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Open-circuit voltage exceeding the outermost HOMO-LUMO offset in cascade organic solar cells

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ABSTRACT

We demonstrate a planar organic solar cell with a four-layer cascade architecture that exhibits an open-circuit voltage (Voc) greater than the offset in energy between the highest occupied molecular orbital (HOMO) of the outermost donor and the lowest unoccupied molecular orbital (LUMO) of the outermost acceptor. The device consists of a subphthalocyanine (SubPc)/fullerene (C60) heterojunction that is modified by inserting one or two additional donor layers between SubPc and the anode. We find that two-, three- and four-layer structures yield similar Voc (1.0 V, 0.91 V and 0.94 V, respectively), even though the outermost HOMO-LUMO offset decreases from 1.4 eV to 1.10 eV, and to 0.9 eV, respectively. Analysis of the turn-on voltage in dark provides further evidence that open-circuit voltage is not limited by the outermost HOMO-LUMO offset.

1. Introduction

Meeting the growing demand for solar energy conversion will require next-generation photovoltaics that are manufactured at low cost and low temperature, over large areas at high throughput, and on flexible substrates. One promising material system consists of organic semiconducting small molecules and/or polymers, although limitations inherent to their excitonic nature, such as low open-circuit voltage (V_{OC}) and poor coverage of the solar spectrum, must be overcome [1]. New device architectures employing multiple molecular species in a cascade energy alignment have begun to address these limitations, demonstrating impressive gains in efficiency by employing two donor materials [2,3], exciton blocking layers [4], interstitial layers at the donor-acceptor heterojunction [5–8], or directed energy transfer [9,10].

The origin of V_{OC}, however, in organic cascade photovoltaics remains unclear. In standard bi-layer cells, V_{OC} depends on the charge-transfer (CT) state energy at the donor-acceptor heterojunction, ideally approaching the offset between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor (ΔE_{DA}) [11,12]. In contrast, the V_{OC} of multiple-layer cells is more difficult to interpret, confounded by the presence of multiple exciton-dissociating interfaces. Here, the limit to V_{OC} has been ascribed to the HOMO-LUMO offset of the outermost semiconducting layers in the device stack [13] or alternately to the lowest value of ΔE_{DA} at each interface [14]. Previous observations of V_{OC} in cascade structures have found that adding an additional layer to a bi-layer cell, resulting in an energy loss step, does not reduce V_{OC} appreciably [4,14]. However, others have observed the opposite [2,15] or mixed results [16,17]. The implications for device theoretical efficiencies and design rules are significant because the lowest value of ΔE_{DA} can be substantially greater than the outermost HOMO-LUMO offset, allowing for higher V_{OC} and a greater number of cascade layers. Furthermore, recent efforts to design material sets with aligned outermost HOMO levels or outermost LUMO levels may not necessarily be required for high V_{OC}.

Here, we attempt to resolve the ambiguity in the origin of V_{OC} in cascade organic photovoltaics by demonstrating an organic small molecule planar cascade structure that exhibits V_{OC} greater than the outermost HOMO-LUMO offset. Our cascade system is constructed with an outermost HOMO-LUMO offset that is lower in magnitude than the lowest ΔE_{DA} energy (Fig. 1). We find that V_{OC} does not correlate with the outermost HOMO-LUMO offset, and instead follows the lowest ΔE_{DA} energy. Analysis of the current density vs.

