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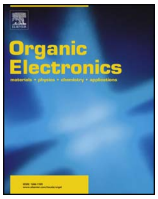

Surface engineering of ITO electrode with a functional polymer for PEDOT:PSS-free organic solar cells

Hussein Awada[a], Giorgio Mattana[b], Aurélien Tournebize[b], Laurent Rodriguez[a], Delphine Flahaut[a], Luc Vellutini[c], Christine Lartigau-Dagron[a], Laurent Billon[a], Antoine Bousquet[a,**], Sylvain Chambon[b,*]

[a] *CNRS/ Univ. Pau & Pays Adour, Institut des Sciences Analytiques et de Physico-Chimie pour l'Environnement et les Matériaux, UMR 5254, 64000, Pau, France*
[b] *Univ. Bordeaux, IMS, CNRS, UMR 5218, Bordeaux INP, ENSCBP, F-33405 Talence, France*
[c] *Univ. Bordeaux, CNRS, ISM, UMR 5255, F-33405 Talence, France*

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ABSTRACT

In this report, surface engineering is used to improve the air-stability of direct polymer solar cells by replacing the PEDOT:PSS hole transporting layer (HTL) by a grafted polymeric layer. For that purpose a poly(3-hexylthiophene) bearing a triethoxysilane function at the end of the chain (P3HT-Si) was synthesized and anchored to the indium-tin oxide (ITO) electrode. The different characterization techniques used (UV–visible and X-ray photoemission spectroscopy) showed that the applied temperature during grafting is a determinant parameter to tune the P3HT-Si layer thickness/density. For low temperature grafting, polymeric chains were laying close to the surface while higher grafting temperature led to polymeric chains pointing upwards. This organization of the polymeric chains in the grafted layer has a direct impact on photovoltaic properties of the devices fabricated with P3HT-Si as HTL. The use of this new self-assembled HTL creates a hole selective membrane which drastically reduces the leakage current. As a result, the power conversion efficiency of such devices was improved compared to devices with bare ITO. Additionally, by replacing PEDOT:PSS by the hydrophobic P3HT-Si, the water penetration in the device is impeded which significantly improved the shelf lifetime of devices.

1. Introduction

Since the discovery of the preparation of robust and flexile polyacetylene films by the Ziegler Natta polymerization, numerous conjugated polymers have been synthesized for various applications: light-emitting diodes, sensors or photovoltaics [1]. The advantages of organic-based devices are the low cost fabrication, lightweight, conformability, flexibility and versatility due to the wide potential of chemical structures. Focusing on organic solar cells (OSCs), the recent development of efficient donor or acceptor molecules together with the smart engineering of device architecture led to the constant increase of the power conversion efficiency above 10% [2–4].

Independently of the active layer materials, the choice of the device architecture (direct or inverted) influences the performance and the stability of the devices. An inverted device exhibits a better air stability than its direct version [5–7]. Indeed, a direct configuration requires the use of low work function materials such as aluminum and calcium, which can therefore be easily oxidized, and materials such as poly (3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) which is sensitive to water exposure. There are evidences that the hygroscopic and acidic nature of PEDOT:PSS is detrimental to the long term performance and stability of devices [8–12]. Specifically, recent reports showed that the water molecules enter devices via the hygroscopic PEDOT:PSS layer and, after travelling through the active layer, corrode the low work function electrode (made of calcium or aluminum) [11,12]. The formation of such insulating oxide leads to the reduction of the device active area which results in a constant loss of short-circuit current (J_{sc}). In inverted devices, it has been shown that the interface between the PEDOT-PSS and active layers could be a weak point subjected to delamination [13]. Because of its higher air-stability, inverted architecture is often preferred but the direct one is still necessary in some cases when the vertical phase segregation induces a favorable distribution of donor and acceptor materials [14]. Therefore, the stabilization of direct solar cells is required and replacing the hygroscopic PEDOT:PSS is a first step. Several studies were already reported on alternative for PEDOT:PSS to improve the stability under humid

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* Corresponding author.
** Corresponding author.
E-mail addresses: antoine.bousquet@univ-pau.fr (A. Bousquet), sylvain.chambon@u-bordeaux.fr (S. Chambon).

