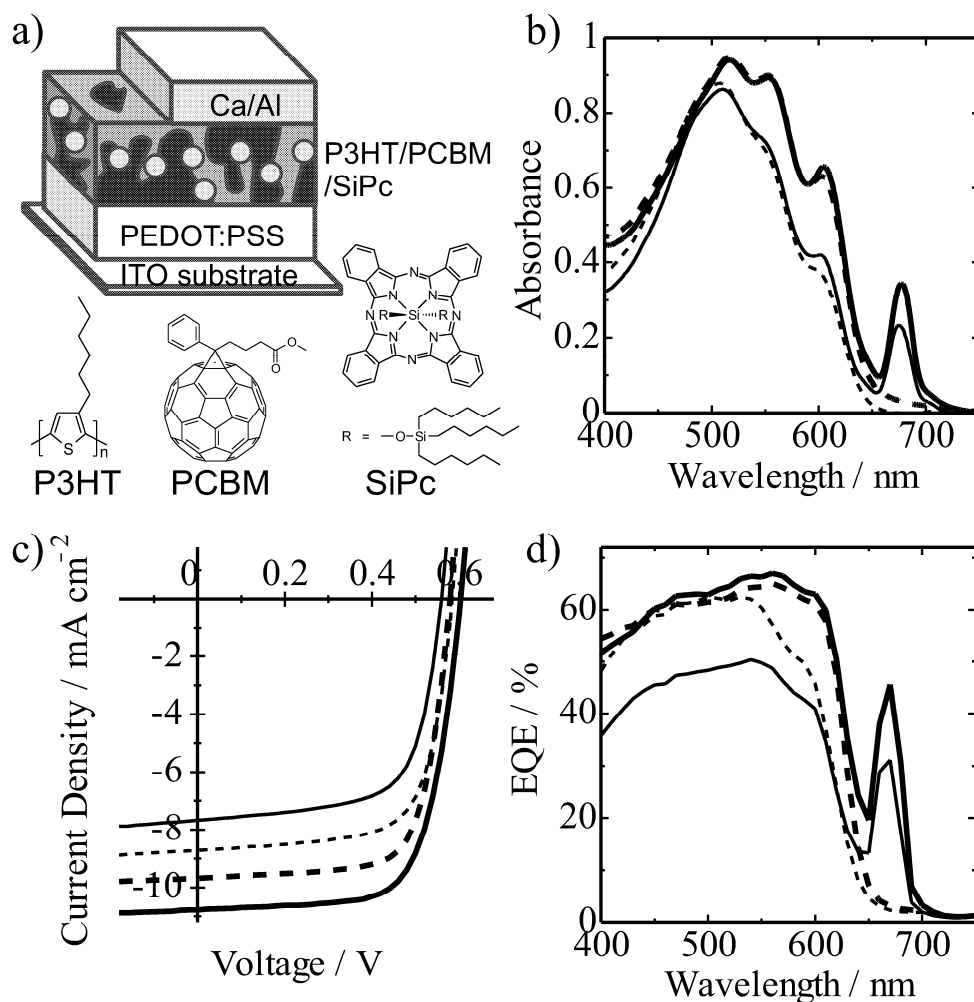


Figure 1. a) Device configuration of ternary blend solar cells. b) Absorption spectra of P3HT/PCBM/SiPc ternary blend films (solid lines) and P3HT/PCBM binary blend films (broken lines) with solvent annealing (thick lines) and thermal annealing (thin lines). c) J - V characteristics and d) EQE spectra of P3HT/PCBM/SiPc ternary blend devices (solid lines) and P3HT/PCBM binary blend control devices (broken lines) with solvent annealing (thick lines) and thermal annealing (thin lines). The weight fraction of SiPc is 4.8 wt%.

