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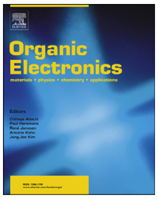

Elucidating the role of current injection on the influence of open-circuit voltage in small-molecule organic photovoltaic devices: From the aspects of charge transfer and electroluminescent spectrum

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We demonstrate that the open-circuit voltage (V_{OC}) of organic photovoltaic (OPV) devices composed of rubrene and C_{60} can be considerably different when the anode and active layer are changed. Two types of anodes and active layers were compared. In plasma-treated indium-tin-oxide (ITO) OPV devices, the parameter V_{OC} exhibits an improvement from 0.68 V to 0.76 V when the device structure is varied from a bilayer to a mixed structure. However, in the OPV devices that use ITO/MoO_3 as the anode, a similar V_{OC} is observed regardless of the device structure. A series of temperature-dependent measurements are conducted to investigate these results. The calculation of barrier height at the rubrene/C_{60} (or rubrene:C_{60}) interface yields the prediction of V_{OC}, suggesting that an excess energetic loss occurs in the mixed structures. The electroluminescent (EL) spectra of these devices show that the mixed structure can completely quench the EL of rubrene single layer. A broad band of the charge transfer (CT) emission is observed clearly. A temperature-dependent measurement for the extracting injection barrier is conducted and shows that the mixed structure is favorable for the hole current injection. The CT properties are obtained using the external quantum efficiency and EL spectra of the OPV devices. We find that the nonradiative recombination loss is highly correlated with the injected current; the lower the injection barrier induced the less the nonradiative recombination loss. Therefore, the parameter V_{OC} can be improved when the injected current is increased.

1. Introduction

Organic photovoltaic (OPV) devices enable the fabrication of applications of large-area and flexible optoelectronic devices [1–3]. Since the first breakthrough that was achieved by Tang, the power conversion efficiency (PCE) of small-molecule OPV devices has been considerably improved over the last decade [4–8]. Because of the fine structure of molecules and the thermal-evaporation fabrication process, small-molecule-based OPV devices enable a high reproducibility over their polymeric counterparts [9,10]. However, the short-circuit current density (J_{SC}) and fill factor (FF) remain challenged because of the narrow absorption band and poor carrier transportation. A possibility for outperforming polymeric OPV devices is to increase the open-circuit voltage (V_{OC}) because of the high band-gap of small molecules that enables an increase of the energy difference of the highest occupied molecular orbital (HOMO) levels of donors and the lowest unoccupied molecular orbital (LUMO) levels of acceptors [11–13]. The combination of complementary absorbing devices in a series connection has shown their possibility for obtaining a PCE approaching that of polymers [4,8,14]. Therefore, the mechanism of the V_{OC} must be clearly understood for realizing high-V_{OC} small-molecule OPV devices [15–17].

In polymeric systems, several groups have demonstrated that the V_{OC} is highly related to the interfacial properties such as morphological change, HOMO-LUMO gap at the donor/acceptor interface, and charge transfer (CT) process [18–23]. There are still relatively few studies discussing the origin of the V_{OC} in small

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molecule-based OPV devices [24–26]. In our previous study, we showed that the interfacial contact between a donor and acceptor has a substantial influence on the V_{OC} [27]. Vandewal et al. demonstrated the influence that is subjected to the CT process [16,23]. Recently, several studies have employed a hole-extraction layer (HEL) for improving the PCE [28–32]. In addition to the improvement of J_{SC} and FF, the V_{OC} can be higher when a HEL is inserted at the anode/organic layer interface [28–32]. The lack of in-depth discussion of the improved V_{OC} renders the mechanism unclear, and, hence, further improvement in V_{OC}. In the current study, we fabricated OPV devices based on rubrene [33,34] as a donor and C_{60} as an acceptor. Because of the high mobility and low absorption coefficient of rubrene [35], the change in thin film structure is expected to be independent of the photocurrent and fill factor, thus allowing for in-depth investigating the relation of V_{OC} to CT states. A standard device with plasma-treated indium-tin-oxide (ITO) has the lowest V_{OC}. A higher V_{OC} was obtained using a mixed structure of rubrene:C_{60}. The insertion of a commonly used HEL, MoO_3, exhibited a higher V_{OC} compared with the device without the HEL. The CT analyses using external quantum efficiency (EQE) and electroluminescence (EL) showed that the energetic losses originated from nonradiative recombination can be suppressed through a high current-injection condition. A temperature-dependent measurement for calculating the injection barrier proved that the high current injection arose from the use of either MoO_3 or mixed structure.