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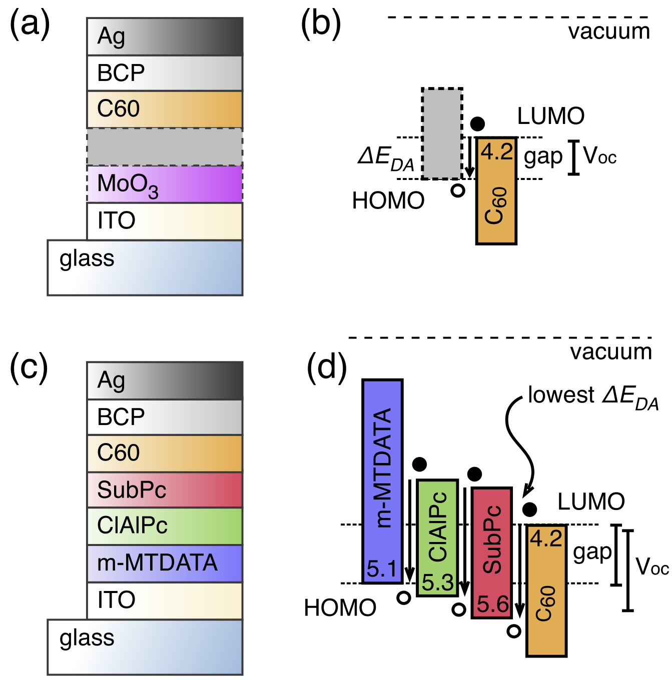

Fig. 1. Schematic of (a) bi-layer structures consisting of either m-MTDATA, ClAlPc, or SubPc donors, indicated in grey (MoO_3 is omitted for the m-MTDATA device), and (c) the four-layer cascade structure. The band diagram in (b) illustrates that V_{OC} is determined by recombination at the charge-transfer (CT) state, which occurs at voltages approaching ΔE_{DA}. In (d), the ambiguity in predicting V_{OC} in cascade solar cells exists because the 0.9 eV gap between the outermost HOMO (of m-MTDATA, −5.1 eV) and the outermost LUMO (of C_{60}, −4.2 eV) is less than the lowest instance of ΔE_{DA}, which occurs at the SubPc/C_{60} interface where $\Delta E_{DA} = 1.4$ eV.

voltage ($J-V$) response in the dark reveals that diode turn-on occurs at voltages greater than the outermost HOMO-LUMO offset, partially accounting for the high V_{OC} in these cascade structures.

2. Materials and methods

We employ two widely studied absorbing species, chloroaluminum phthalocyanine (ClAlPc) [18] and boron subthalocyanine chloride (SubPc) [19], along with a wide bandgap hole transport layer (HTL) 4,4,4-Tris[(3-methylphenyl) phenylamino] triphenylamine (m-MTDATA) [20], and a standard fullerene (C_{60})/bathocuproine (BCP)/silver (Ag) electron-accepting contact. We select m-MTDATA as wide bandgap HTL because it exhibits good diode behavior when paired with C_{60}. SubPc is selected for its ability to produce high V_{OC}. ClAlPc is selected for its energy level alignment, as both its HOMO and LUMO levels lie between those of m-MTDATA and SubPc. Devices are fabricated on half-inch square glass substrates with pre-patterned 20 Ω/sq indium tin oxide (ITO) substrates (Xinyan). After ultrasonic cleaning under micro-90, deionized water, acetone, and isopropanol for 5 min each, substrates are transferred to a glovebox, dried under nitrogen, and directly transferred to a glovebox-integrated plasma cleaner (PE-25-JW, Plasma Etch). Following a 5 min plasma treatment, substrates are loaded into a glovebox-integrated torpedo thermal evaporator (LC Technology) where the remaining layers of the device stack are deposited through a shadow mask (Photo Etch) under vacuum of approximately 3×10^{-6} Torr. In all devices except for those with m-MTDATA, 5 nm of MoO_3 (Aldrich) is evaporated onto ITO as an injection layer. All organic materials are used as-is without further purification (Lumtec). 40 nm thick Ag electrodes are deposited through a shadow mask to obtain a device area of 0.0121 cm^2. Three bi-layer structures are fabricated as controls: (a) ITO/m-MTDATA(30 nm)/C_{60}(30 nm)/BCP(7 nm)/Ag, (b) ITO/MoO_3(5 nm)/ClAlPc(20 nm)/C_{60}(40 nm)/BCP(7 nm)/Ag and (c) ITO/MoO_3(5 nm)/SubPc(13 nm)/C_{60}(32 nm)/BCP (7 nm)/Ag. Three cascade structures are fabricated for comparison: (a) a four-layer cascade structure, ITO/m-MTDATA (10 nm)/ClAlPc(12 nm)/SubPc(18 nm)/C_{60}(30 nm)/BCP(7 nm)/Ag, (b) a three-layer cascade structure without SubPc, ITO/m-MTDATA(10 nm)/ClAlPc(20 nm)/C_{60}(40 nm)/BCP(7 nm)/Ag, and (c) a three-layer cascade structure without m-MTDATA, ITO/MoO_3(5 nm)ClAlPc(10 nm)/SubPc(13 nm)/C_{60}(30 nm)/BCP(7 nm)/Ag. As this work focuses on V_{OC}, we have yet to optimize layer thicknesses to maximize photocurrent and minimize parasitic resistances. $J-V$ characteristics are measured under nitrogen at AM1.5G, 55 mW/cm^2 with a fiber optic solar simulator (Newport) and an electrometer (2400, Keithley).