As shown in Fig. 1b, the solvent-annealed P3HT/PCBM/SiPc ternary blend film exhibited more distinguished vibrational bands at around 500–600 nm, which are

indicative of the crystallization of P3HT (21), than the thermally annealed ternary blend film. Interestingly, the vibrational bands were clearly observed even in the presence of SiPc molecules under both annealing conditions, suggesting that the crystallization of P3HT is not disturbed by the addition of SiPc molecules.

Figure 1c shows the J - V characteristics of P3HT/PCBM/SiPc ternary blend solar cells with solvent annealing (thick line) and thermal annealing (thin line) and the corresponding P3HT/PCBM binary blend control solar cells (broken lines) under AM1.5G illumination from a calibrated solar simulator with an intensity of 100 mW cm^{-2} . The dye concentration was 4.8 wt% for both devices. The solvent-annealed ternary blend solar cell exhibited a substantially improved performance compared to the binary blend control cell: a short-circuit current density of $J_{\text{SC}} = 10.8 \text{ mA cm}^{-2}$, an open-circuit voltage of $V_{\text{OC}} = 0.61 \text{ V}$, a fill factor of $\text{FF} = 0.68$, and $\text{PCE} = 4.5\%$. In contrast, the thermally annealed ternary blend solar cell exhibited a degraded performance of $J_{\text{SC}} = 7.66 \text{ mA cm}^{-2}$, $V_{\text{OC}} = 0.56 \text{ V}$, $\text{FF} = 0.67$, and $\text{PCE} = 2.9\%$. Compared to the binary blend control devices, as shown in Fig. 1d, the solvent-annealed device exhibited a slightly improved external quantum efficiency (EQE) peak (67%) at around 550 nm and a sharp EQE peak (46%) at around 670 nm while the thermally annealed device exhibited a degraded EQE peak (50%) at around 550 nm and a relatively small EQE peak (31%) at around 670 nm.

Table I summarizes device performances of P3HT/PCBM/SiPc ternary blend solar cells with different dye concentrations. For the solvent-annealed device, J_{SC} increased with the increase in the dye concentration up to 4.8 wt% and then decreased at 9.1 wt%. Consequently, the best performance of 4.5% was obtained at a dye concentration of 4.8 wt%. This is the highest efficiency in ternary blend polymer solar cells. For the thermally annealed device, on the other hand, J_{SC} and FF decreased with the increase in the dye concentration and hence the device performance was monotonically degraded. These results suggest that the light-harvesting efficiency of dye molecules is sensitively dependent upon the annealing conditions.

TABLE I. Device Performances for P3HT/PCBM/SiPc Ternary Blend Solar Cells with Solvent and Thermal Annealing.

Anneal	SiPc / wt%	$J_{\text{SC}} / \text{mA cm}^{-2}$	V_{OC} / V	FF	PCE / %
Solvent	0.0	9.70	0.58	0.72	4.0
	1.5	10.2	0.59	0.69	4.1
	3.4	10.4	0.61	0.68	4.3
	4.8	10.8	0.61	0.68	4.5
	9.1	10.3	0.61	0.67	4.2
Thermal	0.0	8.72	0.58	0.69	3.5
	1.5	8.82	0.57	0.70	3.5
	3.4	8.35	0.56	0.67	3.1
	4.8	7.66	0.56	0.67	2.9
	9.1	5.06	0.55	0.60	1.7

In order to discuss these different device performances due to annealing conditions, we carefully examined the dependence of absorption spectra of SiPc molecules on the dye concentration. As shown in Fig. 2a, SiPc molecules doped in P3HT exhibited an

absorption band at 671 nm while SiPc molecules doped in PCBM exhibited an asymmetrical absorption band at 691 nm. The ternary blend films with thermal annealing (thin line) and solvent annealing (thick line) exhibited an absorption band at around 675 and 677 nm, respectively. These bands are similar to that of SiPc molecules doped in P3HT rather than in PCBM, suggesting that SiPc molecules are located in P3HT domains rather than in PCBM domains.

