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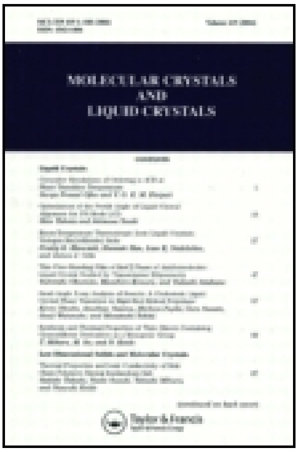

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Near-Infrared Dye Sensitization of Polymer/Polymer Thin-Film Solar Cells

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Near-Infrared Dye Sensitization of Polymer/Polymer Thin-Film Solar Cells

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The dye sensitization method for bulk heterojunction polymer solar cells is applied to polymer/polymer solar cells composed of conjugated donor and acceptor polymers. The power conversion efficiency is successfully improved by addition of a near-infrared (NIR) dye. Spectroscopic analysis and J-V characteristics indicate that the dye molecules effectively contribute to the charge generataion through direct absorption of NIR light and also through the energy transfer from the donor polymers, according to the cascaded HOMO and LUMO potentials. These results demonstrate the versatility of dye sensitization as a useful method for improving the conversion efficiency of photovoltaics.

Keywords Charge generation; dye sensitization; energy transfer; phase separation; polymer/polymer solar cells

Introduction

Development of the polymer-based solar cell is attracting extensive academic and industrial interests, because it is a promising resource of renewable energy in the next generation of human society. The power conversion efficiency of polymer solar cells has made a great progress during the last decade, owing to the development of bulk heterojunction (BHJ) structures, self-organized conjugated polymers, and also owing to intensive synthetic work of low bandgap polymers that harvest long wavelength sun light. Actually, it is a critical issue for polymer solar cells to increase the conversion efficiency for the near-infrared (NIR) light in the wavelength range of 700–900 nm, because the solar spectrum has a broad distribution from visible to NIR wavelengths, but most of organic polymers and fullerene derivatives have little absorption in the NIR region.

We have reported a novel strategy, that is, dye sensitization of BHJ polymer solar cells, which can collect NIR light effectively by addition of an NIR-dye molecule, silicon phthalocyanine (SiPc), into the active layer of poly(3-hexylthiophene) (P3HT) / fullerene derivative (PCBM) composites [1]. The SiPc dyes are selectively allocated at the boundary between phase-separated domains of P3HT/PCBM [2], and successfully improve the charge generation efficiency. The detailed analysis using femtosecond-picosecond transient absorption spectroscopy has clearly revealed the dye sensitization kinetics in each step of

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energy transfer and charge separation processes, taking place at the interface of donor P3HT and acceptor PCBM domains [3, 4].

In this paper, we demonstrate the versatility of this method by applying to polymer/polymer solar cells with another type of NIR-dye, silicon naphthalocyanine (SiNc). SiNc has a strong absorption band at around 800 nm, therefore, it can harvest the photons with wavelength much longer than visible light [5]. On the other hand, polymer/polymer solar cells are realized by controlling the phase-separated structure of blend films composed of conjugated donor and acceptor polymers [6, 7]. All-plastic solar cells thus obtained will have many fascinating characteristics, never expected for conventional fullerene-based organic photovoltaics (OPV). The performance of polymer/polymer solar cells will be further improved by dye sensitization.

Experimental

The ternary blend solutions in *p*-xylene were prepared with regioregular poly(3-hexylthiophene) (P3HT: Aldrich, $M_w = 30{,}000$–$60{,}000$), poly{[*N*,*N*″-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl′-*alt*-5,5′-(2,2′-bithiophene)} (N2200: Pol yera, $M_w = 100{,}000$–$150{,}000$), and silicon[IV]naphthalocyanine bis(trihexylsilyl oxide) (SiNc, Aldrich). About a 100 nm thick active layer (P3HT/N2200/SiNc = 1.0/1.0/0.2 w/w) was spin-coated on an ITO electrode covered with poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS). On the top of the blend film, calcium (20 nm) and aluminum (80 nm) were successively evaporated as a counter electrode.

