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Photocurrent enhancement in polymer:fullerene bulk heterojunction solar cells doped with a phosphorescent molecule

Barry P. Rand,^{1,a)} Claudio Girotto,^{1,2} Alexander Mityashin,^{1,2} Afshin Hadipour,¹ Jan Genoe,¹ and Paul Heremans^{1,2}

¹IMEC, Kapeldreef 75, B-3001 Leuven, Belgium

²ESAT, Katholieke Universiteit Leuven, Kasteelpark Arenberg 10, B-3001 Leuven, Belgium

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We demonstrate photocurrent enhancement of up to 20% in polymer:fullerene bulk heterojunction photovoltaic cells via the incorporation of a phosphorescent dopant, without degradation in the open-circuit voltage or fill factor of the device. The enhancement is shown to originate from multiple sources. First, the phosphor is able to populate the long-lived triplet state of the polymer, leading to longer diffusion length and a larger polymer contribution. Also, there is direct absorption on the dopant leading to enhanced spectral coverage. Finally, the dopant acts as a donor site and therefore increases the fullerene signal. © 2009 American Institute of Physics.

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The performance of organic solar cells has increased steadily in the last few years, thereby offering promise as a low-cost renewable energy source. In an organic semiconductor, photon absorption generates a bound electron-hole pair, or exciton, that must diffuse to and be separated into free charges at a donor-acceptor (DA) interface.^{1,2} One major bottleneck for the efficiency of this process is that exciton diffusion lengths (L_D) are on the order of 3–10 nm for singlet excitons.¹ Therefore, an optimized device must balance the low L_D with active layers thick enough to absorb large fractions of the incident light (typically ≥ 100 nm). A device architecture that is able to achieve a large DA interface area is the bulk heterojunction (BHJ), whereby donor and acceptor materials are intermixed and deposited simultaneously. It is often difficult, however, to achieve a very fine phase separation, on the order of a few L_D , while also maintaining good charge transport.³ If L_D can be increased, then it is possible that phase separation need not be as fine to generate high internal quantum efficiencies. Making use of triplet excitons, which are longer lived and therefore longer diffusing compared with singlet excitons, is one approach which has been applied to BHJ cells.^{4–7} One method to harvest triplet excitons that has been shown recently to increase L_D in bilayer devices is sensitized phosphorescence.^{8,9} With this technique, singlet excitons initially generated in the absorbing host are converted into triplet excitons using a phosphorescent dopant. Here, we show that this process can also be used to enhance the photocurrent of BHJ solar cells.

The material system we use to demonstrate this process for a BHJ cell is the MDMO-PPV:PCBM polymer:fullerene device structure (MDMO-PPV: poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene vinylene] and PCBM: 1-(3-methoxycarbonyl)propyl-1-phenyl-[6,6]-methanofullerene).^{10,11} As a phosphorescent sensitizer for MDMO-PPV, we use platinum octaethylporphyrin (PtOEP). This host:guest system is suitable since the lowest excited singlet state (S_1) of PtOEP is lower than that of MDMO-PPV, allowing efficient energy transfer to S_1 of PtOEP, followed by rapid intersystem crossing to the PtOEP

triplet state (T_1). Furthermore, owing to the larger T_1 of PtOEP (≈ 1.9 eV) compared to MDMO-PPV (≈ 1.6 eV), there is efficient population of the MDMO-PPV T_1 level, as shown previously for PtOEP in PPV hosts.^{8,12} Finally, it is important that the highest occupied molecular orbital (HOMO) of PtOEP is deeper than or equal to that of MDMO-PPV to prevent holes from being trapped on the guest material and ultimately reducing photocurrent. This criterion is satisfied with MDMO-PPV:PtOEP as their HOMO levels are both 5.3 eV. A schematic energy diagram of the MDMO-PPV:PCBM:PtOEP system is shown as an inset to Fig. 1.

