

# Stability and reliability of P3HT:PC61BM inverted organic solar cells



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## ABSTRACT

Improving the stability and reliability of organic photovoltaic (OPV) devices is an area of intense research as it is the major barrier in the commercialization of these devices. We study the stability of inverted structured OPV devices in the present work. A large number of these were fabricated and their shelf life times were recorded. P3HT devices show an average T80 (time in which cell efficiency falls to 80% of its initial value) of 34 days. Some of the devices were tested in actual working conditions outdoors in sunlight. A very low T80 value of 12 h was observed during the outdoor testing. Thermal degradation study was performed on the devices at 65 °C in dark and an average T80 of 200 h was obtained. Signatures of trap formation were observed by analysing and comparing the dark current-voltage characteristics of the pristine and degraded devices. The solar cells degrade due to trap formation in the active layer and formation of charge extraction barriers at the contacts.

## 1. Introduction

Organic solar cells (OSCs) are promising candidates for light-weight and low-cost sources of renewable energy. OSCs also have the potential for rapid roll-to-roll processing and can be fabricated on flexible substrates. A popular form of OSC consists of an active layer blend made up of a conjugated polymer and a fullerene derivative sandwiched between two electrodes. A schematic of the popular OSC architecture is shown in Fig. 1a. Many standard structures of OSCs utilize poly(3,4-ethylenedioxythiophene):poly(styrenesulphonic acid) (PEDOT:PSS) as a hole transporting layer (HTL) or the electron blocking layer (EBL). The acidic nature of can lead to etching of the indium tin oxide (ITO) electrode and thus reduce the device lifetime [1]. It was found that the inverted structure is better suited for improving the stability of OSCs [1]. In this architecture, n-type metal oxides such as TiO<sub>2</sub> or ZnO are deposited on ITO and used as electron transport layer (ETL), while other metal oxides such as NiO, MoO<sub>3</sub> and WO<sub>3</sub> can be used as HTL [1–4]. Schematics of the inverted OSC architecture and the flat band energy levels are shown in Fig. 1b and c respectively. blend forms the active layer, and ZnO and MoO<sub>3</sub> are used as ETL and HTL, respectively.

The major reasons and mechanisms for degradation of OSC device performance and parameters are documented widely in literature. Humidity, oxygen, ultraviolet (UV) light and thermal stresses are

known to degrade the OSC performance significantly [5–9]. The effects of these physical agents can be minimized by proper encapsulation of the device. However, since a solar cell is exposed to light and thermal stresses during its use, the degradation brought about by these stresses cannot be eliminated. Light and heat induce morphological changes in the active layer, which lead to interlayer and electrode diffusion [10,11]. In order to obtain a good insight of device stability, it is essential to study the complete working device under various stresses and observe how the different photovoltaic (PV) parameters evolve with time.

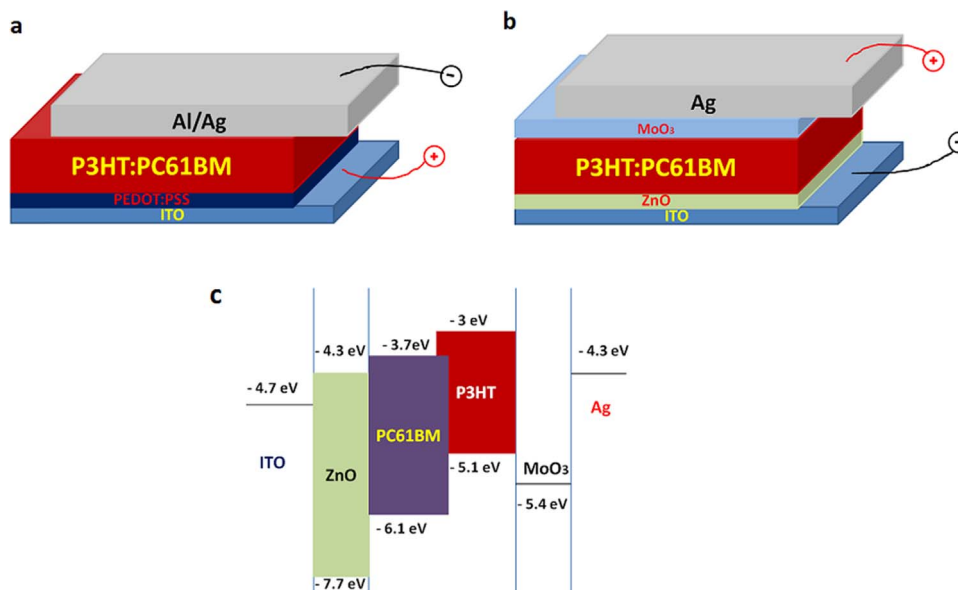
Almost all previous works on stability focussed on standard architecture OPV devices [5–14]. In the present work, we studied the stability of inverted structured OSCs based on P3HT: PC61BM active layer. To obtain statistically significant data sets, more than 90 encapsulated substrates with four devices each were fabricated and their shelf life times were recorded. Some of the devices were stressed in actual outdoor conditions in sunlight to find out the photo-stability and lifetime under light exposure. In addition, some devices were thermally stressed in dark ambient conditions to study the effect of temperature on the device performance. The performances of inverted OSCs were analysed using current density-voltage (*J-V*, measured under solar simulator) and external quantum efficiency (EQE) measurements. Dark current-voltage (*I-V*) analysis has also been performed to observe charge carrier trap signatures in the OSCs.

