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Charge photogeneration and recombination in poly[2-methoxy-5-(2′-ethyl-hexoxy-*p*-phenylene vinylene]:fullerene composite films studied by photocurrent response

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Abstract

The photocurrent spectral responses of poly[2-methoxy-5-(2′-ethyl-hexoxy-*p*-phenylene vinylene]:fullerene (C60) composites are measured as a function of C60 concentration. At low concentration, the relationship between the external quantum efficiency (EQE) and absorption spectra is exhibited as the strengthened antibatic effect, and the EQE of the composite devices declines with increasing concentration of C60. At higher concentration, however, the maximum EQE gradually coincides with the absorption peak (symbatic response) and the EQE of composite devices begins to increase with increasing C60 concentration. It is proposed that at low concentration, dopant C60 increases the self-absorption rate of composite films, and charge trapping by C60 molecules causes the loss of efficiency. At high C60 concentration, the large-scale aggregations in composite films build pathways for charge carrier transport to respective electrodes, inhibiting the self-absorption effect and charge recombination on C60.

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Keywords: Recombination; Photocurrent; Polymer

1. Introduction

In photovoltaic applications, poly[2-methoxy-5-(2′-ethyl-hexoxy-*p*-phenylene vinylene] (MEH–PPV) is a commonly used conjugated polymer due to its solubility and absorption in the visible range. However, in single-layer photocells, the power conversion efficiency (PCE) is limited by the surface of the electrode/polymer contact where a local electric field induces charge separation. Fullerene (C60) and its derivatives have been used as electron acceptors in conjunction with conjugated polymers to enhance PCE. Consequently, interpenetrating conjugated polymer–fullerene networks, known as bulk heterojunctions, have been demonstrated as one of the most promising systems for efficient energy conversion.

Bulk heterojunction photovoltaic devices provide increased charge carrier-generating interfaces, where singlet excitons generated in the polymer layer are dissociated. The dissociated charge carriers are extracted by a built-in potential and are transported to the respective contacts. These separated carriers are responsible for the resulting photocurrent. Photocurrent spectra, therefore, can provide information about the motion of mobile charge carriers [1]. For many organic materials, photocurrent and absorption spectra are either well-matched (symbatic) or almost complement one another (antibatic) [2,3]. If the maximum photocurrent coincides with the strongest photo absorption, the photocurrent response is said to be symbatic with the absorption spectrum. If the maximum photocurrent occurs at photon energies where absorption is weakest, the photocurrent response is said to be antibatic [4]. Several research groups have reported that the relationship between the photocurrent and absorption spectra in undoped organic materials, such as MEH–PPV [5], tris(8-quinolinolato)aluminum and *N*′,*N*′-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine [6], is influenced by the electric field. In this paper, we presented composite devices of MEH–PPV doped with C60 in six different concentrations by weight: 1 wt.%, 2 wt.%, 5 wt.%, 10 wt.%, 20 wt.% and

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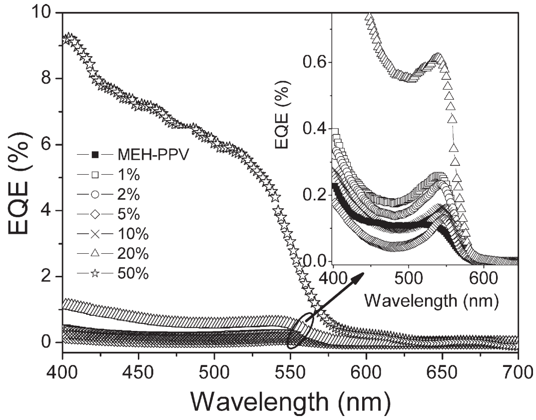

Fig. 1. The external quantum efficiencies (EQE) of undoped MEH–PPV and MEH–PPV:C60 composites at different concentrations for wavelength from 400 to 700 nm are shown. In order to show the relationships of EQE spectra in low concentration range, the inset presents the same EQE spectra at the concentration ranging from 1 wt.% to 20 wt.%.

50 wt.%. It is found that the concentration of C60 significantly influences the photocurrent spectral responses in their shapes and efficiencies.