The device structure of the BHJ solar cell is: indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (40 nm)/BHJ blend (130 nm)/Yb (20 nm)/Al (80 nm). The ITO coated glass substrates were

FIG. 1. Current density vs voltage (J - V) characteristics under 100 mW/cm² AM1.5D solar illumination with the following device structure: ITO/PEDOT:PSS (40 nm)/blend (130 nm)/Yb (20 nm)/Al (80 nm), where the blend is either MDMO-PPV:PCBM (solid curves) or MDMO-PPV:PCBM:PtOEP(5%) (dotted curves). The label denotes the ratio (1:1, 1:3, or 1:7) of MDMO-PPV:PCBM. The inset graph shows the J - V characteristics of the same devices in the dark. The inset also shows the schematic energy diagram of the device structure.

^{a)}Electronic mail: barry.rand@imec.be.

FIG. 2. The short circuit current density (J_{sc}) vs PCBM concentration for the device structure of Fig. 1 under 100 mW/cm² AM1.5D solar illumination either without (open squares) or with (filled circles) 5% PtOEP as the dopant. The data points show the average value of 6 devices. Also shown (open triangles) is the ratio of the doped to undoped J_{sc} values.

solvent cleaned followed by UV/O₃ treatment for 10 min. The PEDOT:PSS (H.C. Starck, Clevis P VPAI4083) solution was spincoated at 3000 rpm for 60 s, followed by baking at 120 °C in N₂. The MDMO-PPV:PCBM blend was dissolved in chlorobenzene at concentrations of 5–10 mg/ml, with 5% doping of PtOEP by weight on the total blend, followed by spincoating for 60 s to yield a thickness of 130 ± 6 nm. The Yb and Al layers were then deposited in a high vacuum chamber (base pressure <1 × 10⁻⁷ Torr). The device area was measured with an optical microscope, with an average area of 3.3 mm². The current density versus voltage (J - V) characteristics were measured using an Agilent 4156C parameter analyzer with illumination from a LOT-Oriel 1000 W Xe lamp fitted with AM 1.5D filters. Calibration was performed by a KG5 band pass filter and a calibrated Si detector. Absorption measurements were carried out on a Shimadzu UV-1601PC. For the measurement of external quantum efficiency (η_{EQE}), light from Xe and quartz halogen lamps were coupled into a monochromator and their intensity calibrated with a Si photodiode. The light incident on the device was chopped and the modulated current signal detected with a current-voltage and lock-in amplifier. Throughout fabrication and testing, cells remained in a vacuum or N₂ environment.

The J - V characteristics of devices with 1:1, 1:3, and 1:7 MDMO-PPV:PCBM blends with and without PtOEP in the dark (inset) and under 100 mW/cm² AM1.5D simulated solar illumination are shown in Fig. 1. The dark curves reveal that the transport in the blend improves with PCBM concentration, a phenomenon thought to arise either from the morphology change with blend ratio, or from ambipolar charge transport on PCBM.^{13,14} Notably, the dark J - V curves are not perturbed with PtOEP doping, indicating that PtOEP does not play a large role in charge transport. Under illumination, the open-circuit voltage (V_{OC}) and fill factor (FF) remain unchanged with and without PtOEP doping. There is a decrease in V_{OC} but an increase in FF with increasing PCBM concentration, with FF > 60% for PCBM concentrations above 80%, in agreement with past studies.¹¹

The short-circuit current density (J_{sc}) versus PCBM concentration for both doped and undoped devices is shown in Fig. 2. The trend in the case of the undoped solar cells is