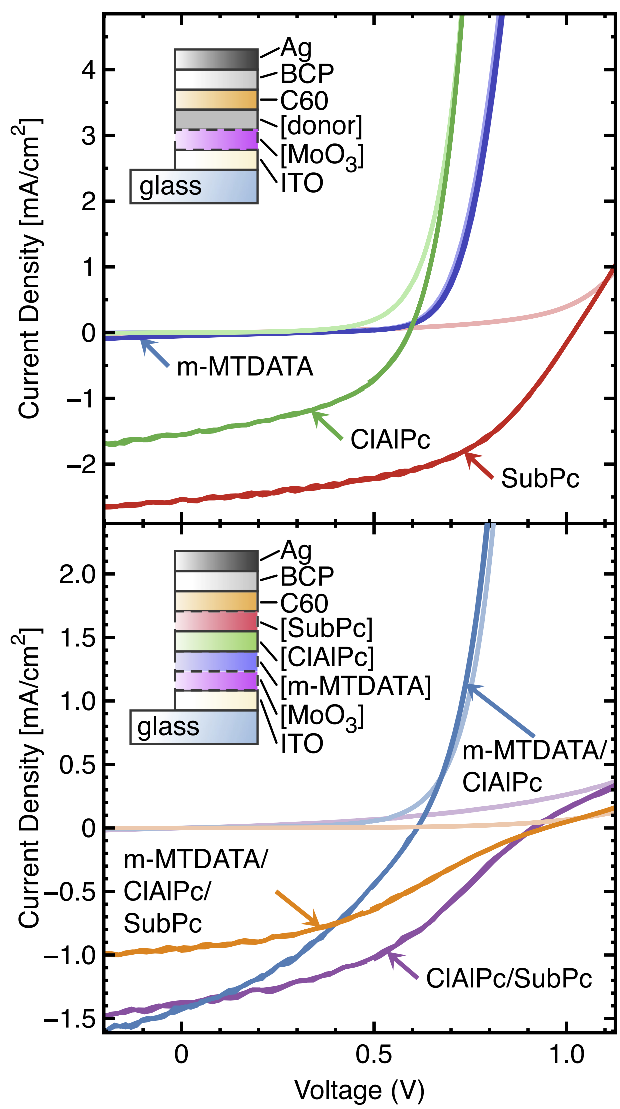

Fig. 2. Linear $J-V$ characteristics in light and dark for bi-layer structures (top) and cascade devices (bottom). A diagram of the bi-layer structure is given in the inset (top), where the donor layer is either m-MTDATA, ClAlPc, or SubPc. The inset (bottom) displays the cascade structures. For three-layer cascades, either m-MTDATA or SubPc is omitted. MoO_3 is not present for devices containing m-MTDATA. Illumination intensity under AM 1.5G is 55 mW/cm^2.