Combining solvents and surfactants for inkjet printing PEDOT PSS on P3HT/PCBM in organic solar cells

Kommeren, Sander; Coenen, Michiel J.J.; Eggenhuisen, Tamara M.; Slaats, Thijs M.W.L.; Gorter, Harrie; Groen, Pim

Important note
To cite this publication, please use the final published version (if applicable).
Please check the document version above.

Combining solvents and surfactants for inkjet printing PEDOT:PSS on P3HT/PCBM in organic solar cells

Sander Kommeren[a], Michiel J.J. Coenen[a], Tamara M. Eggenhuisen[a], ThijsM.W.L. Slaats[a], Harrie Gorter[a], Pim Groen[a,b,*]

[a] Holst Centre, High Tech Campus 31, 5656, AE Eindhoven, the Netherlands
[b] Faculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629, HS Delft, the Netherlands

ABSTRACT

A commonly used strategy in the fabrication of organic electronics involves the use of orthogonal solvents, *i.e.* the alternating use of organic solvents and water for the application of consecutive layers to prevent dissolution of previous layers. This strategy therefore requires the deposition of sequential layers with a large mismatch in surface energy. In case of organic photovoltaics (OPV) a particularly challenging deposition is that of the aqueous Poly(3,4-ethylenedioxythiophene) Polystyrene sulfonate (PEDOT:PSS) on the hydrophobic Poly(3-hexylthiophene-2,5-diyl/Phenyl-C61-butyric acid methyl ester (P3HT/PCBM) layer. The mismatch in surface energy causes dewetting and inhomogeneous layer formation. In inkjet printing individually placed droplets should spread sufficiently far to form a homogeneous closed layer before the solvents in the droplet evaporate. A formulation for the aqueous PEDOT:PSS layer has been developed in which the combination of solvents and surfactants is essential for achieving a homogenous layer on the timescales needed for inkjet printing. Homogenous layers of PEDOT:PSS on P3HT/PCBM were achieved for layer thicknesses from 400 nm to 50 nm. The efficiency of the OPV's fabricated with the new formulation were comparable with reference devices, where evaporated molybdenum oxide (MoO$_x$) was used as a topelectrode. This shows that by the addition of solvents and surfactants a hydrophilic solution can be inkjet printed successfully to form homogenous layers on hydrophobic surfaces and achieve good efficiencies in an inverted organic solar cell.

1. Introduction

In the field of organic electronics or printed electronics the making of devices like organic photovoltaics, OPV, including the more recent perovskite based solar cells and organic light emitting diodes, OLED, by solution processing by roll-2-roll (R2R) production of devices on flexible substrates, at ambient temperatures and at low costs in large quantities [1–6]. Organic solar cells have been fabricated using a broad range of R2R compatible techniques including slot-die coating [1,3,7,8] and gravure printing [4,9]. We recently published the fabrication of partially and fully inkjet printed solar cells [10–12]. These papers mainly focused on the fabrication and characterization of inkjet printed OPV devices rather than on the development of the used inks. In this paper we will address the development of an aqueous solution on a hydrophobic surface which can be a coated and cured layer of the light absorbing layer in case of OPV or the light emitting layer in case of an OLED. In our case we report on research on a poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) ink specifically designed for the deposition on the hydrophobic surfaces, like the poly (3-hexylthiophene)/phenyl-C61-butyric acid methyl ester (P3HT/PCBM) photoactive layer in OPVs. A problem that frequently arises with R2R solution processing techniques is that they require the deposition of sequential layers with large mismatches in surface energy. In case the surface energy of the previous layer is much higher than the surface tension of the desired ink, this ink will spread uncontrollably while in the opposite case, the ink will not wet and no uniform closed layer will be formed. The latter situation occurs when applying a hydrophilic layer of PEDOT:PSS on top of a hydrophobic P3HT/PCBM film. The mismatch between the low surface energy of P3HT/PCBM (24.2 mN/m) and the high surface tension of the used aqueous PEDOT:PSS solution (72.8 mN/m) causes dewetting and inhomogeneous layer formation which makes it difficult to coat PEDOT:PSS properly on the P3HT/PCBM layer [13,14]. P3HT/PCBM is not the only photoactive layer that shows such low surface energy. Other materials such as poly[*N*-9-heptadecanyl-2,7-carbazole-*alt*-5,5-(4,7-di-2-thienyl-2,1,3-benzothiadiazole)] (PCDTBT) give similarly low surface energies [15].