2. Experiments

Materials and Device Fabrication. All materials, MoO_3. rubrene, C_{60}, bathocuproine (BCP) and Al were purchased from Sigma-Aldrich. These materials were used as received without further purification. ITO-precoated substrates with the ITO sheet resistance of approximately 15 Ω/sq were purchased from Luminescence Technology Corporation. The substrates were cleaned through a standard solution-cleaning process by ultrasonic bathes in a series of solutions, detergent, deionized water, acetone, and isopropanol, for ten minutes in each step. Each thin film was deposited in a high-vacuum chamber with a pressure less than 8×10^{-6} Torr. The deposition rate was simultaneously monitored using a deposition controller (Sycon Instruments STM-2XM). The film thicknesses were measured using a surface profiler (Veeco Dektak 3) and ellipsometry (Raditech SE-950). The deposition rate of each thin film was approximately 0.05 nm/s. A rubrene:C_{60} mixture with 1:1 in volume ratio was formed using the same deposition rates. An active area of 0.04 cm^{-2} was defined by the deposition of Al through a shadow mask. All devices were appropriately encapsulated using an UV-curable epoxy resin (Everwide Chemical Corporation Limited EXC345) and a getter-attached cover glass that fitted the active area in a nitrogen-filled glove box. The encapsulation process was completed by exposing the devices to UV illumination.

Characterization. Dark and photo current-density to voltage (*J-V*) characteristics of OPV devices were measured using a source meter (Keithley 2636A) in the dark and under AM 1.5G solar illumination (Newport 91160A) at 100 mW cm^{-2}, respectively. EQE spectra were obtained using a monochromator (Newport 74100) and lock-in amplifier (Stanford Research Systems SR830) chopped at 250 Hz. EL spectra were measured using a spectrometer (USB2000+). Temperature-dependent measurement was performed in a cooled cryostat (Janis VPF-100) connected with a cryogenic temperature controller (Lake Shore 335). The HOMO levels of organic materials and work functions of ITO and Al were measured using a low-energy photoelectron spectrometer (Riken Keiki AC-2). The LUMO levels of organic materials were evaluated from the band-gap obtained using a UV–visible spectrophotometer (Thermo Scientific Evolution 220).

3. Results and discussion

Four types of structures for OPV devices were fabricated. To investigate the influence of inserting an HEL, these devices were divided into two sets; a set with plasma-treated ITO and another with pristine ITO/MoO_3, and each set has a rubrene/C_{60} bilayer and rubrene:C_{60} mixed structures (Supporting Information, Fig. S1). Fig. 1a shows the photo *J-V* characteristics of the OPV devices. The error bars on an average of ten devices are provided. The device with a bilayer structure of plasma-treated ITO/rubrene (7 nm)/C_{60} (30 nm)/BCP (8 nm)/Al (120 nm) shows the lowest V_{OC}. When the mixed structure, rubrene:C_{60} (37 nm) was used, the V_{OC} considerably increased, whereas both the J_{SC} and FF decreased, probably because of a non-optimal mixed ratio that resulted in poor interconnection between rubrene and C_{60}. The thickness of rubrene in a mixed layer is considerably thicker than that in a bilayer structure. However, because of the low absorption coefficient of rubrene, the parameter J_{SC} is expected to be independent of the rubrene thickness. In addition, our ongoing research shows that the J_{SC} remained the same when the thickness of rubrene was changed. Therefore, for improving J_{SC}, an optimal ratio of rubrene to C_{60} is required but beyond the scope of the current study. The devices with a structure ITO/MoO_3/rubrene (7 nm)/C_{60} (30 nm)/BCP (8 nm)/Al (120 nm) has a higher V_{OC} compared to the bilayer OPV device without MoO_3. This result could result from the high work function of MoO_3 and its dipole effect [28,36]. However, when a mixed structure of active layers was used, the V_{OC} exhibits a small increase. The large difference in V_{OC} shift between these two sets may arise from the Fermi energy-level pinning effect of MoO_3, [37] which renders the built-in potential in the devices similar, and hence the V_{OC}. Table 1 summarizes the photovoltaic parameters of the OPV devices. A large change in V_{OC} was observed when various hole-injection conditions were used. The V_{OC} changes from 0.68 V to 0.80 V when the anode varied from plasma-treated ITO to ITO/MoO_3. A possible reason for this phenomenon is that the work function of MoO_3 is larger than that of plasma-treated ITO. However, the plasma-treated set exhibits a very different V_{OC} from 0.68 V to 0.76 V when the device structure varied from bilayer to mixed structure. These results indicated that there are other factors determining the V_{OC} except for the work function of the anode. The J_{SC} and FF primarily depend on the device structure rather than the anode. Fig. 1b shows the EQE spectra of the corresponding devices. The changeless spectrum shape and reduced FF implies that the lower J_{SC} obtained in the mixed structure could result from the poor charge collection efficiency, which includes the exciton dissociation and charge transport.

The Shockley equivalent circuit model is widely used to describe the diode properties of OPV devices [19,24,38]. The general expression of an OPV device can be described by

$$J = \frac{1}{1 + R_S/R_{SH}} \left\{ J_0 \left[\exp\left(\frac{V - JR_SA}{nkT/e} \right) - 1 \right] - \left(J_{PH} - \frac{V}{R_{SH}A} \right) \right\}. \tag{1}$$

Here, R_S and R_{SH} are the series and shunt resistance of the device, J_0 is the reverse saturation current density, A is the active area of the device, n is the ideality factor of the device, k is the Boltzmann constant, T is the temperature, e is the elementary charge, and J_{PH} is the photocurrent. Assuming $R_S = 0$, $R_{SH} \to \infty$, and $J_{PH} = J_{SC}$, and $J = 0$ simplifies Equation (1) to yield the open-circuit condition and the expression of V_{OC}: