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Organic solar cells with an inkjet printed P3HT:O-IDTBR layer based on a green solvent by utilizing a heatable printhead

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Short abstract

In this study we present organic solar cells with an inkjet printed active layer based on a P3HT:OIDTBR bulk heterojunction with a PCE of 2.3 %. The green solvent 2-Methylanisol was used for the ink. The necessary steps for the creation of such cells are explained. The remaining problem of a significant sensitivity to UV radiation is studied. Steps for the improvement of photovoltaic parameters and lifetime of the solar cells are discussed.

Keywords: organic solar cells, inkjet printing, green solvent, UV induced degradation

1. Introduction and background

Organic photovoltaics are a research area that opens up many new fields of application compared to conventional solar cells. In particular they offer potential key features like transparency, flexibility and stretchability (Fukuda, Yu and Someya, 2020). A potential problem however might be that research is often focused on fabrication by spincoating. While this production method works well for lab-scale devices, reaching power conversion efficiencies (PCE) of up to 19 % (Cui, et al., 2021), it is inherently difficult to upscale for industrial applications. Consequently, it is crucial to explore alternative possibilities suitable for industrial production, primarily printing technologies.

In this work we use inkjet printing, which offers many advantages compared to other printing methods. While its throughput is lower than for example slot-die coating, the ability to freely create new patterns without the need for a mask makes it a potent contender for niche applications (Gertsen, et al., 2020).

Organic solar cells (OSCs) are built around a photoactive layer consisting of an acceptor and a donator polymer. In this study we used an inverted layout, which means that the substrate is serving as the cathode. This layout was shown to increase the lifetime and stability of the solar cells under ambient conditions (Hau, Yip and Jen, 2010).

We used an indium tin oxide (ITO) coated glass substrate as it is common in research and does not influence the studied active layer. OSCs require electron and hole transport layers to extract the charge carriers out of the active layer. In this study we used zinc oxide (ZnO) as the electron transport layer and molybdenum trioxide (MoO_3) as the hole transport layer. A schematic displaying the layers of our solar cell is shown in Figure 1.

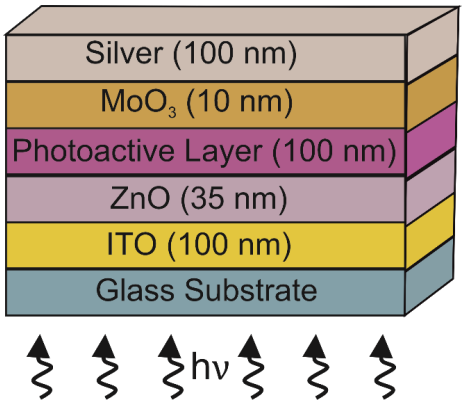

Figure 1: Schematic cross section of the used architecture for the studied solar cells

In the majority of OSCs the components of the active layer are intermingled to maximize the surface between the components, thus creating a bulk heterojunction solar cell. In recent years, new polymers were developed to increase the PCE with impressive results. The creation of nonfullerene acceptors (NFAs) significantly increased the PCE and stability of organic solar cells, since their absorption spectrum can be tailored to match with new highly efficient donators. However, from a commercial perspective, it would be preferable to combine specifically tailored NFAs with the well-researched donator poly(3-hexylthiophen-2,5-diyl) (P3HT) due to its low cost of production and high stability under ambient conditions (Li, McCulloch and Brabec, 2018). As such, for this work we used the NFA (5Z,5'Z)-5,5'-((7,7'-(4,4,9,9-tetraoctyl-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(benzo[c][1,2,5]thiadiazole-7,4-diyl))bis(methanylylidene))bis(3-ethyl-2-thioxothiazolidin-4-one) commonly referred to as O-IDTBR because of its excellent stability and good synergy with P3HT (Holliday, et al., 2016).

Inkjet printing of OSCs based on P3HT was already demonstrated in the past, however mostly with toxic halogenated solvents (Hoth, et al., 2007). Even when the used solvents were halogen-free, they still had unwanted health effects like the narcotic properties of the often used o-xylene or toluene.