Fig. 1. A schematic representation of the inverted OPV stack (a), A picture of an inkjet printed layer of our standard CH8000 based, inkjet printing formulation (b) and a printed layer of CH8000 + 0.1 wt% Capstone FS-3100 (c). Both printed layers show inhomogeneous layers due to dewetting of the ink in the substrate.

Hydrophobic surfaces are often treated with UV-ozone to improve wetting of hydrophilic solutions, however, this method is undesirable and detrimental for the photoactive layer [9,16]. Although the surface energy of the photoactive layer can be raised by using UV-ozone or plasma treatments, this practice might affect the surface chemistry of the layer [9,14,17]. The use of a plasma treatment can also require several minutes of treatment, rendering it very expensive in R2R processes operating at speeds of several tens of m/min.

Other methods to improve the wetting of PEDOT:PSS on the photoactive layer is the addition of solvents, usually isopropanol or dimethyl sulfoxide and/or surfactants, usually Zonyl FS-300 or Capstone FS-31, which improve layer formation in several coating techniques but are not effective for inkjet printing on hydrophobic surfaces [9,14,18–27]. Most techniques for the wet-chemical fabrication of organic electronics such as spin coating, wire bar coating, slot-die coating and slide coating deposit the layer as one continuous wet film [7]. With inkjet printing the deposition of the ink is different as many small droplets are deposited on the surface and which have first have to flow together and merge to form a homogenous, closed film, before the solvent in the droplets evaporates. Given that such processes only take milliseconds to seconds, one must consider not only the static, equilibrium surface tension, but also the dynamic surface tension. Here, we report on the influence of a co-solvent and a surfactant on the dynamic surface tension and how these can be combined to inkjet print uniform PEDOT:PSS layers on top of hydrophobic P3HT/PCBM photoactive layers. After evaluation of the starting formulation, the dynamic surface tension of different PEDOT:PSS ink formulations was investigated using bubble tensiometry. Suitable combinations were subsequently evaluated using high speed camera imaging. Finally, devices in which the several PEDOT:PSS inks based on the newly developed formulations were inkjet printed on top of P3HT/PCBM were fabricated, evaluated and compared a reference device made with a conventional top electrode made from Molybdenum oxide (MoO$_x$).

2. Experimental methods

P3HT/PCBM samples were made with 2 wt% solution of both P3HT (Merck Lisicon SP001) and PCBM (99% Solenne BV) in Chlorobenzene (99.9%, Sigma Aldrich). Upon mixing, the solution was stirred overnight at 70 °C and filtered through a 0.45 μm filter before use. Glass plates with sizes of 3 × 3 cm^2 or 15 × 15 cm^2 were cleaned using multiple ultrasonic cleaning steps at elevated temperature in baths containing Teepol soap, followed by extensive rinsing in deionized water and drying in an oven at 80 °C. Substrates were treated with UV/ozone for 5 min prior to spincoating. Approximately 0.5 mL of solution for the 3 × 3cm^2 or 4 mL of solution for the 15 × 15 cm^2 substrates was then spincoated on the glass plates at 550 rpm with an acceleration of 2000 rpm/s for 95 s. This yielded P3HT/PCBM layers with thickness of 250–300 nm, as measured with a Dektak 8 M profilometer (Veeco). The spincoated layers were annealed at 130 °C for 10 min.

