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Enhanced power conversion efficiency of p-i-n type organic solar cells by employing a p-layer of palladium phthalocyanine

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We demonstrate an enhancement in the power conversion efficiency (PCE) of p-i-n type organic solar cells consisting of zinc phthalocyanine (ZnPc) and fullerene (C60) using a p-layer of palladium phthalocyanine (PdPc). Solar cells employing three different device structures such as ZnPc/ZnPc:C60/C60, PdPc/PdPc:C60/C60, and PdPc/ZnPc:C60/C60 with varying thickness of mixed interlayers were fabricated by thermal evaporation. The mixed i-layers were deposited by co-evaporation of MPC (M=Zn, Pd) and C60 by 1:1 ratio. PCE of 3.7% was obtained for optimized cells consisting of PdPc/ZnPc:C60/C60 while cells with device structure of ZnPc/ZnPc:C60/C60 showed PCE of 3.2%. © 2010 American Institute of Physics. [doi:10.1063/1.3507387]

Solar cells based on small molecular weight organic semiconductors have been gaining much attention in major part due to their low cost, relative ease of materials synthesis, and inherent flexibility, since Tang et al.1 reported p-n type heterojunction solar cells. One of the limitations in a power conversion efficiency (PCE) of p-n type organic heterojunction cells arise due to a low exciton diffusion efficiency, ascribed to short exciton diffusion lengths (∼10 nm) of most organic semiconductors.2 The exciton diffusion efficiency can be enhanced by blending donor and acceptor materials in order to enlarge the donor/acceptor (D/A) interface, thus enabling almost all the excitons generated by incident photons to reach D/A interfaces for subsequent dissociation and generation of charge carriers.3 However, intermixing of donor and acceptor results in inevitable reduction in carrier mobility as carrier transport is disrupted by fine domain size of donor and acceptor. This leads to poorer charge collection in a D/A mixed layer compared to a D/A bilayer. A thin mixed layer of donor (CuPc or ZnPc) and acceptor (C60) sandwiched by neat films of donor and acceptor has been demonstrated to generate photocurrent, efficiently.4 Such device structure is termed p-i-n type heterojunction.5 In p-i-n type organic solar cells, charge carriers are generated not only in the i-layer but also in both the p-layer and the n-layer. Therefore, a longer exciton diffusion length in the pristine layers is beneficial to producing large photocurrent. Recently, we have reported that replacement of centered metal ions with palladium in widely used planar metallophthalocyanines (MPCs) such as CuPc and ZnPc resulted in a longer exciton diffusion length.6 In this article, we report the enhancement of PCE in p-i-n type solar cells of ZnPc and C60 by substituting palladium phthalocyanine (PdPc) for the ZnPc p-layer. In addition, charge carrier collection efficiency in mixed layers of MPC and C60 is also discussed.

ZnPc, PdPc and perylene tetracarboxylic diimide with hexyl (PTCDI-C6) were synthesized following procedures detailed in literature.7,8 Bathocuproine (BCP), which is typically used as an exciton blocking layer, and C60 were purchased from Alfa Aesar and MER Corp., respectively. All organic materials were purified by thermal gradient approach prior to their deposition in a thermal evaporation system. Indium tin oxide (ITO) glass substrates were plasma-ashed before thin film deposition. Figure 1 illustrates three device structures used in this study. First, a p-layer of MPC having a 20 nm thickness was deposited, followed by a mixed i-layer of MPC and C60 with varying thickness of 10–30 nm. C60 (30 nm), PTCDI-C6 (5 nm), and BCP (15 nm) were deposited sequentially. The C60 served as the n-layer, while the PTCDI-C6 was used to achieve good Ohmic contact between C60 and BCP/Ag.9 Lastly, silver was evaporated through a shadow mask defining a device area of 0.2 cm2. Mixed i-layers of MPC and C60 were coevaporated at 1:1 volume ratio, which were reported to be favorable for efficient charge collection.4 p-n type cells without the mixed i-layer were also fabricated and compared. Current-voltage charac-

FIG. 1. Schematic representation of three p-i-n type device structures: MPC (20 nm)/mixed layer (0–30 nm)/C60(30 nm)/PTCDI-C6 (5 nm)/BCP (15 nm)/Ag (100 nm).