In this work we used an inkjet printer to fabricate a P3HT based OSC utilizing a truly green solvent, the food additive 2-Methylanisole (2-MA). While this solvent has successfully been used in other production methods like spincoating (An, Zhong an Ying, 2020), it has not yet been demonstrated to be compatible with inkjet printing. This is most likely due to the rapid clumping that occurs at low temperatures when in contact with even very small amounts of P3HT.

Thus, the aim of this study is to research the possibilities and difficulties of using 2-MA as the singular solvent for inkjet-printing of the active layer.

2. Materials and methods

2.1 Materials

Prepatterned ITO substrates (S211) were purchased from Ossila. ZnO was purchased in the form of a commercial ink (Helios'Ink H-SZ01034, semi conductive ink) from Sigma-Aldrich. These glasses have a transmittance of > 80 % for wavelengths between 400 nm and 750 nm. For wavelengths below 400 nm, the transmittance starts falling and is approximately 77 % at a wavelength of 350 nm. The active layer materials P3HT (molecular weight: 24 480, 93.6 % regioregularity) and O-IDTBR were acquired from Ossila. The 2-MA and silver pellets were ordered from SigmaAldrich. MoO_3 was purchased from Evochem.

2.2 Device fabrication

The ITO substrates were cleaned in acetone and isopropanol and then coated with 35 nm of the commonly used electron-injection layer zinc oxide, applied via inkjet printing of the commercial ink as received. For all the printing in this work a MD-P-826 printing system (one nozzle, printing speed 50 mm/s) from microdrop Technologies was used.

The active layer consisting of P3HT:O-IDTBR in a 1:1 weight ratio was prepared by dissolving each material in 2-Methylanisol. The concentration of P3HT was 4 mg/ml. The ink was heated to 85 °C and stirred overnight. Since the solution quickly hardened at room temperature the ink was kept printable by using a heatable printhead MD-K-801 (microdrop Technologies) with a heated storage container. High ink temperatures lead to a significantly reduced viscosity, which is unwanted since it causes the generation of satellite droplets. We used a printhead temperature of 85 °C as a compromise between viscosity and the risk of nozzle blocking. 2-MA proved well suited for this application because its viscosity (14.32 mPa·s at room temperature) is relatively high for a solvent, such preventing satellite droplets. The ink was printed in ambient atmosphere. Optimal substrate temperature during the printing process was determined to be 57 °C. In order to investigate the influence of the coating process on the characteristics of the OSCs, we produced additional samples by using a spincoater inside a glovebox to deposit the active layer. Those cells only serve as a reference and were not optimized in terms of electrical parameters.

For both production methods, the thickness of the active layer was approximately 100 nm. After both inkjet-printing and spincoating the samples were annealed for 5 minutes at 100 °C in vacuum. The back electrode consisting of a 10 nm MoO_3 and a 100 nm silver layer, was applied by physical vapor deposition.

The data of the cells with inkjet printed active layer is based on 5 ITO substrates with 8 solar cells produced on each substrate. Each cell had an active area of 4 mm^2. 7.5 % of the cells were unusable due to short circuits and thus are not included in the following discussion. 30 cells with spincoated active layers were used for comparison.

2.3 Measurements

For measuring the solar cell parameters a solar cell I-V test system (Ossila) in conjunction with a HAL-320 solar simulator, supplying an AM1.5G spectrum, was utilized. In this setup, an ultraviolet (UV) blocking PET film procured from Edmund Optics could be inserted, in order to investigate the UV sensitivity. It blocked wavelengths below 400 nm and its transmittance in the visible part of the spectrum was approximately 80 %. This reduction in light intensity was considered, when calculating the photovoltaic parameters PCE, J_{SC}, V_{OC} and *FF* based on the measured *J*-*V*-curves.