2.1. Ink formulation and characterization

Inkjet inks were based on either low conductive PEDOT:PSS (Clevios CH8000 from Heraeus) or high conductive HILHC5i (Agfa Gevaert N.V.). To these dispersions various surfactants such as Capstone FS-3100 (DuPont), 4-dodecylbenzenesulfonic acid (DBSA, Sigma Aldrich), Sodium dodecylbenzene sulfonate (SDBS, Sigma Aldrich), N-dodecyl-N,N-dimethyl-3-ammonio-1-propanesulfonate (DDAPS, Sigma Aldrich)) and alcohols (Ethanol (Biosolve BV), 1-propanol (Sigma Aldrich), isopropanol (Fluka), 1-butanol (Merck), 2-butanol (Sigma Aldrich), 1-pentanol (Sigma Aldrich)) were added. Inks were stirred for several hours prior to use. The contact angle measurements were made on an Easydrop Standard (Krüss), with 2 μL drops. The equilibrium surface tension measurements were made on the same apparatus using the pendant drop method. These contact angle and pendant drop measurements were performed at room temperature (22 °C). Dynamic surface tensions were measured on a Krüss Bubble Tensiometer (BP2) with a glass capillary (KR SH2031, Krüss) with an inner diameter of 0.2 mm and a hydrophobic silane coating. These measurements were performed over a range of 5 m s to 10000 ms at a temperature of 20 °C.

2.2. Inkjet printing and jetting evaluation

The jetting experiments were performed on a LP50 platform (OTB, Roth&Rau) with a Konica Minolta KM-512LN printhead having 512 nozzles with a nominal drop volume of 42 pL. Prior to inkjet printing the PEDOT:PSS ink formulations were filtered with a 0.45 μm hydrophilic PVFE filter. To calculate the dry layer thickness of the PEDOT:PSS ink the following formula is used:

$$T_{dry} = \frac{V_d \cdot f_{wt}}{DP \cdot LP}$$

Here, DP is the dotpitch, LP is nozzle spacing which on a KM-512LN printhead is 70 μm, Vd is the volume of an individual droplet (42 pL) and f$_{wt}$ is the weight fraction of the dispersed PEDOT:PSS. In this research the expected dry layer thickness for the PEDOT:PSS layer are shown for ink formulations with several dotpitches.

2.3. High speed imaging

The landing and spreading of individually jetted droplets was performed using a phantom v310 high speed camera equipped with a long-range microscope objective capturing at 15600 frames per second, a resolution of 512 × 384 pixels and an overall magnification of 0.22 μm/pixel. Individual droplets were jetted from disposable Fujifilm Dimatix DCM-11610 cartridges with a nominal droplet volume of 10 pL. The droplets landed on spincoated films of P3HT/PCBM on glass which were prepared as described above.

2.4. Device preparation

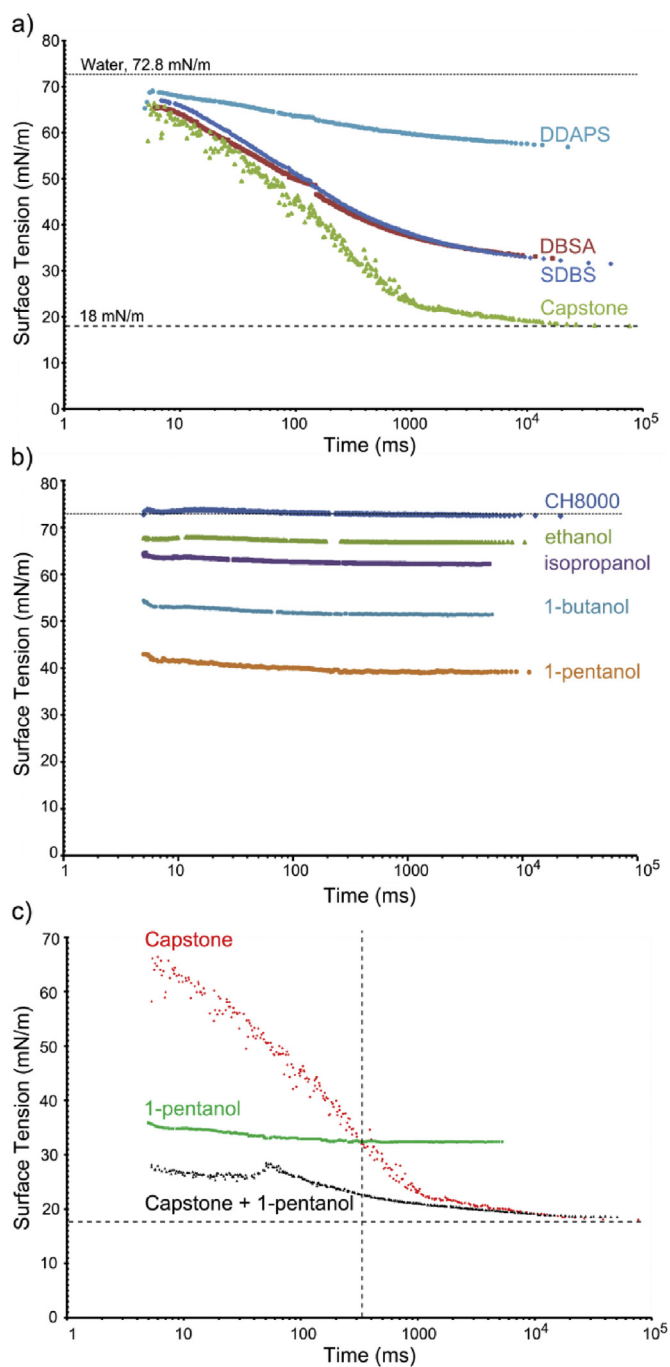The solar cells were made on 30 × 30 mm^2 glass/indium tin oxide

