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Photocurrent Enhancement in Bulk Heterojunction Organic Photovoltaic Devices

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I. INTRODUCTION

Organic photovoltaic (OPV) devices that can convert sunlight into electricity in organic semiconductors have been subject of active research over the past two decades. Significant advances on the development of smart materials and innovative device architecture have boosted the power conversion efficiency up to 10.6 % [1]. In particular, bulk heterojunction consisting of a spatially distributed donor/acceptor interface can greatly increase the exciton dissociation efficiency approaching an unity, yielding a higher short-circuit current (Isc). The major obstacle for achieving high power conversion efficiency is in balancing the absorption needed for photocurrent generation with the charge transport properties of the blended layer. Especially the charge carrier mobilites in the blended layer are orders of magnitude lower than those of homogeneous layers, and it requires a delicate control on the composition and thickness of the blended layer. Zhang *et al.* recently modified this bulk heterojunction concept by employing non-absorbing donor material, 1,1-bis(4-bis(4-methly-phenyl)-amino-phenyl)-cyclohexane (TAPC), doped into fullerene (C_{70}) acceptor, in conjunction with molybdenum oxide as anodic buffer layer [2]. Surprisingly, with a very low concentration of TAPC of only 5%, a three-fold increase in Isc with an extraordinarily high open-circuit voltage (Voc) of 0.91 V had been obtained. These yielded a high power conversion efficiency of 5.23%, which is the highest ever reported for a cell with fullerene as the sole absorber. On the other hand, the exact mechanisms and the underlying physics for the performance improvement are still unclear. In particular, such high Voc cannot be explained by the common energy gap law. Here, the effects of different non-absorbing organic materials as donor on the performance of OPV devices with the modified bulk heterojunction have been studied and the correlation between the energetic properties of donor materials and the photovoltaic responses is discussed.

II. EXPERIMENTAL

OPV devices were fabricated with the configuration of indium-tin oxide/WO_3/C_{60}/ bathophenoline (BPhen)/aluminum, in which 5% non-absorbing organic materials were doped into C_{60} as donor. Two well-known hole-transporting materials, namely, 4,4',4"-tris(*N*-carbazolyl) triphenylamine (TCTA) and *N*,*N*'-diphenyl-*N*,*N*'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), and two electron-transporting materials, namely, 3-(4-biphenyl)-4-phenyl-5-(4-tert-butylphenyl)-1,2-4-triazole (TAZ) and 1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB), were used as donor materials. A control C_{60}-only device had also been prepared for comparison. The photocurrent of OPV devices was measured under illumination with an intensity of 1 sun from an Oriel 300 W solar simulator equipped with AM1.5 G filter and the light intensity was calibrated by a Newport reference cell equipped with a KG5 window to minimize the spectral mismatch.

III. RESULTS AND DISCUSSION

Under light illumination, the C_{60}-only device showed a poor performance with Isc = 1.22 mA/cm^2, Voc = 0.87 V, fill factor = 0.36, and power conversion efficiency of 0.38%. The incorporation of hole-transporting donor material, e.g. TCTA or TPD, can improve the photovoltaic responses. The Isc was dramatically increased to 3.21 and 3.68 mA/cm^2, for the TCTA- and TPD-doped devices, respectively. More importantly, the Voc of the device increased from 0.87 V to 0.95 V for the TCTA-doped device. These correspond to high power conversion efficiencies of 1.20% for both devices, much higher than that of the C_{60}-only device. In sharp contrast, the doping of electron-transporting donor material, e.g. TAZ or TmPyPB, would degrade the device performance. Particularly, the Isc of the TAZ- and TmPyPB-doped devices dropped to 0.82 and 0.77 mA/cm^2, respectively; while the Voc decreased to 0.54 and 0.48 V, respectively. It is quite surprising that the use of donor material with a very low dopant concentration (i.e. 5%) can lead to a significant

change on the photovoltaic responses. To investigate the role of donor materials, an incident-photon-to-current efficiency (IPCE) measurement was performed. Figure 1 depicts the IPCE spectra of OPV devices doped with different non-absorbing donor materials. Apparently, the incorporation of 5% donor materials can significantly enhance the IPCE and thus the exciton dissociation efficiency, in which the IPCE dramatically increased from 16.0% for the C_{60}-only device to 36.7% and 41.2% for the TCTA- and TPD-doped devices at the C_{60} absorption at 440 nm. This enhanced exciton dissociation efficiency definitely increases the Isc of OPV devices. It is also found that the Voc of OPV devices are strongly dependent on the highest occupied molecular orbital (HOMO) level of the donor materials. To investigate the controlling factors governing the Voc, the Voc of the devices were re-plotted as a function of HOMO level of donor materials. As depicted in Figure 2, the Voc of OPV devices generally increased with increasing the HOMO level of donor material and reached a maximum at 0.95 V when the HOMO level increased up to 5.7 eV (i.e. TCTA was used as donor material). The Voc increase is due to the increase on the energy difference between the HOMO level of donor and the lowest unoccupied molecular orbital level of C_{60}. On the other hand, a further increase in the HOMO level would lead to the reduction in the Voc of the devices. The close proximity of the HOMO levels of donor and C_{60} may restrict the exciton dissociation in C_{60} and accounts for the Voc reduction [3].

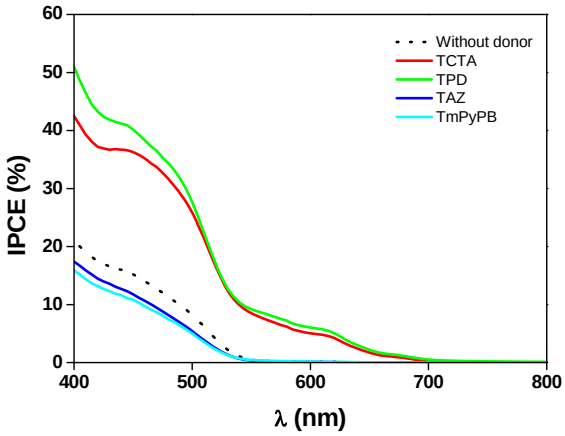

Figure 1. IPCE spectra for OPV devices doped with different donor materials.

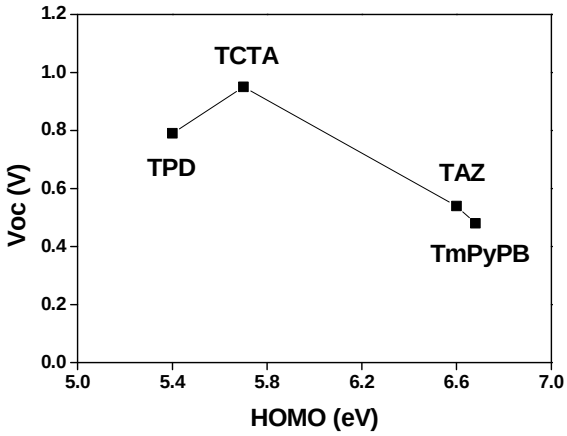

Figure 2. Voc of OPV devices as a function of HOMO levels of donor materials.

IV. CONCLUSION

In summary, the influences of different non-absorbing organic materials as donor on the performance of OPV devices with modified bulk heterojunction had been studied. The photovoltaic responses of OPV devices were found to be sensitive to the choice of the donor materials, even if a very low donor concentration of only 5% was employed. Particularly, the Isc showed a three-fold increase when a hole-transporting material was doped into C_{60} to form bulk heterojunction, which might be due to an enhanced exciton dissociation efficiency. A strong dependence of HOMO level of donor material on the Voc of OPV devices was also found.

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