3. Results and discussion

By using the measurement setup described above, we determined PCEs of up to 3 % for the cells with inkjet printed active layer, which is a reasonable value for the used materials. However, most of the cells showed a massively reduced lifetime compared to the spincoated OSCs, when exposed to the light of the solar simulator. Further investigations revealed that placing a UV-filter in between solar simulator and solar cells prevented this effect, which indicates that wavelengths below 400 nm are the origin of the degradation.

To get a better understanding of the UV induced degradation of the inkjet printed cells we used the following procedure: First, a *J*-*V*-curve was measured, while the UV-filter was protecting the sample. Then the PCE was calculated and depicted in Figure 2 as M_0. Afterwards the UV filter was temporarily removed and

the sample exposed to UV light for 0.5 seconds. Now, a second *J-V*-curve was measured, while protecting the sample from UV by using the filter. Based on this measurement the PCE was calculated and plotted as $M_{0.5}$ in Figure 2. By removing the filter again for 0.5 seconds, the cumulated UV exposure was increased to 1 second, another *J-V*-curve was measured, and the result depicted as M_1. Following this procedure, measurements of up to 5 seconds of cumulated UV exposure were performed. These measurements were done for the printed cells as well as the spincoated cells, resulting in a plot of PCE vs. exposure time.

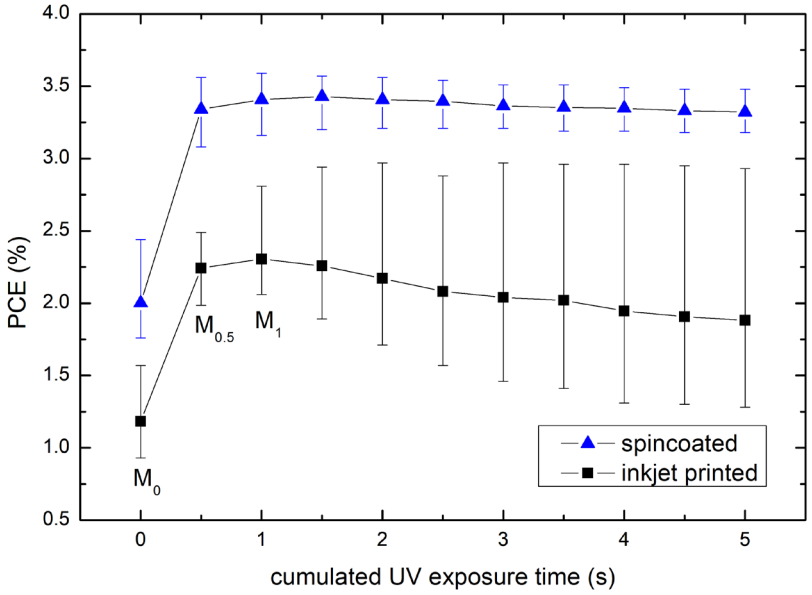

Figure 2: The average PCE of the inkjet printed and the spincoated solar cells versus cumulated UV exposure time; the error bars represent the maximal and minimal measured PCE

From Figure 2 it can be seen that for exposure times of up to approximately 1 second the PCE increases, a phenomenon well known as the light soaking effect (Kim, et al., 2012). This means that ZnO is dependent on regular exposure to UV radiation to maintain its functionality. Otherwise, a drastically reduced fill factor is observed. This effect is theorized to originate from the absorption of oxygen into the ZnO layer leading to a shift in the work function (Sundqvist, et al., 2016). Even short amounts of exposure to UV radiation leads to the ZnO adsorbing the oxygen and increasing the PCE of the cell.

The PCE of the cells with spincoated active layers remains almost constant for high UV exposure times. This behavior is expected, since the UV induced degradation of the cells usually happens on a larger time scale. For the inkjet printed cells however, the average PCE can be seen to quickly decrease. Since UV radiation is required to activate the ZnO, protecting the cells with a UV filter is not a viable option.

However, the upper ends of the error bars shown in Figure 2 reveal that it is possible to fabricate printed cells that do not show a significant degradation effect. This strongly suggests that it is possible to minimize efficiency losses by carefully optimizing the printing process.

