Understanding the effect of triplet sensitizers in organic photovoltaic devices

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ABSTRACT

The effect of PtOEP as a dopant on the performance of MEH-PPV/C_{60} photovoltaic devices was studied. Bilayer heterojunction devices with various compositions and layer structures were used to determine the possible pathways by which the photogeneration efficiency is enhanced. A key finding is that photocurrent generation enhancement always occurs in the MEH-PPV absorption region, regardless of the PtOEP dopant concentration or the MEH-PPV layer thickness. This result suggests that the presence of PtOEP in the donor MEH-PPV layer is primarily responsible for increasing the triplet exciton diffusion length of MEH-PPV by acting as a triplet sensitizer, rather than as an additional absorber for direct photogeneration. Values obtained from simulation show that the enhancement of exciton diffusion length of MEH-PPV can be more than a factor of 2 with optimal PtOEP concentrations. Further support for the role of PtOEP as a triplet sensitizer in MEH-PPV was obtained in experiments incorporating a blocking layer between MEH-PPV and C_{60}, whereby the various exciton transfer processes can be differentiated.

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1. Introduction

Organic photovoltaic (OPV) devices have shown impressive improvements in the past decade. Yet, there are still some fundamental material and device issues that limit their performance. It is generally understood that photovoltaic charge generation is a sequence of processes involving exciton generation in an absorber, consisting typically of a bulk heterojunction (HJ) of donors and acceptors, exciton diffusion to a donor/acceptor (DA) interface, exciton dissociation at the DA interface to produce electron—hole pairs, and transport of the mobile charges to the collecting electrodes. In many OPV devices based on bulk HJ, nearly 100% quantum efficiency in photovoltaic charge generation has been achieved, mainly, by manipulating the composition and morphological properties of the bulk HJ to overcome the limitation of short exciton diffusion length (L_D) (<10 nm), which is common among molecular solids, including polymers. While exciton generation and dissociation can be highly efficient in bulk HJ, charge collection can be compromised because separate and continuous pathways

necessary for the transport of electrons and holes can be difficult to achieve. An alternative approach is to reexamine the use of bilayer HJ in which the L_D of the absorber can be deliberately extended. Phosphorescent materials have been proposed as possible absorbers due to their long triplet exciton lifetimes [1–3]. However, only limited improvements have been observed using the latter approach. Used as dopants in host:guest systems, phosphorescent materials were intended to extend the L_D of the host [4–7]. Several studies have reported the poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]:platinum octaethylporphyrin (MEH-PPV:PtOEP) host:guest system, with modest efficiency improvements [6,7]. These results support an extension of the L_D, from external quantum efficiency (EQE) calculations. Although this method provides a simple manner to determine the L_D, it can be quite challenging when there is a considerable absorption overlap between the absorbing materials, as it is the case for MEH-PPV and C_{60}. A detailed thickness dependence study would evaluate the effect of PtOEP at different doping concentrations, in addition to differentiating the contribution of MEH-PPV and C_{60} for a more comprehensive analysis of EQE to determine the extension of the L_D. In this study, we investigated a bilayer HJ device based on MEH-PPV:PtOEP/C_{60} with the aim of supporting the role of PtOEP as a triplet dopant in the donor MEH-PPV:PtOEP layer and further

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differentiate the contribution of the dopant excitons from the host excitons to photogeneration, by altering the device architecture. We also aimed to exclude the contribution of dopant absorption to photogeneration in these devices.

2. Experimental

OPV devices were fabricated on pre-patterned ITO (90–100 nm) glass substrates (1.5 × 1.5 inches) with a surface resistance of 15 Ω/sq and an optical transparency of ~90%. The ITO substrates were cleaned with an initial scrubbing with detergent solution. Then they were rinsed and subjected to 10 min agitation in ultrasonic baths of DI water, acetone, and isopropanol (IPA), sequentially. Following a final IPA rinse, the substrates were dried with nitrogen and treated with oxygen plasma (2:15 min, 400 W and 5 × 10^{-1} Torr). The substrates were then transferred into a nitrogen-filled glove box, where the OPV devices were fabricated by thermal deposition and spin coating. MoO_x, C_{60}, bath-ophenanthroline (Bphen), and Al were deposited under a vacuum of 5.0 × 10^{-6} Torr. MEH-PPV (Sigma–Aldrich, MW: 150,000–250,000) was dissolved in a chlorobenzene:chloroform (1:1) mixture, with concentrations ranging from 2.5 to 5 mg/mL. PtOEP (Frontier Scientific) was added to the MEH-PPV solution at 5% and 10% (wt.) doping concentrations. The organic solutions were deposited by spin-coating, using 300 μL of solution on each substrate (ITO/MoO_x), at different rpm for 60 s, in order to obtain the desired thicknesses. The devices were completed with vacuum deposition of C_{60}, followed by Bphen and Al. For the blocking layer experiment, 20 nm of 2,5,8,11-tetra-*tert*-butyl-perylene (TBP) were evaporated on top of the MEH-PPV layer before C_{60} deposition. Three identical OPV devices with an active area of 0.1 cm^2 were produced on a single substrate.

The thicknesses of the films were initially measured with an AlphaStep D-100 profilometer. The thicknesses of MEH-PPV films were later corrected using its absorption coefficient. The absorption spectra were obtained with an Ocean Optics DT-Mini-2 light source (200–2000 nm) and an Ocean Optics USB4000 detector (200–1100 nm). The current density–voltage (JV) characteristics were recorded with a Keithley 2400 source meter in the dark and under irradiation at 100 mW/cm^2 generated by an Oriel xenon lamp solar simulator equipped with an AM 1.5 G filter. The intensity was calibrated with a Hamamatsu S1787-04 silicon photodiode traceable to the National Renewable Energy Laboratory. External quantum efficiency (EQE) measurements were performed with a calibrated Newport Cornerstone 260 Monochromator.