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conditions. Voroshazi et al. showed that molybdenum (MoO_3) dramatically reduces the degradation under storage in air with ~35% relative humidity (RH) [12]. Similarly, Züfle et al. used vanadium oxide (V_2O_5) and MoO_3 as an alternative to PEDOT:PSS and showed that, in certain conditions, the stability under storage in humid conditions (45, 75, 85% RH) can be improved [11].

Among the electrode interlayer materials used to replace PEDOT:PSS in direct architectures, organic surface modifiers such as self-assembled monolayers (SAMs) have also been explored [15–17]. They enable device fabrication on flexible substrates using only low-temperature solution processing. The SAMs strategy leads to the self-organization of ordered structures at the molecular level via chemical absorption and has been utilized to alter the work function of the electrodes leading to an ohmic contact between active layer and electrode [18,19]. Specifically, the modification of ITO using self-assembled monolayers with a permanent dipole moment has been employed to tune the work function of the anode to improve device performances [20,21]. A series of silane-based SAMs with different end units (CH_3, NH_2, CF_3) have been self-assembled on the surface of ITO before depositing a P3HT:$PC_{61}BM$ active layer [22]. The SAM with the electron withdrawing CF_3 group can effectively increase the work function of ITO from 4.7 to 5.16 eV, providing a better match with the HOMO level of P3HT for efficient hole collection. In addition, the change of surface energy upon surface modifications was also found to be important in determining the morphology of the upper active layer. The hydrophobic surface induced by the CF_3 group alleviated destructive phase segregation and crystallization of the upper P3HT:$PC_{61}BM$ film. More recently, Heeger et al. used chlorobenzoic acid SAMs to produce a high work function ITO electrode achieving PCE of 8.5% (compared to 7.5% for PEDOT:PSS) [23]. This improvement was attributed to increased light absorption within the active layer because of higher transparency in visible wavelength region, efficient hole extraction from the active layer to anode by cascade energy level alignment, and reduced contact resistance at the ITO/active layer interface. Similarly, Yang et al. developed a method to grow a semi-conducting polymer brush by surface initiation of 3-methylthiophene from ITO which will act as HTL [24]. They show that, after an additional doping of grafted P3MT layer, they could obtain similar initial performances to PEDOT:PSS. This "grafted-from" method showed for the first time the potentiality of replacing the commonly PEDOT:PSS HTL by a grafted polymer on ITO surface. Nevertheless this surface modification is a three-step synthetic procedure and is hardly viable at an industrial scale. Moreover the authors did not study the stability of the solar cell over time.

In the present paper, we report an easy method to further explore the potentiality of electrode surface modification at the border between SAMs and polymer brush approaches. The commonly used HTL PEDOT:PSS was replaced by a triethoxysilane terminated poly(3-hexylthiophene) (P3HT-Si) (Fig. 1). Contrary to Yang et al., we used a "grafting onto" one-step method [25,26], which highly facilitates the processability of this novel HTL. We show that this graftable polymer improves the charge selectivity by creating a p-type layer between the active layer and the ITO electrode. Additionally, we prove that the replacement of PEDOT:PSS by P3HT-Si as HTL enhances the device stability under shelf lifetime conditions in air and without doping. This work opens new directions in order to fabricate air-stable direct architecture for organic photovoltaic devices.

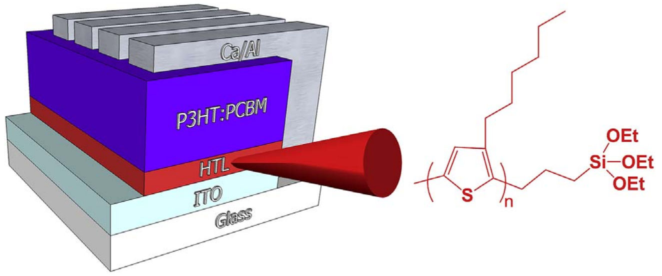

Fig. 1. Architecture of a direct organic solar cell and chemical structure of the triethoxysilane terminated poly(3-hexylthiophene) (P3HT-Si) used as HTL.