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characteristics of solar cells were measured under air mass 1.5 global 100 mW/cm² illumination at room temperature using a solar simulator (Oriel 300 W). External quantum efficiency (EQE) of solar cells was measured at various light wavelengths from 300 to 900 nm using a custom-setup EQE measurement system (Optronic Laboratories).

Figures 2(a)–2(d) show characteristics of solar cells having device structure A, B, and C with varying mixed layer thickness. In the case of p-i-n type cells without a mixed i-layer, the PdPc/C_60 cell exhibits a PCE of 2.7%, whereas the ZnPc/C_60 cell shows 1.9% as shown in Fig. 2(a). The higher PCE of PdPc/C_60 cell is due to its larger short circuit current density (J_{sc}) when compared with that of ZnPc/C_60 cell. This stems from a longer exciton diffusion length in PdPc (~10 nm) compared to ZnPc (~6 nm). Insertion of a mixed i-layer of ZnPc:C_60 leads to enhancement in PCE (A- and C-type cells). The PCE increases with increasing thickness of the mixed layer up to 20 nm. C-type cells exhibit a PCE as high as 3.5%, whereas A-type cells exhibit a maximum of 3.2%. A further increase in the thickness of the i-layer results in slight reduction in the PCE of the both structures. In Fig. 2(b), J_{sc} of A- and C-type cells increases as the thickness of the i-layer is increased up to 30 nm. Moreover, J_{sc} of C-type cells is consistently larger than that of A-type cells at given i-layer thicknesses. As shown in Figs. 2(c) and 2(d), the fill factor (FF) and open circuit voltage (V_{oc}) of A- and C-type cells are almost similar, although FF of C-type cells is slightly lower than A-type cells. In contrast, B-type cells show a decrease in the PCE with insertion of the mixed PdPc and C_60 i-layer despite the increase in J_{sc} for the thickness of up to 20 nm. Such decrease in PCE can be ascribed to a combination of decreasing FF and V_{oc} with increasing i-layer thickness compared to A and C-type cells.

EQE measurements provide further understanding the origin of the relatively larger J_{sc} of C-type cells. Figure 3 shows that EQE spectra of A-, B-, and C-type cells with 20-nm-thickness i-layer, along with p-n type cells of ZnPc/C_60 and PdPc/C_60. Peak values in EQE spectra around 600–610 nm are due to MPC. p-n type cell of ZnPc/C_60 has broadened EQE spectra with a peak value of 25% at ~610 nm, whereas that of PdPc/C_60 is 44% at ~600 nm. With insertion of 20-nm-thickness i-layer of ZnPc:C_60, the EQE values at 600–610 nm for A- and C-type cells increase significantly with virtually no enhancement observed in the range of 400–500 nm in which there is dominant absorption by C_60. The peak EQE value for C-type cell lies at ~600 nm, suggesting a substantial contribution from PdPc. Although the peak EQE value of B-type cell is the highest among all cells, its narrower EQE spectra results in similar J_{sc} to that of A-type cell. Therefore, efficient photocurrent contribution from the PdPc p-layer coupled with broadened spectral response due to the ZnPc:C_60 i-layer is considered to be a reason for the larger J_{sc} of C-type cell.