Fig. 2. Dynamic surface tensions of different CH8000 PEDOT:PSS formulations comprising various surfactants at concentrations of 0.13 wt% (a), various alcohols at 1 wt% (b), and the same PEDOT:PSS dispersion with 0.1 wt% Capstone FS-3100 (red), 2 wt% 1-pentanol (green) and the combination of the two (black) (c). The dynamic surface tension of the pure CH8000 is also given in (b) and can be seen to remain constant at the surface tension value of pure water. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

(ITO) substrates each containing 4 devices with active areas of 9, 16, 25 and 100 mm². The glass/ITO substrates were cleaned in advance using the same protocol as described above. Prior to spincoating, the glass/ITO substrates were treated with UV/ozone for 10 min. Zinc oxide nanoparticles are made as described by Krebs et al. [28] The P3HT/PCBM solution is made with 2 wt% solution P3HT (Merck Lisicon SP001) and 2 wt% PCBM (99% Solenne BV) in 1,2-Dichlorobenzene (Reagentplus, 99%, Sigma-Aldrich). The P3HT/PCBM solution is stirred overnight on

a hotplate at 70 °C and filtered with a 0.45 µm filter prior to use. The HilHC5i + 0.1 wt% Capstone +2 wt% pentanol and Clevios CH8000 + 0.1 wt% Capstone +2 wt% pentanol are prepared as described above. A reference cell was made with Orgacon EL-P 5015 diluted with isopropanol in a 1:1 ratio. Zinc oxide is spin coated at 1000 rpm for 60 s, after which the layers are dried at room temperature and subsequently annealed at 200 °C for 5 min in air. The P3HT/PCBM layer was spun at 550 rpm for 95 s, dried at room temperature in air and annealed at 130 °C for 10 min under N₂ atmosphere. The reference Orgacon 5015 PEDOT:PSS layer was spun at 1000 rpm for 60 s, dried at 110 °C for 2 min in air and then annealed at 130 °C for 8 min under N₂ atmosphere. The modified PEDOT:PSS formulations were inkjet printed using the same procedure as described above, dried on a hotplate in air at 110 °C for 2 min and subsequently annealed at 130 °C for 8 min under N₂ atmosphere. After annealing of the PEDOT:PSS layers, 100 nm of silver is thermally evaporated on the PEDOT:PSS to complete the devices.

2.5. Electrical characterization of layers and devices

The conductivity of the printed PEDOT:PSS layers is measured with a digital multimeter (Keithley, Model, 2001) and a four-point probe setup. Current-voltage (I/V) measurements were done on a solar simulator, containing a Keithley 2400 SourceMeter wired to a sample holder in a nitrogen-filled glove box. The sample was illuminated by a halogen lamp. Samples were illuminated through an illumination mask with a well-defined aperture area. An automated rotating filter wheel was used to record the current densities at various wavelengths for external quantum efficiency (EQE) measurement. A silicon reference cell with known spectral response was used for calibration purposes. This enabled the measurement program on the computer to calculate an estimation of the short-circuit current density (J_{sc}) of the organic solar cell under 1000 W/m², AM1.5 illumination.

