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# Large area slot-die coated organic solar cells on flexible substrates with non-halogenated solution formulations



Florian Machui<sup>a,\*</sup>, Luca Lucera<sup>1,b</sup>, George D. Spyropoulos<sup>a</sup>, Johann Cordero<sup>a</sup>, Abid S. Ali<sup>a</sup>, Peter Kubis<sup>a</sup>, Tayebbeh Ameri<sup>a</sup>, Monika M. Voigt<sup>a,b</sup>, Christoph J. Brabec<sup>a,b</sup>

<sup>a</sup> Institute Materials for Electronics and Energy Technology (i-MEET), Department of Material Science and Engineering, Friedrich-Alexander University of Erlangen-Nuremberg, Martensstrasse 7, 91058 Erlangen, Germany

<sup>b</sup> Bavarian Centre of Applied Energy Research (ZAE Bavaria), Haberstrasse 2a, 91058 Erlangen, Germany

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## ABSTRACT

The transfer from lab scale to industrial application is one of the challenges for organic photovoltaics. For this, non halogenated formulations are a decisive need for the upscaling process, as are roll-to-roll (R2R) compatible methods. Devices processed with *o*-xylene using slot-die coating as a sheet-to-sheet technique show a reduced efficiency on a larger scale compared to lab scale solar cells. By using a mixture of high and low volatile solvents which selectively dissolve one component, the film homogeneity and the efficiency is dramatically improved. The slot-die coated active layers for solar cells processed from non-halogenated solvents show device efficiencies above 3% on flexible substrates.

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## 1. Introduction

Printed, organic solar cells gained considerable academic and industrial attention offering the advantages of a cost-effective and highly efficient technology, which is a promising candidate to compensate the rising worldwide energy demand [1,2]. Solution processed polymer solar cells are currently reaching efficiencies over 10% and are on their way to proof the feasibility of the predicted efficiencies of 15–20% by Denzler et al. and Li et al. [3–5]. Compared to their inorganic counterparts organic solar cells offer the advantage of a low temperature, solution processable technique. The active layer of organic solar cells consists in most of the cases of a bulk-heterojunction (BHJ), an interpenetrating network of a donor and an acceptor material. Commonly used materials are poly(3-hexylthiophene-2,5-diyl) and [6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM) as donor and acceptor, respectively. Generally, best device efficiencies can be achieved with halogenated, aromatic solvents, i.e. chlorobenzene (CB) and ortho-dichlorobenzene (DCB) [6]. Due to their toxicity and their harmful impact on the environment, these solvents are not suitable for industrial manufacturing since this would lead to an increased expense for additional personal protection equipment

and containments. Often mentioned alternative solvents are *o*-xylene, toluene and tetrahydronaphthalene (THN) [6–8]. Compared to halogenated solvents, the solubility for most materials in these solvents is lower. When toluene is used, a cluster formation is observed which is not beneficial for the charge transfer process and therefore for the device efficiency [9,10]. Nevertheless it has been shown that *o*-xylene can be used for device fabrication resulting in comparable efficiencies [11,12]. One drawback of *o*-xylene as solvent is the P3HT agglomeration and the tendency to form gels which can lead to clogging of the coating equipment [13,14].

Lange et al. used different solvent and solvent blends for inkjet printed devices with an amorphous polymer in the active layer [15]. The poly[9,9-dioctylfluorenyl-2,7-diyl-co-(10,12-bis(thiophen-2-yl)-3,6-dioxooctyl-11-thia-9,13-diaza-cyclopenta[b]triphenylene)] (PFDTBTP):PCBM solar cells showed a 3.5% power conversion efficiency when inkjet printed from chlorobenzene/trichlorobenzene solutions and led to efficiencies below 3% when processed from anisole/THN, *p*-xylene/THN and *p*-xylene/mesitylene/THN mixtures. A coarser phase separation and pinholes were found for the devices processed with the non-halogenated solutions compared to the use of chlorinated solvents. Vanlaeke et al. and Zimmermann et al. showed P3HT:PCBM device with efficiencies above 3% spin-coated from THN solutions on ITO glass [7,8].

The most used method for processing of organic solar cells is spin-coating, since it requires only few formulation efforts and homogeneous films can be fabricated with a high reproducibility

\* Corresponding author: Tel.: +49 9131 85 27717; fax: +49 9131 85 28495.

E-mail address: [florian.machui@ww.uni-erlangen.de](mailto:florian.machui@ww.uni-erlangen.de) (F. Machui).

URL: <http://www.i-meet.ww.uni-erlangen.de/> (F. Machui).

<sup>1</sup> These two authors have contributed equally to this work.

[16]. However restriction of substrate size and incompatibility with a continuous processing does not establish it as a mass production method. One of the challenges in the upscaling process is the transfer from lab scale devices to large area roll-to-roll processed solar cells. Slot-die coating offers the possibility of a sheet based coating technology that can be transferred to a full roll-to-roll process. This technique uses a coating head that fills the gap between the die and the substrate with ink and through a slot. A meniscus is then formed between the moving web and the slot-die head. The coating result depends strongly on the velocity, the slot-die gap and other parameters. Therefore, we determined recently the processing window for slot-die coated layers of an organic solar cell (OSC) stack [17]. Usually the transfer from spin-coating to doctor-blading or slot-die coating requires several modifications. The processing, drying behavior and resulting film are completely different for the two deposition techniques.

