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## Investigation of photodegradation in polymer solar cells blended with different fullerenes derivatives

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## ABSTRACT

To fabricate long lifetime polymer solar cells, understanding the fundamental aspects controlling the performances, stability and degradation of the devices is essential. In this study, we compare the chemical and electrical degradation behaviors of polymer solar cells based on active layers of semi-crystalline p-type polymer poly(3hexylthiophene) (P3HT) and different fullerene derivatives as acceptors. Photodegradation study by UV–visible and Fourier transform infrared (FTIR) spectroscopy and photovoltaic performance study by current–voltage measurement were done to understand and compare air stability of P3HT blended with different fullerenes. The used acceptors are indene-C(60) bisadduct (ICBA) and phenyl-C61–butyric acid methyl ester (PCBM). The obtained results show that solar cells fabricated from PCBM as acceptor are more stable than those based on ICBA. Based on the spectroscopic and electrical measurement results, it is safe to conclude that PCBM contributes more to stability of P3HT than ICBA, and that the degradation behavior is compatible with recently proposed mechanisms. Chemical properties of ICBA such as the low electron affinity could be responsible for the relative low stability of the device.

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## 1. Introduction

Organic semiconductors are becoming crucial in a number of important technologies. In recent years organic semiconductors have been extensively investigated due to their electrical, optical and magnetic properties. These materials have wide applications in the electronic technology, such as organic solar cell, biosensors, field effect transistor, light emitting diodes and lasers [1–7].

Bulk heterojunction (BHJ) organic solar cells having active layers comprising blended organic semiconducting polymers and fullerenes offer the advantage of low fabrication cost, lightness, simple solution-based device fabrication process and flexibility [8,9]. The phase separated active-layer blend structure provides a highly nanostructured internal morphology that both decouples the exciton diffusion length ( $< \sim 10$  nm) [10] from the thickness of the active layer and increases the heterojunction area available for exciton dissociation [11].

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Recently high efficiency (10.6%) polymer solar cells [12] have been reported and in the near future polymer solar cells fulfilling some of the requirements of commercial applications can be envisaged. Despite the growing efficiency of polymer based solar cells, their short working life time remains an obstacle to their practical use owing to chemical and physical degradation mechanisms when the device is exposed to oxygen, moisture, light and high temperature [13–18]. In order to realize polymer based solar cells for practical use, it is imperative to investigate the stability of the polymer and polymer based solar cells under different working conditions.

In many papers it is reported that polymer BHJ films can be easily degraded and destroyed through various pathways of physical and chemical degradation. On the other hand, a recently published paper [19] mentions that the fullerene acceptors donate photogenerated electrons to oxygen molecule and result in the formation of superoxide radical anion  $O_2^-$ , which degrades the polymer. According to the authors, the fullerenes with low electron affinity are prone to easily donate photoexcited electrons to oxygen molecule. In this study, the goal is to elucidate the effect of fullerene with different electron affinity on the air stability of P3HT based polymer solar cells. The fullerene-derivatives used as

electron acceptor are ICBA and PCBM. ICBA has lower electron affinity than PCBM. Both acceptors are widely used for the fabrication

of polymer solar cells. To compare the air stability of the active layer and solar cell fabricated from P3HT and the two fullerene acceptors, we used spectroscopic and electrical measurement techniques.

## 2. Experimental details

### 2.1. Materials and solutions

Regioregular poly(3-hexylthiophene) (P3HT) polymer used in this work was obtained from Rieke Specialty Polymers, Rieke Metals Inc. The fullerene acceptors, [6,6]-phenyl C<sub>61</sub>-butyric acid methyl ester (PCBM) >99.5% purity was obtained from Sigma-Aldrich and indene-C<sub>60</sub> bisadduct (ICBA) from Lumtec Luminescence Technology Corp. The hole transporting polymer PEDOT:PSS was obtained from Abs. H. C. Starck. 1, 2 dichlorobenzene (Sigma-Aldrich 99%) was used as a solvent. The molecular structure of P3HT, PCBM and ICBA is shown in Fig. 1.

### 2.2. Device fabrication

The devices were fabricated on indium tin oxide (ITO) coated glass substrate with a sheet resistance of 15 Ω/cm<sup>2</sup>. ITO (2.5 mm × 2.5 mm) was partly protected with photoresist and the exposed ITO was etched with a mixture of HCl+HNO<sub>3</sub>+H<sub>2</sub>O, 48:4:48 by volume. The etched portion of the ITO/glass provides a convenient region for the aluminum contact pads subsequently deposited. The photoresist was removed using acetone and then the surface was cleaned using a standard cleaning procedure consisting of a sequence of four ultrasonication steps in detergent, distilled water, acetone and isopropanol for 15 min each. After rinsing in deionized water and blowing them dry with nitrogen, the ITO coated substrates were treated by oxygen plasma for 3 min.