The measured results are summarized in Table 1. Samples with a spincoated active layer showed an average PCE of 3.41 % after 1 second of exposure to UV radiation. It should be noted, that the used P3HT had a relatively low molecular weight to reduce aggregation and thus minimize the risk of nozzle clogging. However, Khan, et al. (2019) showed that a low molecular weight leads to a high loss of efficiency. As such the PCE of these unoptimized OSCs was expected to be lower than the efficiency of comparable cells in literature. The corresponding average PCE of the printed cells is 2.28 %, which is less than the PCE of the spincoated cells due to the different coating process.

Table 1: Averaged photovoltaic parameters of the inkjet-printed and spincoated OSCs after 1 second of UV exposure

Production method	PCE (%)	J_{SC} (mA/cm^2)	V_{OC} (V)	*FF* (%)
Inkjet printing	2.28	−5.44	0.69	48.07
Spincoating	3.41	−6.49	0.74	57.10

Additionally, it can also be seen from Figure 2 that it is possible to produce cells with an inkjet printed active layer able to achieve higher values of up to 3 % efficiency, while also minimizing degradation. To compare the photovoltaic parameters, averaged *J-V*-curves of the 4 best performing inkjet printed and the 5 best performing spincoated cells are shown in Figure 3. It can be seen that the V_{OC} and the J_{SC} of spincoated and inkjet printed cells are almost identical, indicating that these parameters will achieve high values for an optimized printing process. The current problems are likely occurring because only one line at a time can be printed with a singlenozzle system. This may result in drops drying separately instead of forming a homogeneous layer, which is highly relevant for the photovoltaic parameters and should be a focus of further research.

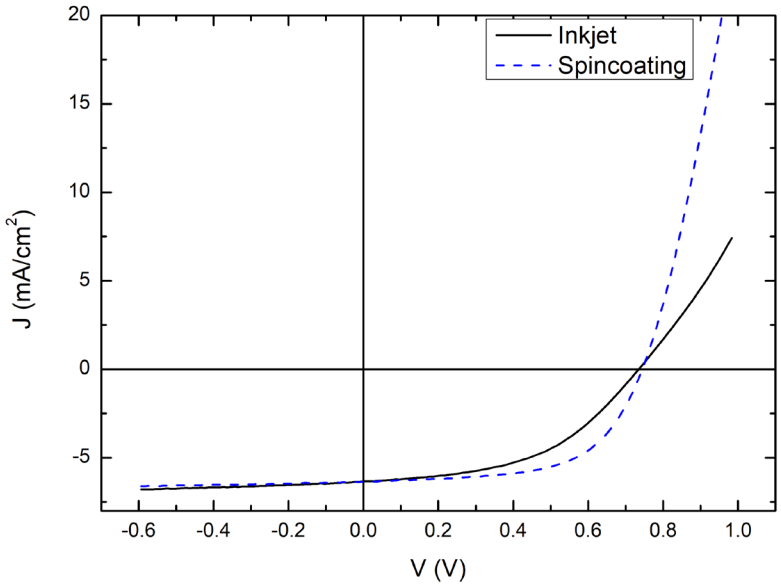

Figure 3: Averaged J-V-Curves of the 5 best performing devices for spincoated (dashed) and the 4 best performing devices for inkjet printed (solid) solar cells

4. Conclusions

We found that it is indeed possible to produce inkjet printed organic solar cells using a truly green solvent. The use of a printhead with a heatable storage bin and hose allowed us to print the 2-MA based ink without damaging the nozzle, producing cells of up to 3 % efficiency. However, the study revealed stability issues for the majority of our printed cells. While further research will be necessary to fully understand the problem, our results strongly suggest that it can be overcome by optimization of the printing process. Our best inkjet printed cells showed photovoltaic parameters and UV stability comparable to the fabricated reference cells, demonstrating the potential of inkjet printed OSCs from an environmental perspective. This shows a possible path towards industrialization for niche products, where the digital flexibility of inkjet printing might prove to be invaluable.

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