2. Experimental details

Fullerene without any side functional groups was used as an electron acceptor. C60 with its single sphere structure has a low solubility in most solvents, while toluene is an exception [7]. MEH–PPV, doped with C60 was dissolved in toluene at concentrations of 1 wt.%, 2 wt.%, 5 wt.%, 10 wt.%, 20 wt.% and 50 wt.% (where wt.%$=M_{C60}/M_{MEH-PPV}$). Composite devices were fabricated using a structure of indium–tin oxide (ITO)/poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS)/MEH–PPV:C60/Al. The ITO-coated glass substrate was cleaned by detergent and distilled water, respectively, in an ultrasonic bath. PEDOT:PSS was spin-coated on top of ITO-coated glass substrates as the polymer anode. This is followed by thermal treatment for several minutes, leaving a 20-nm-thick film. The MEH–PPV and C60 in toluene solution was deposited on top of PEDOT:PSS by spin-coating. By controlling the speed of spinning, a composite film with a thickness of approximately 100 nm was obtained. Finally, an Al cathode was deposited by thermal evaporation through a shadow mask on top of the active layer in a vacuum lower than 10^{-3} Pa. The shadow mask defines an active area of 3.5 mm^2. All resulting samples were encapsulated in a glove box filled with dry nitrogen. In the glove box, the concentrations of both O_2 and H_2O were lower than 5 ppm. An undoped MEH–PPV film device also was fabricated using the same processes for comparison.

All devices were illuminated through the ITO electrodes. The absorption spectra were detected by a Shimadzu UV-3101 PC Spectrophotometer. The photoluminescence emission was obtained by a SPEX-Fluorolog 3. The photocurrent was recorded with a Keithley 2410 Source Measure Unit. A monochromator was used to select an illumination wavelength from a Xe lamp between 400 and 700 nm. The concomitant power spectrum of the Xe-lamp/monochromator system was recorded using the same setup to correct the photocurrent spectra.

For the time-of-flight (ToF) measurements, a Continuum Company Surelite SSP-2 Nd:YAG laser was used to generate short light pulses (4.7 ns length) to excite the samples through the ITO electrode. The illumination wavelength was 520 nm. The resulting transients were detected with a digital Tektronix oscilloscope (TDS 540D). The thickness of the composite film for ToF measurements was of ~1 μm. The external electric field was 2×10^5 V/cm.

3. Results and discussion

Fig. 1 shows the external quantum efficiency (EQE) spectra of the MEH–PPV:C60 blends at different C60 concentrations of 1 wt.%, 2 wt.%, 5 wt.%, 10 wt.%, 20 wt.% and 50 wt.% for a wavelength range from 400 to 700 nm. The inset in Fig. 1 presents the detailed change of EQE spectra for C60 concentrations from 1 wt.% to 20 wt.%. As can be seen, the EQE of the blends declines with increasing C60 concentration from 1 wt.% to 5 wt.%, followed by a gradual increase from 5 wt.% to 20 wt.%, and even a sharp rise from 20 wt.% to 50 wt.%. At a wavelength of 500 nm, the EQE of the MEH–PPV:C60 blend at a C60 concentration of 50 wt.% is two orders of magnitude larger than that of the blend at 5 wt.%.

Figs. 2a–g show the relationship of EQE (solid square) and absorption (line) spectra in the range of 450–700 nm for undoped MEH–PPV and each blend. For undoped MEH–PPV (Fig. 2a), the EQE spectrum shows a sharp onset at $\lambda\approx580$ nm followed by a slight decrease in the region of highest absorption. Since the light illuminates through the ITO electrode, the strongest absorption is within the active layer near the anode (ITO). For single-layer devices of polymer materials, excitons are generated in the film upon the absorption of photons, and dissociation of excitons into free carriers occurs at metal–polymer interfaces in short-circuit conditions [8]. Before dissociating, therefore, photogenerated excitons must travel to the far electrodes, and then in the built-in potential, hole can be produced from excitons dissociated at the cathode (Al) and

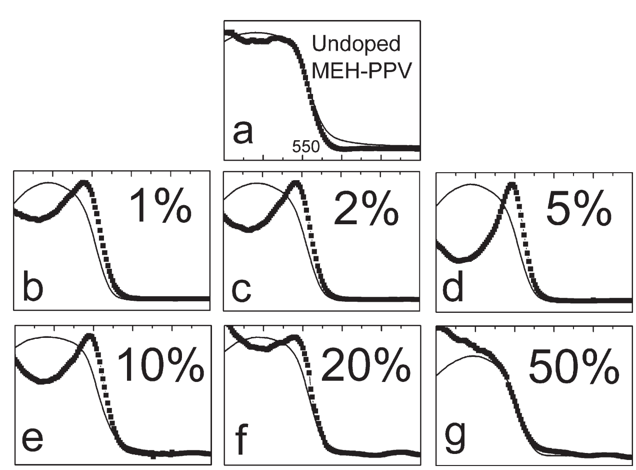

Fig. 2. The relationship of EQE (solid square) and absorption (line) spectra in the range of 450–700 nm for undoped MEH–PPV and each composition.