The aqueous PEDOT: PSS dispersion was spin coated onto the cleaned ITO coated substrates at 3000 rpm for 40 s to produce a film thickness of around 30 nm. The PEDOT:PSS coated substrates were dried on a hotplate at 150 °C for 15 min to remove water residues. Then the samples were directly transferred into the glove-box system, for spin-coating films of P3HT blends with different fullerene.

Prior to device fabrication, a solution consisting of P3HT:fullerene in blend ratio of 1:1 (wt/wt%) and blend concentration of 30 mg/ml in dichlorobenzene was stirred at 40 °C for 36 h inside glove-box. P3HT:fullerene solution spin-casted onto a PEDOT:PSS coated substrate at 800 rpm for 50 s inside glove-box. Finally through shadow mask 100 nm thick aluminum contacts were vacuum evaporated at a pressure of approximately  $2 \times 10^{-6}$  Torr. After aluminum evaporation the devices were annealed at 140 °C for 30 min inside glove-box. The sandwich structure ITO/PEDOT:PSS/P3HT:fullerene/Al provides a means for current-voltage measurements. The structure of the device used in this work is shown in Fig. 2.

### 2.3. Device characterization

The thickness of PEDOT:PSS and P3HT:fullerene film was measured using Alpha-Step 500 Surface Profiler. To characterize the polymer solar cell, the current-voltage characteristics were measured by using Agilent Technologies B1550A Semiconductor Device analyzer. The set-up was controlled by the easyExpert software package. *J-V* characteristics of the P3HT:fullerene based polymer solar cell were obtained in ambient air and room temperature under dark and white light illumination at 100 mW/cm<sup>2</sup> using AM1.5G ABET TECHNOLOGIES Sun 2000 Solar Simulator immediately after removing the sample from the glove-box. For degradation measurements in ambient air, the samples were kept in an open sample holder, exposed to simulated AM1.5G irradiation from a Solar Simulator of intensity 100 mW/cm<sup>2</sup>. The photovoltaic cell characteristics, the power conversion efficiency ( $\eta$ ), short circuit current density ( $J_{sc}$ ), open circuit voltage ( $V_{oc}$ ) and fill factor ( $FF$ ) were measured at different irradiation time. The laboratory relative humidity during the *J-V* measurement was between 30% and 40%. All devices were not sealed. UV-visible spectra were measured by Perkin Elmer Lambda 35 UV/vis spectrometer.

### 2.4. FTIR measurements

FTIR spectra of P3HT, PCBM, ICBA and their blends were recorded in transmission mode at the SISSI beamline of Elettra-Sincrotrone Trieste with a Bruker Vertex70 interferometer using a DTGS detector. Spectra were obtained averaging 512 scans with 4 cm<sup>-1</sup> spectral resolution. Samples were prepared by spin coating the test materials onto 1 mm thick CaF<sub>2</sub> IR windows, having a very thin nanometric layer of sputtered silicon on the top. The silicon layer does not affect the IR transparency of the IR substrate [20] while improves the wettability by the solution and the adhesion of the polymer and the blends on it. The samples have been measured immediately after preparation; the photo-degradation test was made by exposure to simulated AM1.5G

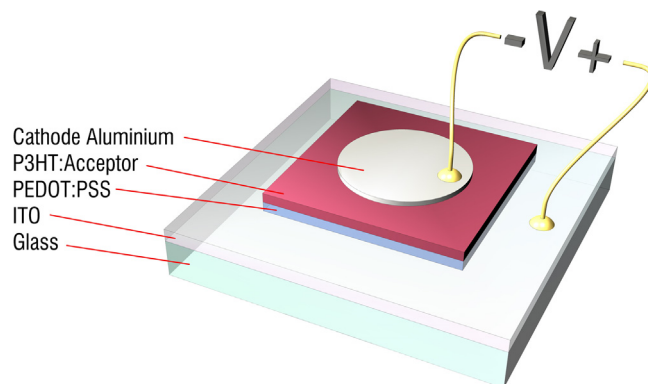


Fig. 2. Device structure of ITO/PEDOT:PSS/ P3HT:fullerene/Al solar cell.

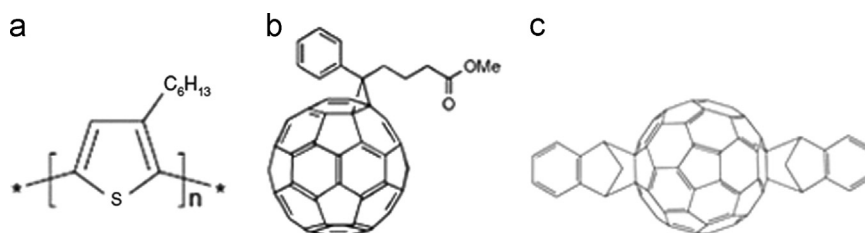


Fig. 1. The chemical structure of organic compounds used in this work (a) P3HT, (b) PCBM, and (c) ICBA.

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