very similar to trends reported previously, where J_{sc} increases until 75%–80% PCBM, after which J_{sc} begins to decrease.¹¹ The initial rise is caused by an improvement in photocurrent extraction, while the ultimate drop is due to the lack of polymer absorption in cells with high PCBM content. In all cases, the addition of 5% PtOEP produces an increase in J_{sc} , and therefore an increase in power conversion efficiency (η_p). For example, the J_{sc} of the 1:4 cell increases from 3 mA/cm² to 3.4 mA/cm², and η_p from 1.4% to 1.6% with PtOEP doping. The ratio of the J_{sc} of the doped devices to that of the undoped devices is also shown in Fig. 2, and reveals that at both low and high PCBM concentrations, J_{sc} is enhanced significantly (15%–22%), with only a modest (5%) increase at the peak. It should be noted that the surface morphology of the blend does not change with doping, as confirmed by atomic force microscopy of doped and undoped 1:1 and 1:3 blend films (data not shown), indicating that PtOEP molecules are likely uniformly distributed throughout the blend film. Given this, and with consideration of the energy diagram in Fig. 1, the photocurrent enhancement can come from one or more of three main sources: (1) sensitized phosphorescence allowing for increased harvesting of MDMO-PPV excitons, (2) charge transfer of a PCBM exciton to a nearby PtOEP donor molecule, or (3) direct absorption on the PtOEP dopant followed by charge transfer to PCBM or triplet energy transfer to MDMO-PPV.

To gain a better understanding of which of these multiple sources of photocurrent enhancement are responsible, we consider the η_{EQE} spectra of doped and undoped devices in Figs. 3(a)–3(c). The absorption spectra of MDMO-PPV, PCBM, and PtOEP are shown in Fig. 3(d) in order to discriminate between the various contributions. The η_{EQE} spectrum of the doped 1:1 blend [Fig. 3(a)] shows an enhancement that comes both from direct absorption on PtOEP with peaks at wavelengths of $\lambda = 390$ and 540 nm, as well as from an increase of the MDMO-PPV signal in its absorption window (450 nm < λ < 550 nm). Here, the enhanced MDMO-PPV signal originates from a higher percentage of excitons that can reach the DA interface as a result of increased L_D . This is consistent with the high content of polymer in the 1:1 blend, where it is not always obvious that a DA interface is nearby the location of exciton generation.

Phase separation of the MDMO-PPV:PCBM blend sets in at between 60%–70% PCBM concentration, with the PCBM domain size steadily increasing with PCBM content.^{10,11} In a 1:3 blend ratio, the phase separation is ideal for exciton dissociation, with PCBM domains of 50–80 nm, slightly larger than $2L_D$. This fact is confirmed in the η_{EQE} spectra [Fig. 3(b)], where the main contribution to the 5% increase in photocurrent comes from direct absorption on PtOEP molecules, and not from an enhancement of the MDMO-PPV or PCBM signals. In the 1:3 blend device, the PtOEP therefore only acts to harvest a slightly larger percentage of solar illumination, similar to other studies for incorporating small molecules into polymer:fullerene blends.^{15–17} Finally, in the 1:7 blend, PCBM domains are ≈ 100 –175 nm, reducing the diffusion efficiency of PCBM excitons to the DA interface. In Fig. 3(c), we see that direct absorption on PtOEP again plays a role in enhancing photocurrent, but that the main increase comes throughout the PCBM absorption spectrum, where there is a 10%–15% increase, in agreement with the increase in J_{sc} shown in Fig. 2.

FIG. 3. Measured external quantum efficiency (η_{EQE}) spectra for the device structures of Fig. 1 with a MDMO-PPV:PCBM layer in a ratio of (a) 1:1, (b) 1:3, and (c) 1:7, either undoped (solid curves) or doped (dashed curves) with 5% PtOEP. (d) The absorption spectra for the three active materials in the device.

In summary, we have demonstrated photocurrent enhancement in BHJ solar cells of over 20%, where we have introduced a small amount of a phosphorescent dopant. The dopant, which has no negative impact on charge transport,

was found to enhance the photocurrent via multiple pathways. First, at low acceptor concentrations, the donor polymer signal was enhanced by the process of sensitized phosphorescence, whereby optically excited singlet excitons are transferred to farther-diffusing triplet excitons. Second, the dopant is able to absorb light and contribute directly to photocurrent. Finally, the dopant also acts as a donor site to improve the acceptor signal in blends containing a high concentration of acceptor. These multiple pathways mean that for well-chosen dopants, it should be possible to enhance the performance of BHJ solar cells optimized for arbitrary polymer:fullerene ratios.

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