In order to understand the noticeable decrease in FF of C-type cells with increasing i-layer thickness, two solar cells having a mixed layer of ZnPc:C_60 and PdPc:C_60 sandwiched between ITO glass and BCP (10 nm)/Al (100 nm) were fabricated and tested under illumination at a light intensity of AM 1.5G 100 mW/cm². Figure 4 shows the dependence of normalized photocurrent (J_{ph}/J_{calc}) of the two devices on effective bias (V_{0}–V), where J_{ph} is the photocurrent density...
determined by subtracting the dark current density from the current density under illumination, and $J_{\text{calc}}$ is the maximum possible photocurrent calculated based on the assumption that all the absorbed photons in a mixed layer are converted into electricity. Absorption in a mixed layer was calculated using a transfer matrix algorithm with refractive indices determined by spectroscopic ellipsometry (J.A. Woollam M-2000). $V$ is the bias voltage and $V_0$ is the compensation bias voltage for a zero photocurrent. In Fig. 4, both of the cells exhibit a linear increase in normalized photocurrent with increasing bias up to a few tenths of a volt, followed by saturated photocurrent at higher bias. ZnPc:C$_{60}$ cells generate larger normalized photocurrent than that of PdPc:C$_{60}$ cells at a given bias voltage in the range of 0.01 to 3.0 V, which indicates a more efficient collection of photogenerated charge carriers in ZnPc:C$_{60}$ devices. At 3.0 V, 99% of absorbed photons in ZnPc:C$_{60}$ are converted into electricity, whereas the conversion is only 87% in PdPc:C$_{60}$ cell. For further characterization, we fabricated two devices with cell structure of ITO/ZnPc:C$_{60}$ (100 nm)/Au and ITO/PdPc:C$_{60}$ (100 nm)/Au in order to measure the hole mobility in a mixed layer using a space charge limited current model. In this case, a zero field hole mobility of $8.3 \times 10^{-5}$ cm$^2$/V s and $9.1 \times 10^{-6}$ cm$^2$/V s was obtained in ZnPc:C$_{60}$ and PdPc:C$_{60}$ mixed layers, respectively. The zero field hole mobility of PdPc:C$_{60}$ is one order of magnitude lower than that of ZnPc:C$_{60}$. In addition, AFM images reveal relatively different surface morphology of the mixed layers as shown in Fig. 4. The ZnPc:C$_{60}$ film shows uniform-sized domains of approximately 30–50 nm and clear domain boundaries, whereas the PdPc:C$_{60}$ film shows the presence of finer domains and less defined domain boundaries, suggesting that phase separation between PdPc and C$_{60}$ is more hindered than ZnPc and C$_{60}$. A lower hole mobility and finer phase separation in PdPc:C$_{60}$ film appears to result in stronger dependence of electron-hole recombination on electric field, which can be a possible reason for a faster decrease in FF of $B$-type cells with increasing $i$-layer thickness.

Further optimization of $C$-type cells by varying the thickness of $p$-layer PdPc was performed. We found that cells with 15-nm-thick PdPc $p$-layer (labeled as C-1) led to a PCE of 3.7% due to an increased FF. Device parameters for A, B, C, and C-1 cells with 20 nm $i$-layer are summarized in Table I.

In conclusion, the PCE of $p$-$i$-$n$ type organic solar cells consisting of ZnPc and C$_{60}$ was enhanced by using a $p$-layer of PdPc. Such improvement is due to a more efficient exciton diffusion in PdPc compared to ZnPc. An optimized cell structure exhibits a PCE of 3.7% at a light intensity of AM 1.5G 100 mW/cm$^2$. However, the mixed layer of ZnPc:C$_{60}$ has more efficient charge carrier collection than PdPc:C$_{60}$ due to higher hole mobility and more favorable phase separation in ZnPc:C$_{60}$ than PdPc:C$_{60}$. Further work is under way to achieve higher PCE than 3.7% by enhancing charge carrier mobility of the $i$-layer through elaborate morphology control.

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### Table I. Device parameters of $p$-$i$-$n$ type cells with a 20-nm-thick mixed layer. The thickness of MPc $p$-layer is 20 nm for cells with the structure of A, B, and C, and 15 nm for cells with the structure of C-1.

<table>
<thead>
<tr>
<th>Device structure</th>
<th>PCE (%)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>3.2</td>
<td>9.4</td>
<td>0.60</td>
<td>56</td>
</tr>
<tr>
<td>B</td>
<td>2.4</td>
<td>9.7</td>
<td>0.55</td>
<td>46</td>
</tr>
<tr>
<td>C</td>
<td>3.5</td>
<td>10.8</td>
<td>0.60</td>
<td>54</td>
</tr>
<tr>
<td>C-1</td>
<td>3.7</td>
<td>10.5</td>
<td>0.60</td>
<td>58</td>
</tr>
</tbody>
</table>