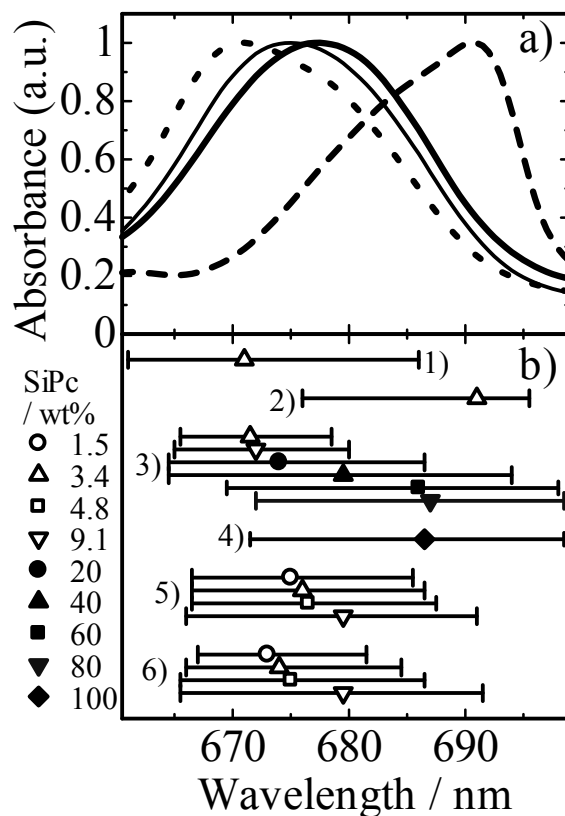


Figure 2. a) Absorption spectra of SiPc in P3HT neat films (dotted line), PCBM neat films (broken line), solvent-annealed ternary blends (thick solid line), and thermal annealed ternary blends (thin solid line). b) Peak wavelengths and FWHM of the SiPc absorption in various matrices: 1) a P3HT neat film, 2) a PCBM neat film, 3) PS films, 4) a SiPc neat film, 5) solvent-annealed ternary blend films, 6) thermally annealed ternary blend films.

Figure 2b summarizes the peak wavelength (symbols) and full width at half maximum (FWHM) (bars) of the dye absorption spectra in different matrices at various dye concentrations. Figures 2b-1 and 2b-2 represent the peak wavelength and FWHM of SiPc molecules doped in P3HT and in PCBM, respectively. Figure 2b-3 shows the peak wavelength and FWHM of SiPc molecules doped in polystyrene (PS) with different dye concentrations: SiPc molecules are likely to be dispersed relatively homogeneously in amorphous PS films. As shown in the figure, the peak position was red-shifted from 672 to 687 nm and FWHM was widened from 13 to 27 nm with increasing SiPc concentration, and consequently approached to that of SiPc neat film (Fig. 2b-4) at higher concentrations (>60 wt%). The peak wavelength of the SiPc neat film is still shorter than

that of SiPc in PCBM, suggesting that the ground-state interaction between SiPc and PCBM causes the largest peak shift. For ternary blend films, the absorption was red-shifted and broadened with increasing SiPc concentration, as is the case with that of SiPc molecules doped in PS films. As we have previously proposed, the crystallization of P3HT and PCBM would expel dye molecules from each crystalline domain. Therefore, these results suggest that SiPc molecules are located in amorphous P3HT domains, which would be interfacial area between crystalline P3HT domains and aggregated nanocrystalline PCBM domains.

