Pivotal factors in solution-processed, non-fullerene, all small-molecule organic solar cell device optimization

CrossMark

Jessica M. Topple [a], Seth M. McAfee [b], Gregory C. Welch [b, **], Ian G. Hill [a, *]

[a] Department of Physics, Dalhousie University, 1459 Oxford Street, Halifax, Nova Scotia B3H 4R2, Canada
[b] Department of Chemistry, Dalhousie University, 1459 Oxford Street, Halifax, Nova Scotia B3H 4R2, Canada

ARTICLE INFO

ABSTRACT

The importance of device structure and active-layer processing when screening non-fullerene acceptors was demonstrated through the organic solar cell device performance optimization of a solution processable non-fullerene, all small-molecule bulk heterojunction (BHJ) blend. Key tuning parameters were identified; notably, the largest improvement in performance was achieved by switching from the conventional device architecture (ITO/PEDOT:PSS/D-A BHJ/Ca/Al) to an inverted structure (ITO/ZnO/D-A BHJ/MoOx/Ag), approximately doubling the power conversion efficiency from best cells of 0.5%—1.0%, demonstrating the importance of investigating more than a single architecture when screening novel non-fullerene acceptors.

1. Introduction

The potential for sustainable, low-cost, clean-energy generating technology motivates research in the development of solution-processable small-molecule organic solar cells (OSCs) [1]. Although a wide variety of small-molecule electron donors have been explored [2—5], because of the widespread success and popularity of solubilized fullerene derivatives [6,7], relatively few non-fullerene electron-deficient small-molecules have been studied [8—10]. Alternatives to fullerenes are desirable, given their relative production expense [11] and energy cost [12], as well as their limiting weak optical absorption [13] and tendency to photo-oxidize [14] which may potentially limit device performance and longevity. The majority of high performance non-fullerene acceptors (achieving power conversion efficiencies in excess of 3%) are perylene diimide (PDI) based [15—22]. Given the inability to tune energy levels and their tendency towards crystallization [23], alternatives to PDI-based acceptors are also desirable.

We recently reported the preliminary OSC performance for a sustainable low-cost electron deficient fullerene-alternative small-molecule, Oct-II(ThPhth-1EP) [24,25]. Here, we extend our study of bulk heterojunction (BHJ) blends of Oct-II(ThPhth-1EP)$_2$ as the electron acceptor with a prototypical electron donor, p-DTS(FBTTh$_2$)$_2$. [26,27] While optimizing parameters such as the blend ratio, processing solvent, active layer thickness and device architecture, a surprisingly strong dependence on the device architecture was observed. In this contribution, we have identified key factors in improving OSC performance learned during the device optimization process — lessons which may apply to other all small-molecule, non-fullerene systems.

2. Experimental

BHJ OSC devices (Fig. 1) were fabricated using commercially available ITO-coated glass substrates (Lumtec; 15 Ω/□), cleaned by sequentially ultrasonicating in detergent and deionized water, acetone, and ethanol, followed by UV/ozone cleaning.

For conventional devices, PEDOT:PSS (Clevios P VP AI 4083) was spin cast through a hydrophilic PVDF filter at a speed of 5000 RPM, then annealed at 140 °C in air for 10 min, for an typical thickness of 40 nm. For inverted devices, ZnO was deposited as a sol—gel precursor solution, following the method of Sun et al. [28] Zinc acetate dihydrate was dissolved in 2-methoxyethanol (100 mg/mL; 5 mL total) with 142 uL of ethanolamine and stirred overnight at room
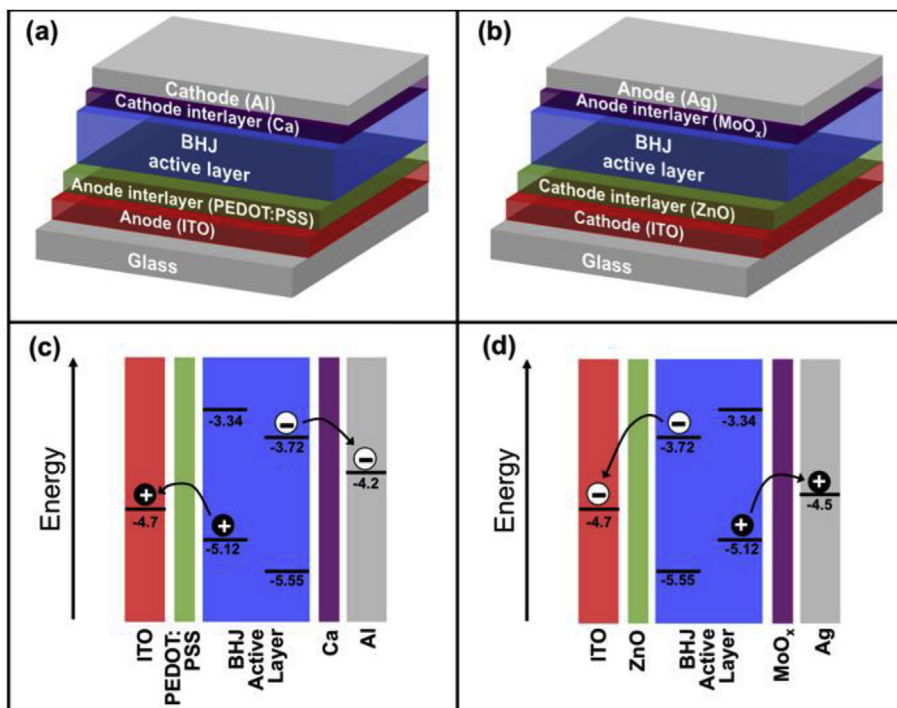
Fig. 1. Architecture illustrations and energy level diagrams for conventional (a, c) and inverted (b, d) devices.