3. Results and discussion

To fabricate devices of OPV of the inverted stack design in Fig. 1a, a highly conductive hole conducting PEDOT:PSS layer must be deposited on top of the photoactive layer (PAL). This P3HT/PCBM layer is very hydrophobic and was found to have a surface energy of 24.2 mN/m, which is well below the surface tension of water (72.8 mN/m) and aqueous solutions will therefore not wet this surface. Fig. 1b, shows the poor layer formation when inkjet printing the same PEDOT:PSS dispersion as we previously reported as hole injection layer in inkjet printed OLED devices [29]. This formulation consists of a CH8000 PEDOT:PSS dispersion with an added AGFA proprietary surfactant. The poor layer formation by this ink is due to its surface tension of 33.3 mN/m which is above the surface energy of the PAL layer. Better wetting was obtained by using a modified formulation in which the surfactant was replaced by the Capstone FS-3100 fluorosurfactant (Fig. 1c), as fluorosurfactants are capable of lowering the surface tension of aqueous solutions to values as low as 15 mN/m, however no homogeneous dry layer was formed despite the equilibrium surface tension of 18 mN/m of this ink [30].

The effects of surfactants on the surface tension is not instantaneous as they need to diffuse from the bulk of the liquid to the interface, reorientate and absorb [31]. While in many coating techniques, such as spin coating, slot-die coating and blade coating, the ink is deposited as one uniform and continuous thin film, in inkjet printing the liquid film is created by depositing many small ink drops. While in other coating techniques the surfactant needs to prevent this liquid film from breaking up, in inkjet printing the surface tension must be reduced sufficiently and sufficiently fast to allow the individual droplets to merge to a uniform wet layer. This layer then must dry to a homogeneous thin solid film. When examining the dynamic surface tension of different surfactants (Fig. 2a), the initial surface tensions, i.e. within the
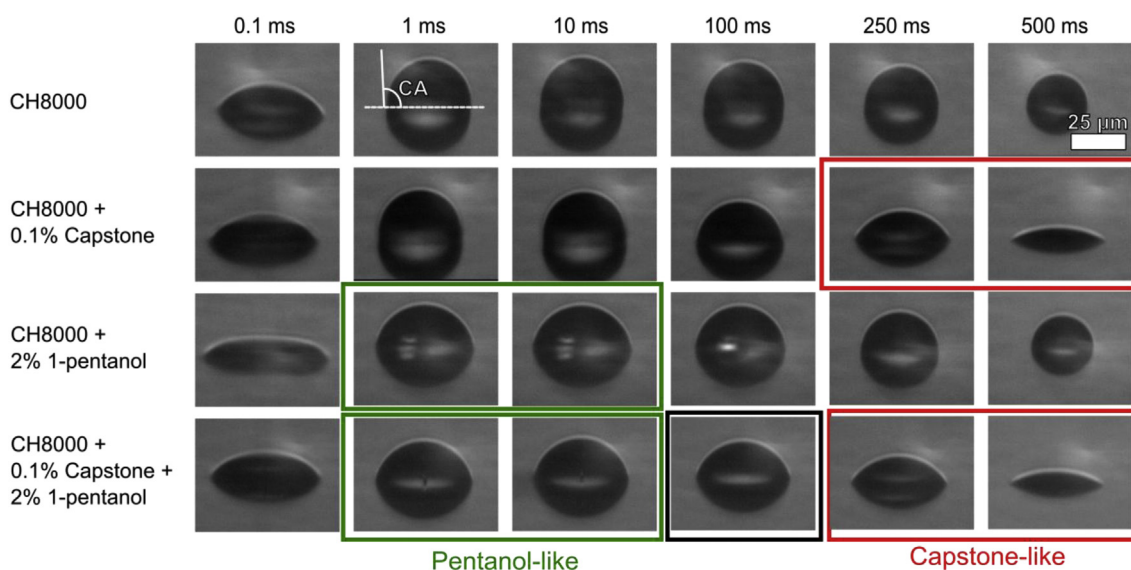
Fig. 3. Characteristic frames obtained with a high-speed camera after the landing of different PEDOT:PSS formulations on a spin coated P3HT/PCBM layer. The boxes highlight droplet spreading dynamics that are characteristic of added 1-pentanol (green), added Capstone FS-3100 (red) and the combined effect of the two at intermediate timescales (black). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
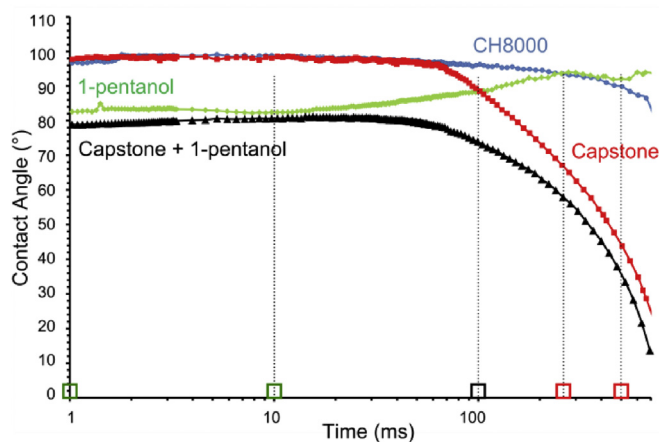