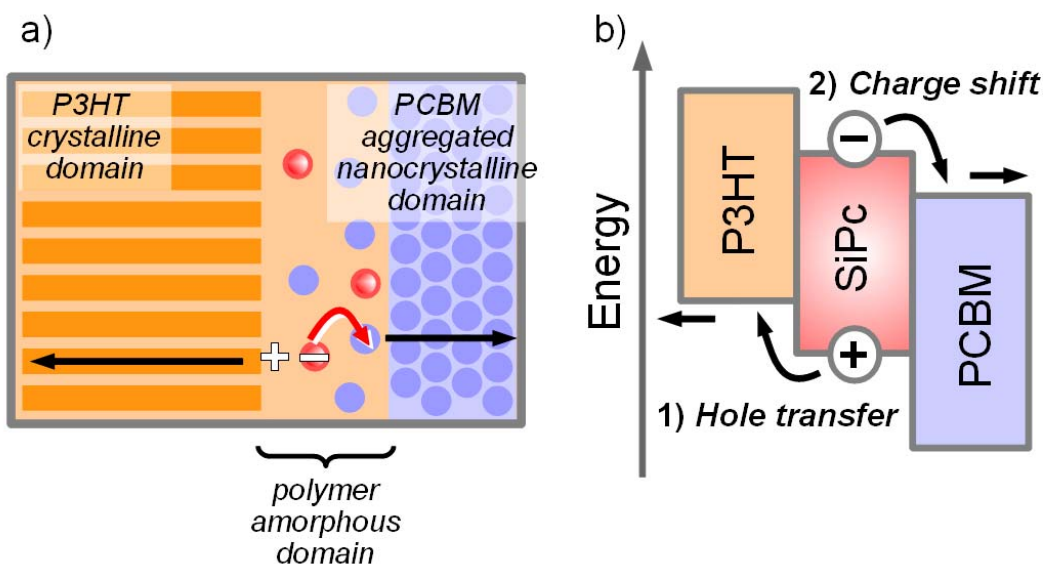


Figure 3. a) A schematic drawing of phase separated structure for a P3HT/PCBM/SiPc ternary blend solar cell. b) HOMO–LUMO potentials of P3HT/SiPc/PCBM components and sequential charge transfer processes upon photoexcitation of SiPc .

Figure 3 depict a schematic drawing of phase separated structure at the interface of a ternary blend and potential levels of three components. On the basis of the concentration dependence of the peak wavelength of SiPc in PS films, the local concentration of SiPc molecules was roughly estimated to be ~30 wt% for the solvent-annealed device and ~20 wt% for the thermally annealed device, which is much higher than the original weight ratio of 4.8 wt%. This higher local concentration of SiPc molecules is consistent with higher crystallization of P3HT by solvent annealing, which would reduce interfacial amorphous P3HT domains more effectively and consequently shorten the separation distance from SiPc molecules to each crystalline domain. We thus speculate that SiPc excitons accept electron first from the surrounding amorphous P3HT and then SiPc anion can easily migrate into the neighboring crystalline PCBM domains because of the relatively high local concentration of SiPc molecules, which is beneficial for the dye sensitization in the ternary blend devices.

Conclusions

We have shown highly efficient polymer/fullerene/dye ternary blend solar cells with a PCE of 4.5%. The device performance is strongly dependent upon the annealing processing employed for the active layer: the solvent annealing improves J_{SC} mainly with increasing dye concentration up to 4.8 wt%, while the thermal annealing degrades J_{SC} mainly with increasing dye concentration. The absorption spectra of dye molecules in ternary blends suggest that dye molecules are located in amorphous P3HT domains rather than in PCBM domains. In other words, the majority of dye molecules are selectively located at the amorphous P3HT domains that would be interface between P3HT and PCBM crystalline domains. One of driving forces for such a selective loading is due to the crystallization of P3HT and PCBM, which would expel dye molecules from each crystalline domain into amorphous regions. It is noteworthy that the solvent annealing is more suitable for the selective loading of dye molecules because it enhances the crystallization of P3HT more efficiently than the thermal annealing. Furthermore, the solvent annealing has an advantage that it can effectively suppress diffusion and aggregation of small molecules although dye molecules loaded are likely to serve as a plasticizer in amorphous P3HT domains. With a suitable selection of near-IR dye molecules and also annealing conditions, the device performance of ternary blend polymer solar cells can be improved furthermore.

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