temperature. The room temperature solution was spin-cast unfiltered at a speed of 5000 RPM, then annealed at 200 °C in air for 1 h, for an expected thickness of 30 nm.

Active layer solution blends of p-DTS(FBTTh$_2$)$_2$ and Oct-II(ThPhth-1EP)$_2$ were prepared with a total concentration of 20 mg/mL in chlorobenzene (CB) with 0.4 v/v% 1,8-diiodooctane (DIO, TCI Chemicals) additive. Solutions were heated to 80 °C and stirred overnight prior to hot-casting through a PTFE filter and spinning at a speed of 1000 RPM.

For conventional devices, top contacts of 7.5 nm of calcium followed by 100 nm of aluminum were thermally deposited under vacuum. For inverted devices, top contacts of 5.5 nm of molybdenum oxide followed by 110 nm of silver were thermally deposited under vacuum. The active areas of resulting devices were 0.04 cm^2.

Completed devices were then transferred directly into an argon-filled glovebox and tested using a xenon short arc lamp fully reflective solar simulator (Sciencetech SS-0.5k). Light from the simulator was passed through AM1.5G and neutral density filters resulting in a power density of 100 mW/cm^2 at the sample (calibrated with a standardized silicon photodetector/KG5 glass filter immediately prior to use).

Purity of the active layer materials is of utmost importance, where the presence of even trace impurities can be detrimental to device performance [29,30]. This lesson became apparent when several rounds of devices showed a drastically reduced performance with approximately half the previously achieved PCE values. The performance decrease was determined to be a result of residual impurities in the acceptor material (discussed in detail in the Supporting information).

3. Results and discussion

Donor–acceptor blends with weight ratios of 2:1, 1:1, 1:2, 1:3, and 1:4 were initially screened in conventional architecture devices on substrates with small sample sizes (see Supporting information). The best performing blend ratios, 1:1, 1:2 and 1:3 were selected for further study, discussed in detail below. The use of high acceptor ratio blends is preferable in these devices, as Oct-II(ThPhth-1EP)$_2$ is relatively lower cost and synthetically sustainable than p-DTS(FBTTh$_2$)$_2$.

Thin-film ultraviolet–visible spectroscopy was performed for neat films of the donor (p-DTS(FBTTh$_2$)$_2$) and acceptor (Oct-II(ThPhth-1EP)$_2$), as well as donor–acceptor blends with weight ratios 1:1, 1:2 and 1:3 (Fig. 2). All films were spin-cast from solutions heated to 80 °C onto clean glass substrates. Neat films of p-DTS(FBTTh$_2$)$_2$ and Oct-II(ThPhth-1EP)$_2$ were spun from CB at 10 mg/mL at 3000 RPM, while blend films were spun from CB with 0.4 v/v% DIO solvent additive at 20 mg/mL at 1000 RPM. The absorption profiles of neat p-DTS(FBTTh$_2$)$_2$ and Oct-II(ThPhth-1EP)$_2$ complement one another and blends show good coverage of the visible range from 300 to 800 nm. In blends with lower mass fractions of p-DTS(FBTTh$_2$)$_2$, the p-DTS(FBTTh$_2$)$_2$ absorption band intensity decreases and the intensity of the total absorption of the blend at 700 nm is reduced below that at 625 nm.

The morphology of the blend films at each weight ratio was measured with TappingMode™ atomic force microscopy (AFM) (Fig. 3). All films were relatively smooth with similar morphology, though taller features appeared (white) as roughness increased slightly with the Oct-II(ThPhth-1EP)$_2$ mass fraction. The visible granular domain sizes are similar to typical exciton diffusion lengths reported in the literature, on the order of tens of nanometers, which may be a hallmark of a favorable active layer film morphology [26]. A review article by Liao et al. suggests that in order to tune the morphology of an active layer blend, a balance between phase separation and over-crystallization must be achieved [31]. In our experience, non-fullerene acceptors tend to over-crystallize, and various approaches, including molecular design, solvent selection, fabrication conditions, and substrate choice are required to obtain favorable blend morphologies.

The optimal method for spin casting 1:1 p-DTS(FBTTh$_2$)$_2$:Oct-