2. Experimental section

Materials. All reactions were performed under pre-dried nitrogen using flame-dried glassware and conventional Schlenk techniques. Syringes used to transfer reagents or solvents were purged with nitrogen prior to use. Chemicals and reagents were used as received from Aldrich (France) and ABCR (Germany) and stored in the glove box. Solvents (Baker, France) were used as received; THF was distilled over sodium and benzophenone under nitrogen.

Instrumentations. ^1H and ^{29}Si Nuclear Magnetic Resonance (NMR) spectra were recorded using a Bruker 400 MHz instrument in $CDCl_3$ at ambient temperature. Gel Permeation Chromatography (GPC) was performed using a bank of 4 columns (Shodex KF801, 802.5, 804 and 806) each 300 mm × 8 mm at 30 °C with THF eluent at a flow rate of 1.0 mL min^{-1} controlled by a Malvern pump (Viskotek, VE1122) and connected to Malvern VE3580 refractive index (RI) and Malvern VE3210 UV–visible detectors. Calibration was against polystyrene standards.

The X-ray photoelectron spectroscopy analyses (XPS) were performed with the Thermo K-alpha spectrometer with a hemispherical analyzer and a microfocused (analysis area was ca. 200 μm^2) monochromatized radiation Al Kα line (1486.6 eV) operating at 75 W under a residual pressure of 1×10^{-7} mbar. The spectrometer pass energy was set to 20 eV for core peak records. Surface charging was minimized using a neutralizer gun which sprays the low energy electrons and Ar^+ ions over the sample surface. All the binding energies were referenced to the C 1s peak at 285.0 eV originating from the adventitious carbon (always detected at the surface of materials). Core peaks were analysed using a nonlinear Shirley-type background [27]. and peak positions and areas were obtained by a weighted least-squares fitting of model curves (70% Gaussian, 30% Lorentzian to the experimental date. Quantification of surface composition was based on Scofield's relative sensitivity factors [28].

UV–Visible spectrophotometry was performed on a SAFAS Monaco UV MC2 instrument. Transmission spectra were recorded from 300 to 800 nm with a 1 nm step.

Contact Potential Difference (CPD) was measured using a Kelvin Probe set up from Besocke Delta Phi. The work function (Wf) of the difference substrate was estimated using freshly cleaved highly ordered pyrolytic graphite (HOPG) as a reference (4.65 eV) [29].

Atomic Force Microscopy (AFM) analyses were carried out in tapping mode with a Bruker Innova SPM and using Olympus cantilevers (OMCL AC-160-TS).

Contact angles were performed on a Krüss DSA 100 goniometer, at 20 °C in static mode. The results correspond to the mean of at least 3 measurements.

Synthesis of allyl-terminated P3HT. High regioregularity, allyl-terminated P3HT was synthesized using a previously reported procedure [30]. The GRIM method was applied to synthesize the desired polymer in a flamed-dried 100 mL round flask bottom under inert atmosphere at room temperature. Initially 2,5-dibromo-3-hexylthiophene (1) (3.06 mmol) and freshly distilled THF 10 mL were added into the flask. After mixing for several minutes, isopropyl magnesium chloride (3.06 mmol) was then added via a syringe and stirred for 2 h at room temperature. The reaction mixture was diluted to 50 mL with dried THF, and 1,3-bis(diphenylphosphino)propane nickel-(II) chloride Ni (dppp)Cl_2 (0.087 mmol) was added. The polymerization proceeded for 10 min before adding allyl magnesium bromide (1.53 mmol) and then the reaction continued for another 30 min to ensure high end-group functionalization before quenching with methanol. The resulting solid polymer was washed by Soxhlet extraction using ethanol and acetone,