3. Results and discussion

MEH-PPV/C_{60}, a bilayer HJ OPV device with MEH-PPV as the hole-transport donor and C_{60} as the electron-transport acceptor, was the basis of this study. The typical layer structure is the following: ITO/MoO_x(8 nm)/MEH-PPV/C_{60}/Bphen(8 nm)/Al(100 nm), which includes MoO_x as the hole-injection layer and Bphen as the electron-transport layer. First, we investigated the thickness dependence of MEH-PPV from 4.5 nm to 47.8 nm, a range that exceeds its L_D (5–8 nm) [8,9]. The C_{60} layer was fixed at 40 nm, a thickness that is approximately equal to its L_D [10,11]. As indicated by the JV curves in Fig. 1A, the short-circuit current density (J_{sc}) increases from 1.44 mA/cm^2 to 3.73 mA/cm^2 with the addition of a very thin layer of MEH-PPV (4.5 nm), whereas the open circuit voltage (V_{oc}) decreases from 0.9 V to 0.5 V. Such a large change in both J_{sc} and V_{oc} is expected because of a shift from a MoO_x/C_{60} Schottky-like junction (with a large built-in potential (V_{bi}) due to MoO_x [12,13]) to a MEH-PPV/C_{60} HJ (with a smaller V_{bi} defined by the HOMO-LUMO energy offset). With increasing MEH-PPV

thickness, the device efficiency decreases monotonously. This is largely due to a steep decrease in both J_{sc} and fill factor (FF) while the V_{oc} remains unchanged at 0.5 V. The J_{sc} drops by more than an order of magnitude from 3.73 mA/cm^2 to 0.26 mA/cm^2 over the 4.5–47.8 nm range. Correspondingly, the FF decreases from 0.47 to 0.21. The reduction in J_{sc} and FF with increasing MEH-PPV thickness can be attributed to primarily two factors: 1) short L_D and 2) range limitation of the hole transport. On one hand, with a bilayer HJ configuration and incident light from the ITO side, a short L_D would result in MEH-PPV layer acting as a light filter. On the other hand, a short hole carrier range would result in a build-up of hole space charges in the MEH-PPV layer, which in effect produces an internal electric field that opposes the hole-transport to the ITO anode. MEH-PPV, with an L_D of only 5–8 nm and low hole mobility of 10^{-7} cm^2/V s [14,15], represents a poor donor material for OPV devices with a bilayer HJ configuration such as in this study. Fig. 1B shows the EQE spectra between 350 nm and 750 nm that span the absorption regions of both MEH-PPV and C_{60}. It is clear that the spectral response contains contributions from both MEH-PPV and C_{60}, although it appears that it is mostly from C_{60}. The contribution of MEH-PPV is evident only as a shoulder at around 500 nm. It can be seen that, in general, the EQE response is symbatic to the absorption of MEH-PPV and C_{60}, except for the thicker MEH-PPV layers, in which the EQE response appears to be antibatic with a reduction in EQE around 500 nm, the peak absorption of MEH-PPV. This is clearly evident for the thickest MEH-PPV (47.8 nm), where the EQE response is antibatic with a local minimum around 500 nm and a peak shifted to around 560 nm, which is outside the absorption maximum. This EQE response with respect to the absorption spectra has been previously reported and explained in terms of an internal filter effect [16–20].

Focusing on photogeneration and charge transport in MEH-PPV, the MEH-PPV/C_{60} layer structure was modified with C_{60} reduced from 40 nm to 4 nm, a thickness that is sufficient to form a bilayer HJ structure, but limited in absorption relative to MEH-PPV. Furthermore, the thickness of MoO_x was increased to 20 nm to ensure a uniform and continuous layer. Fig. 2A and B summarize the device performance of MEH-PPV/C_{60} (4 nm) devices where MEH-PPV is varied between 11.6 nm and 29.9 nm. It should be noted that compared to the MEH-PPV/C_{60} (40 nm) devices (Fig. 1), the overall J_{sc} of the MEH-PPV/C_{60} (4 nm) is much smaller, ranging from 0.74 mA/cm^2 to 0.30 mA/cm^2. This is due to the reduced absorption of the C_{60} layer and confirms that MEH-PPV contributes only marginally to the photogeneration. The J_{sc} decreases with an increase of MEH-PPV thickness, a trend that is independent of the C_{60} thickness. The same behavior is observed in the EQE spectra, as shown in Fig. 2B. The EQE spectral response correlates well with the absorption of C_{60} and MEH-PPV. Because the C_{60} layer is thin, the EQE spectra clearly show the contribution of MEH-PPV with a broad maximum that is symbatic with the MEH-PPV absorption maximum around 510 nm. Antibatic response is more noticeable for the thicker MEH-PPV films with a gradual red shift of the EQE maxima, as shown in the insert of Fig. 2B. This red shift is characteristic of PPV derivatives with antibatic response [17,18,20]. Harrison et al. explained this enhancement in the exciton generation in regions where the absorption coefficient is low as a result of intermolecular charge separation between neighboring molecules with more planar and extended structure [18].

Next, we investigated the effect of PtOEP doping in MEH-PPV. The device structure is the following: ITO/MoO_x(20 nm)/MEH-PPV:PtOEP/C_{60}(4 nm)/Bphen(8 nm)/Al(100 nm), where MEH-PPV:PtOEP is the doped layer. Fig. 3A summarizes the J_{sc} dependence on the thickness and PtOEP dopant concentration of the doped layer. Similar to the devices without the PtOEP dopant, the J_{sc} for the PtOEP doped devices show a monotonous decrease with