



The effect of charge transfer state on the open-circuit voltage of small-molecular organic photovoltaic devices: A comparison between the planar and bulk heterojunctions using electroluminescence characterization



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ABSTRACT

This work studies the open-circuit voltage (V_{OC}) of planar and bulk heterojunction organic photovoltaic (OPV) devices by means of electroluminescent (EL) technique to resolve the charge transfer (CT) states between donor and acceptor. The OPV devices containing a small part of bulk heterojunction increases the V_{OC} as a result of the enhanced CT process as compared with a complete planar structure. Red shift of the CT charge transfer was observed by increasing the bulk volume, which indicates the increased degree of interaction between both molecules and excitons. By characterizing the EL spectra of OPV devices and relating them to the CT absorption, the interfacial property between the donor and acceptor is shown to be crucial for determining the V_{OC} in small-molecule OPV devices. Detailed analysis of the energetic loss was also used to interpret the V_{OC} under the effect of CT states.

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1. Introduction

Open-circuit voltage (V_{OC}) is as important as short-circuit current density (J_{SC}) and fill factor (FF) for improving the power conversion efficiency (PCE) of organic photovoltaic (OPV) devices due to the linear proportion of PCE to V_{OC} , J_{SC} and FF [1,2]. However, improving V_{OC} involves complex mechanisms, such as thermodynamic losses [3,4], charge behavior [5], interfacial energetics [6], electronic properties [7] and charge transfer (CT) states [8]. Several efforts have been made to simplify the explanation of V_{OC} . For example, the work function matching at the collecting electrode

[9,10], the energy difference between donor and acceptor [11], the donor/acceptor coupling [12], and the built-in potential at the Schottky junction [13] are systematically studied and shown to be valid for the V_{OC} estimation. Recently, Rau derived a rigorous theorem of the reciprocity relation between external quantum efficiency (EQE) and electroluminescent (EL) emission in photovoltaic devices, giving the direct connection of V_{OC} and EL [14]. Meanwhile, Goris et al. observed the subgap absorption in polymeric system which provided evidence for the CT states suggested by Vandewal et al. [15,16]. Direct observation of the EL spectra of polymeric OPV devices have also been shown to be useful in detecting the CT states as proposed by Tvingstedt et al. [17]. A complete and comprehensive study relating V_{OC} to CT states was then accomplished and fully discussed, revealing the importance of nonradiative and radiative losses from CT states [18].

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In contrast to their polymeric counterparts, less research attention with the focus on CT states has been paid in small-molecular OPV devices. Nevertheless, CT is a nature of organic materials that is omnipresent as a result of inter- and/or intra-molecular π - π interactions [19]. Sanchez-Diaz et al. and Chou et al. employed transient absorption decay and time-resolved photoluminescence to observe the CT process in small-molecule OPV devices [20,21]. These approaches allow for the detailed evaluation of bimolecular recombination and interfacial properties between donor and acceptor. More recently, the EL properties of a rubrene/ C_{60} -based OPV device were characterized by Huang et al., showing the existence of CT states [22]. Precise calculation of the CT absorption band was performed by Graham et al. comparing tetracene and rubrene as donors and C_{60} as acceptor, revealing a consistent relationship between V_{OC} and CT energy as obtained in a polymeric system [23]. The most complete study of CT states was published by Bernardo et al., using N,N'-bis(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine mixed with C_{60} as the active layer, showing the influence of crystallinity on CT states depending on the mixing ratio of donor to acceptor [24]. These studies used non-absorbing donors and few studies have used the conventional absorbing donors like zinc phthalocyanine [25]. In addition, none of the reported studies measured EL spectrum to ensure the accurate CT absorption band from the existence of CT states [26]. Here, we demonstrate that the V_{OC} of subphthalocyanine (SubPc)/ C_{60} based OPV devices could be related to the properties of CT states by using the EL measurement without special techniques. The increased degree of interaction between donor and acceptor was shown to contribute to the improvement in V_{OC} . Energetic losses caused by CT states could be reduced by enhancing the EL efficiency as observed in the decreased nonradiative recombination. A detailed analysis of CT properties was also performed.

2. Materials and methods

Organic materials, SubPc, C_{60} , bathocuproine (BCP) were purchased from Sigma-Aldrich and used as received without further purification. Devices were fabricated onto pre-patterned indium-tin-oxide (ITO) substrates in a high vacuum chamber ($<8 \times 10^{-6}$ Torr). Four kinds of structures based on planar, mixed-planar, bulk heterojunctions, and bulk heterojunction followed by a thick planar layer that are distinct from the active layers were used as shown in Table 1. For the sake of simplicity, the devices with four different structures are denoted as p/n, i/n, I, and I/n, respectively. Prior to the thin film deposition, the ITO

surface was treated by oxygen-plasma to meet a better work function matching at the hole-collecting anode [27,28]. The deposition rate and thickness were monitored with a quartz crystal microbalance calibrated by a surface profiler (Veeco Tektak 150). The typical deposition rate of organic materials was 0.1 nm/s. For the mixed structure, the deposition rates of SubPc and C_{60} were independently controlled at 0.1 nm/s to form a 1:1 volume ratio. The device active area was defined as 0.04 cm² by the deposition of Al through a shadow mask. A total of ten devices were simultaneously fabricated on two different substrates to avoid deviation between devices. A home-made *in-situ* and independently controlled shutter system was used to fabricate devices with different structures in one run without breaking the vacuum, thus avoiding deviation between production runs. Following the fabrication process, the devices were well encapsulated and measurements were carried out in the air. Current density–voltage (J - V) characteristics were performed using a source-meter (Keithley 2400) and an AM 1.5G solar simulator (Newport 91160A) with 1-sun intensity (100 mW/cm²) calibrated by a silicon reference cell (PV measurement; area: 3.91 cm²). EQE spectra were recorded using a monochromator (Newport 74100) to select the wavelength ranging from 400 to 800 nm and a lock-in amplifier chopped at 250 Hz (Stanford Research Systems SR830) for the photocurrent reading. EL spectra were measured using a spectrometer (Ocean Optics USB2000).

3. Results and discussion

Fig. 1(a) shows the J - V characteristics of OPV devices with different structures under AM 1.5G simulated solar illumination. The data were collected in one run and the standard deviation at each point is given. Table 1 summarizes the corresponding performances on an average of ten devices, with the standard deviation to highlight the reliability of the work. The conventional planar heterojunction (p/n, i/n) devices show a typical diode behavior, while the devices with bulk heterojunction (I, I/n) deviates significantly from the ideal property, probably due to the non-optimum mixing ratio and/or discontinuous interpenetrating network between donor and acceptor resulting in the poor carrier transport [29,30]. It should be noted that the deviation refers to the unpredictable J - V curve based on an ideal diode, which generally exhibits a dramatic increase in current after the maximum power point. On the contrary, the devices with bulk heterojunction show a slow increase in current with applied voltage, indicating a pronounced carrier recombination in these devices. A comparable FF was obtained for both the p/n and i/n

Table 1
Device structures of the OPV devices with different active layers.

Device	Anode	Active layer	Buffer	Cathode
p/n	ITO	SubPc (5 nm)/ C_{60} (30 nm)	BCP (10 nm)	Al (100 nm)
i/n		SubPc: C_{60} (1:1; 5 nm)/ C_{60} (30 nm)		
I		SubPc: C_{60} (1:1; 35 nm)		
I/n		SubPc: C_{60} (1:1; 35 nm)/ C_{60} (30 nm)		

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