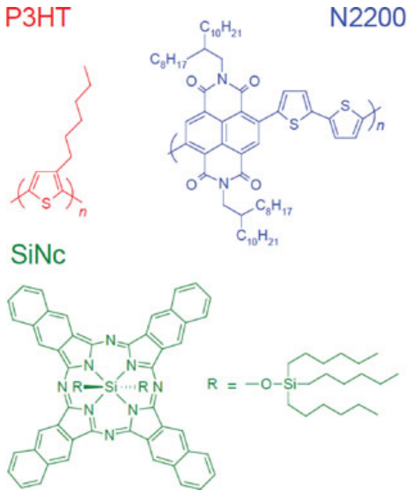
For absorption and fluorescence measurements, binary (P3HT/N2200, P3HT/SiNc, N2200/SiNc) and ternary (P3HT/N2200/SiNc) blend films were prepared by spin-coating on glass substrates. The spectra were measured with a spectrophotometer (Hitachi U-3500) and a fluorescence spectrophotometer (Hitachi F-4500 and Horiba NanoLOG-Symphony).

The *J*-*V* characteristics of the devices were measured in a N_2 atmosphere in the dark and under illumination with AM1.5G simulated solar light at 100 mW cm^{-2}. The photocurrent action spectra were measured with a digital electrometer (Advantest, R8252) under monochromatic light illumination from a 500 W xenon lamp (Thermo-Oriel).

Results and Discussion

The conjugated polymers employed in this study are P3HT as an electron donor and N2200 as an acceptor, both of which are known to have high mobility of hole and electron charges, respectively. Scheme 1 shows the chemical structures of the materials used, including the NIR dye, SiNc. These three components are simply blended and spin-coated on substrates with a thickness of ca. 100 nm.

Figure 1 depicts absorption spectra of each component. They have large and distinct absorption bands from visible to NIR region, and cover a wide range of wavelength up to 850 nm (P3HT: 450–600 nm, N2200: 400 nm, 600–800 nm, and SiNc: 760–800 nm). We previously reported that SiPc can effectively harvest longer wavelength light than P3HT, and increase the photocurrent of the P3HT/PCBM cells [1]. Instead of PCBM, which has very weak absorption at longer wavelengths, the low bandgap polymer N2200 is employed in this study. This conjugated polymer can collect NIR light, furthermore, the use of SiNc expands the light-harvesting ability. Hence, we expect that the new ternary blend P3HT/N2200/SiNc films would have high photo-conversion efficiencies, particularly in the NIR region.



Scheme 1. Chemical structures of materials used in this study.

From these absorption spectra and fluorescence spectra, the bandgap energy of each component was determined. In addition, the ionization potentials were measured by photoelectron yield spectroscopy (PYS). Using these spectroscopic data, we evaluated the HOMO-LUMO levels of three components as shown in Fig. 2. It is an absolute requirement for dye sensitization that both of the HOMO and LUMO potentials are lined up in the order of P3HT, SiNc, and N2200. The present three component system meets this energetic requirement of the cascaded potentials, as shown in Fig. 2. Upon the photo-excitation of SiNc, the hole charge can transfer to the HOMO of P3HT, and the electron can transfer to the LUMO of N2200, consequently the cation and anion charges are separated effectively according to the potential levels.

Indeed, we observed a large increase in the short-circuit current density (J_{sc}) by doping SiNc into P3HT/N2200 devices. Figure 3 shows absorption spectra (a) and the J-V curves (b) of P3HT/N2200 blend films with and without SiNc dye. The addition of 10 wt%

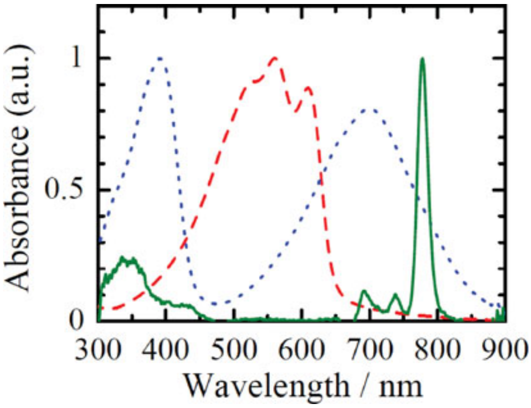


Figure 1. Absorption spectra of P3HT film (broken line), N2200 film (dotted line), and SiNc in solution (solid line). The spectra are normalized at the peak wavelength.

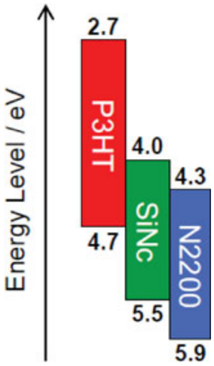


Figure 2. Potential energy diagram of P3HT, SiNc, and N2200.

dyes provides the best performance, and results in largely enhanced absorbance around 750–800 nm, corresponding to the absorption band of SiNc shown in Fig. 1. In Fig. 3b, J_{sc} is clearly improved by addition of dye molecules from 3 mA cm^{-2} to 5 mA cm^{-2}, while a little increase in the open-circuit voltage V_{oc} from 0.45 V to 0.49 V. Consequently, the ternary blend cells exhibit an improved power conversion efficiency (PCE) of 1.03% (J_{sc} = 4.9 mA cm^{-2}, V_{oc} = 0.49 V, FF = 0.43), that is, double of the PCE = 0.51% for the control binary blend P3HT/N2200 solar cells.

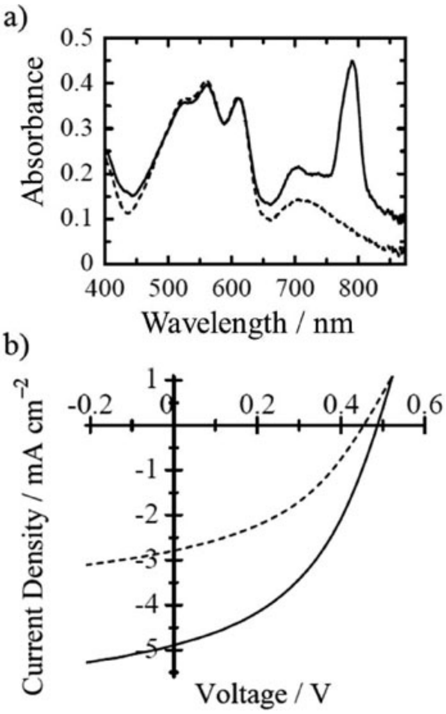


Figure 3. Absorption spectra (a) and J-V curves (b) for P3HT/N2200 blend films with SiNc dye (solid line) and without SiNc dye (broken line).

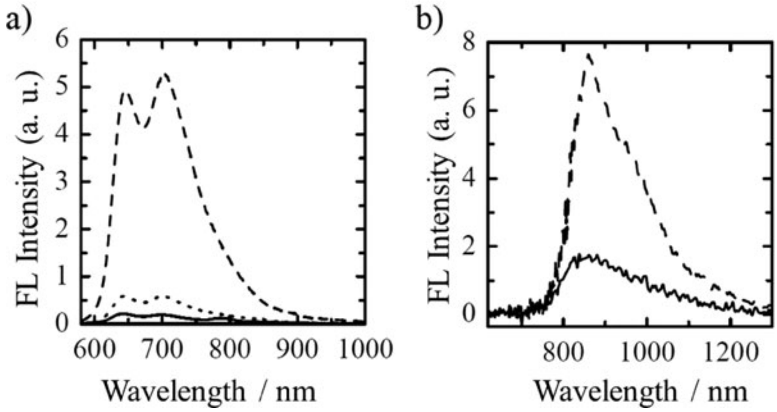


Figure 4. (a) Fluorescence spectra of P3HT neat film (broken line), P3HT/N2200 blend film (dotted line), and P3HT/N2200/SiNc ternary blend film (solid line), with excitation of P3HT at 550 nm; (b) Fluorescence spectra of N2200 neat film (broken line) and N2200/SiNc blend film (solid line), with excitation of N2200 at 600 nm.

To discuss the sensitization mechanism, we performed quenching experiments for the P3HT and N2200 films. Figure 4 shows fluorescence spectra of these polymer films, measured with blending quenchers for the excited state. As to P3HT films (Fig. 4a), the fluorescence intensity around 650–750 nm becomes very weak for the P3HT/N2200 blend films, indicating efficient energy transfer and/or electron transfer from P3HT excitons to N2200. The large quenching efficiency about 90% suggests that although these donor and acceptor polymers are incompatible and phase-separated [6–8], the size of P3HT domains should be nearly equal to or smaller than the diffusion length of P3HT exciton. By the addition of SiNc, the quenching efficiency further increases to 97%, suggesting the fast energy transfer reaction from P3HT exciton to SiNc, probably due to the long distance of Förster-type energy transfer. Therefore, SiNc can collect photon energies not only by direct excitation but also through energy transfer from P3HT.

Figure 4b shows N2200 fluorescence spectra, whose intensity is quenched by SiNc. Judging from the peak wavelengths of fluorescence (850 nm for N2200, and 785 nm for SiNc), this quenching takes place with electron transfer mechanism from SiNc to the excited state of N2200, and will contribute to the charge separation between them.

Figure 5 shows the action spectra of external quantum efficiency (EQE) with and without SiNc dyes; EQE values are plotted vs. wavelength of incident light. The large increase in EQE is found not only at the wavelength of dye absorption band at 750–800 nm, but also at the wavelengths of P3HT absorption band at around 500 to 600 nm. Of course, the former increase is due to direct light absorption by dye molecules, but the latter indicates the presence of indirect sensitization, mediated by energy transfer through the P3HT exciton, as mentioned above.

Based on these experimental results, we propose three types of dye-sensitization mechanisms as shown in Fig. 6.

1) SiNc dye excitation with NIR light, followed by charge separation to P3HT polaron and N2200 anion.
2) Electron transfer to N2200 excited state, and successive hole transfer from the dye cation to P3HT.

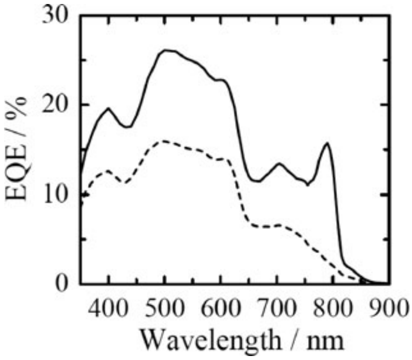


Figure 5. EQE spectra of P3HT/N2200 blend films with SiNc dye (solid line) and without SiNc dye (broken line).

3) Energy transfer from P3HT excitons to SiNc dyes, yielding P3HT polaron and N2200 anion as same as the latter part of mechanism 1).

All these mechanisms cooperatively work in the ternary blend films. Therefore, the individual components harvest a wide range of wavelength light, and then center most of the photon energies on dye molecules, which act as the starting point of charge generation. Although this successful result suggests that the dye molecules were preferentially introduced at the interface region as shown in Fig. 6, it is really hard to get the evidence of localization by microscopic methods. Previously, a work using P3HT and polystyrene blends showed that hydrophobic dye molecules tend to segregate at the interface of polymer/polymer blend [2]. The behavior observed in the current study on polymer/polymer solar cells is very similar to the dye sensitization reported for P3HT/PCBM systems, indicating the versatility of dye sensitization to boost photo-conversion efficiency of various OPV systems.

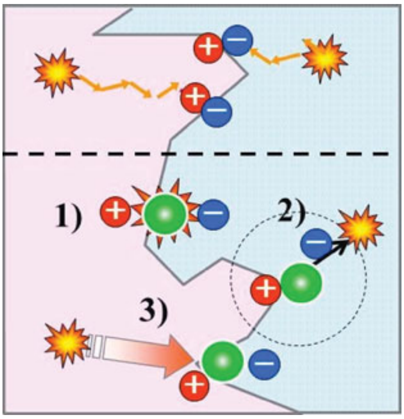


Figure 6. Schematic illustration of charge generation processes in P3HT/N2200 binary blend films (upper), and proposed dye-sensitization mechanisms for P3HT/N2200/SiNc ternary blend films (lower).

Acknowledgments

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