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**Fig. 1.** (a) Standard OPV structure for P3HT:PC61BM as the active layer. (b) A schematic of the inverted organic solar cell architecture fabricated in the present work. (c) Schematic energy levels of the inverted device under open-circuit (flat-band) conditions.

## 2. Experimental

### 2.1. Device fabrication

Electron donor polymer P3HT and fullerene electron acceptor PC61BM were purchased from Sigma Aldrich and used as received without any purification. The inverted OSC structure was a stack of ITO/ZnO/P3HT:PC61BM/MoO<sub>3</sub>/Ag layers. The ITO substrates of size 5 cm were patterned using photolithography technique to obtain four different sizes of ITO strips. Patterned ITO substrates were cleaned sequentially in soap water, de-ionized water and propanol. The cleaned ITO substrates were subjected to oxygen plasma treatment prior to device fabrication. A thin layer (~30 nm) of ZnO was formed by spin coating at 3000 rpm a solution of zinc acetate and 2-methoxyethanol on top of ITO. The ZnO coated substrates were annealed in air at 250 °C for 15 min and transferred to a N<sub>2</sub> filled glove-box for further processing. The active layer materials P3HT/PC61BM were dissolved in dichlorobenzene in 1:1 wt ratio and a concentration of 20 mg/ml. This solution was dropped on ZnO coated ITO substrates using a glass syringe attached with a 0.45 μm Polyvinylidene Difluoride (PVDF) filter. The active layer was then spin coated at 500 rpm for 1 min for obtaining a targeted final thickness of ~120 nm. The active layer coated substrates were annealed inside the glove box at 110 °C for 30 min and subsequently transferred to a glove box integrated thermal evaporator for MoO<sub>3</sub> and Ag deposition. A thin (~3 nm) layer of MoO<sub>3</sub> was deposited using shadow masks. The thickness of deposited Ag electrode was ~100 nm. This completed the device fabrication and cell pixels of four different areas were obtained: C1 (0.7 cm), C2 (1 cm), C3 (1.2 cm) and C4 (1.3 cm). These pixels were characterised by covering with square metallic masks to define four different active areas: A1 (0.5 cm), A2 (0.7 cm), A3 (0.9 cm) and A4 (1 cm). In the subsequent sections of this paper, the devices C1, C2, C3 and C4 refer to cells with active areas 0.25 cm<sup>2</sup>, 0.49 cm<sup>2</sup>, 0.81 cm<sup>2</sup> and 1 cm<sup>2</sup>, respectively (see supplementary **Fig. S1**).

### 2.2. Encapsulation of organic solar cells

Encapsulation is a critical step in device processing and determines, to a great extent, its stability and reliability in actual working conditions. The devices were encapsulated using a grooved glass and UV-curable epoxy glue (Epoxy Technology, USA). The encapsulation

process was performed inside the glove box using a semi-automated system. Initially, grooved glasses were cleaned by sonicating them in DI water, isopropanol and acetone for 10 min each. Afterwards, the grooved glasses were dried using a nitrogen gun and transferred to a nitrogen filled glove box housing the semi-automatic encapsulation system. Epoxy glue was applied on the grooved glass using a robotic dispenser. The grooved glass with epoxy and the solar cell substrate were aligned manually with the help of custom made holders. The aligned glass and device were pressed together using a mechanical press and kept under a UV lamp for 2 min. The epoxy was cured by UV rays to which it was exposed, solidifying the initially liquid epoxy. The cured epoxy held together the grooved glass and the solar cell substrate. The epoxy layer was expected to be a barrier against oxygen and moisture ingress into the device.

### 2.3. Device characterization

The PCEs of the fabricated PTB7 and P3HT devices were determined from current density-voltage (*J-V*) curves measured using Keithley 2400 source-meter under 1 sun AM1.5 G illumination from a solar simulator (Class AAA, Newport-Oriel, USA). The illumination intensity was adjusted using a calibrated reference silicon solar cell. To ensure well defined active areas, the *J-V* measurements were performed using laser-cut stainless steel square masks. Incident photon to current conversion efficiency (IPCE) of inverted OSCs was measured using a custom-built apparatus consisting of a tungsten lamp, monochromator, chopping wheel, lock-in amplifier and current pre-amplifier. The incident monochromatic light was chopped at 11 Hz and the measurements were taken in the range 330–850 nm with an interval of 5 nm. All the measurements were performed at room temperature in ambient conditions.

### 2.4. Stability testing of organic solar cells

Stress testing of OSCs to study their aging process was carried out according to the consensus stability testing protocols defined by Reese et al. [15]. Three sets of experiments were performed. In the first case, the shelf lifetime of inverted OSCs based on PTB7 and P3HT were compared. In the second case, the OSCs were placed outdoors and their photovoltaic (PV) parameters were studied periodically. In the third set of experiment, the OSCs were stored at 65 °C in the dark. The PV

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