Several process changes need to be adapted for the transfer from a lab scaled to a roll-to-roll (R2R) compatible process. This includes the change from rigid to flexible substrates, larger area coatings with comparable film homogeneity and a fully solution based processing. Different publications already addressed aspects of the upscaling process. Wengeler et al. compared different coating techniques for P3HT:PCBM with CB as solvent for the active layer on glass substrates [18]. Schrödner et al. reported the slot-die coating of PEDOT:PSS and P3HT:PCBM layers on PET foils [19]. By comparing different solvents for the active layer the PCE ranged from 1.17% for *o*-xylene, to 1.26% for DCB and 1.37% for CB processed devices. A completely ITO and vacuum free R2R process has been established by Krebs et al. which allows the processing of all layers of the device without moving the substrate to different equipment [20–26]. For these experiments usually halogenated solvents, such as CB, DCB and chloroform are used. Slot-die coated devices processed with DCB reached 2.3% in a fully R2R compatible process [27]. For solution processing the resulting dry film homogeneity is one of the major criteria for the process stability. Found artifacts can be separated in coating defects which occur directly during the coating and drying defects resulting from the evaporation of the solvent system [28,29].

In this manuscript we demonstrate that the device performance of slot-die coated active layers for OSC can be improved by solvent formulation. Within non-halogenated solvents *o*-xylene was chosen as the most promising candidate, due to reasonable solubility values and comparable drying dynamics to CB. Sheet to sheet devices processed with a slot-die coater, using *o*-xylene as solvent for the active layer, did not show comparable device performance as lab scale solar cells. Using a combination of a low and a high volatile solvent led to improved drying kinetics, increasing the phase separation of the blend system and to higher device efficiencies. Here two different solvent formulations are suggested and analyzed. A general printing quality control of the layers had been carried out and compared to the mean value device performance.

## 2. Experimental

### 2.1. Materials and solutions

P3HT (with weight average molar mass ( $M_w$ ) 65,600 g/mol, polydispersity (PD) 2.04, and regioregularity (RR) 96.6 from Merck), and PCBM (99% from Solenne BV) were used as received. All solvents were obtained from commercial chemical suppliers in high purity grades. For the solubility measurements saturated solutions were stirred for at least twelve hours at room temperature and centrifuged at 15,000 rpm for ten minutes. The absorption is compared to standard curves with known concentrations. The measurements have been performed at 25 °C.

### 2.2. Simulation

For the simulation of the evaporation behavior of the used solvent systems the HSPiP software was used [30]. For the calculations of the simulations a wet film thickness of 9 μm and a solute content of 2 wt% were utilized. The curves were normalized to the evaporation time of pristine *o*-xylene at 65 °C which is the processing temperature for xylene and xylene:THN (75:25) solutions.

### 2.3. Processing and characterization of solar cells

For small scale solar cells pre-structured ITO-glass (Nuremberg Weidner Glas GmbH) was used with an ITO layer thickness of 260 nm and a sheet resistance of  $< 10 \Omega/\square$ . As a reference to PET substrates, the devices were processed in ambient atmosphere. An electron injecting layer (EIL) composed of aluminum-doped zinc oxide (AZO) was doctor-bladed with an approximated layer thickness of 40 nm to enable electron selective charge carrier collection. The synthesis, the processing and the conversion are already described elsewhere [31]. Subsequently the active layer consisting of P3HT:PCBM was doctor-bladed with an approximated layer thickness of 120 nm at 65 °C for *o*-xylene and *o*-xylene:THN processing. For anisole:THN solutions the temperature was raised to 80 °C due to limited solubility resulting in gel formation of P3HT at 65 °C. The used concentrations were (9+9) mg/ml (P3HT+PCBM)/*o*-xylene, (9.2+9.2) mg/ml (P3HT+PCBM)/*o*-xylene:THN (75:25) and (10+10) mg/ml (P3HT+PCBM)/anisole:THN (70:30). A hole injection layer (HIL) consisting of PEDOT:PSS (Clevios AI 4083 from Heraeus) with approximately 40 nm layer thickness was doctor-bladed on top of the active layer. A thermal evaporated 100 nm silver electrode was deposited as final layer which also defined the active area. All solar cells were annealed at 140 °C for 5 min under ambient conditions. For all doctor bladed layers a gap size of 400 μm was used.

In order to upscale the coating to larger areas with the slot-die technique, PET foils pre-sputtered with a transparent conductive oxide (ITO (40 nm)/Ag (10 nm)/ITO (40 nm) with a sheet resistance of  $7.7 \Omega/\square$ ) were used. Based on results from bending tests it was shown that the mechanical and electrical properties of these foils were not affected [32]. The dimensions of the foils were 160 × 110 mm. The foils were patterned with a layout of nine adjacent single substrates, with dimensions of 25 × 25 mm and contained 54 single devices with a cell size of 10.4 mm<sup>2</sup>. The layout can be seen in Fig. 1. Laser marking lines were used to mark the single substrates. They were used to cut the foils to smaller substrates after the coating procedure. In order to make these lines visible a higher laser fluency was used which is visible in the PET foil and can cause local dewetting.

Furthermore devices with a cell size of 250 mm<sup>2</sup> have been investigated. Patterning of the transparent conductive oxide (TCO) deposited on the foil and the ITO on the glass substrates was done with a LS-7xxP setup built by LS Laser Systems GmbH (München, Germany) including a Laser source femtoREGEN TM UC-1040-8000 fs Yb SHG from High Q Laser GmbH. A detailed description of the ablation thresholds of each layer is presented in reference [33]. An AZO layer with an approximated layer thickness of 40 nm was doctor-bladed on top of the substrate according to previous description. For device processing both techniques, doctor-blading and slot-die coating of the active layer, were used. The solution preparation and processing temperatures were adapted from doctor-blading experiments. A slot-die coater LBA BCM SD100 1713 from FMP Technology GmbH was used for coatings of the active layer in a sheet-to-sheet setup. A die head (model SD 100) with a coating width of 100 mm and a slot lip gap of about 100 μm was chosen. An optimized wet film thickness of 9 μm and

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