Fig. 4. Contact angles of the different PEDOT:PSS formulations as a function of time as obtained from the high-speed camera measurements. The times at which the frames in Fig. 3 were recorded are indicated with squares of the same color on the horizontal axis. Shown are the dynamic contact angle of the un-modified CH8000 (blue), and the same PEDOT:PSS dispersion with added 2 wt % 1-pentanol (green), added 0.1 wt% Capstone (red), and with the combination of these two (black). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 5. Inkjet printed layers of CH8000 + 0.1 wt% Capstone FS-3100 + 2 wt% pentanol on a spincoated layer of P3HT/PCBM. The layers are inkjet printed with dotpitches (DP) of DP = 120 μm (a), 62 μm (b), 41 μm (c) and 31 μm (d). The corresponding layer thicknesses are indicated.

first 10 m s, are still above 60 mN/m. Only after times in excess of 1000 m s, do the examined surfactants reach their equilibrium surface tension. The addition of Capstone FS-3100 lowers the equilibrium surface tension of the PEDOT:PSS formulation to 18 mN/m, well below the surface energy of the P3HT/PCBM layer of 24 mN/m. The effects of added alcohols on the surface tension of PEDOT:PSS formulations is much faster than that of the surfactants, as can be seen in Fig. 2b. The effect of a 1 wt% addition of the various alcohols on the equilibrium surface tensions is much lower than for most of the surfactants, but these surface tensions reach their equilibrium values below the detection threshold of our bubble tension meter, which is about 8 m s. As it is anticipated that the slow onset of the Capstone surfactant underlies the poor film formation during inkjet printing, a combination of the slow, but powerful Capstone surfactant and the fast 1-pentanol was investigated further. In Fig. 2c the influence of each of these additives, as well as their combined effect can be seen. The addition of both
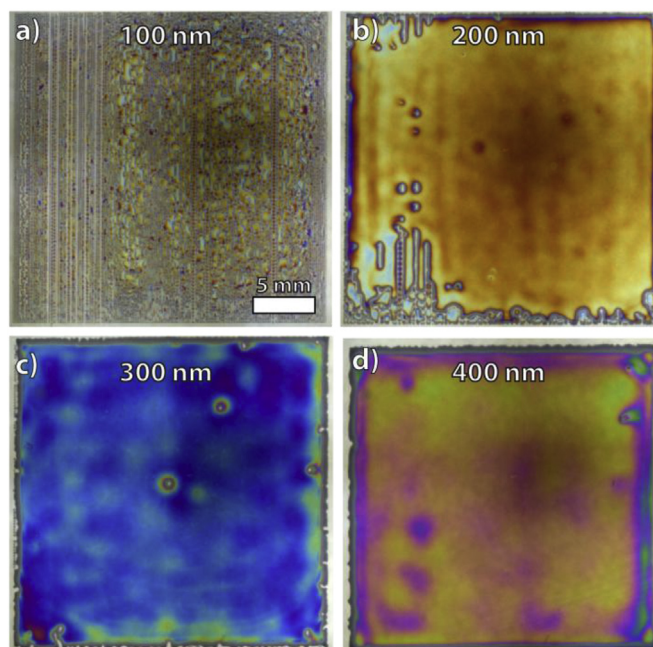
components indeed leads to a low initial surface tension of 29 mN/m which decreases over time to similar values as obtained with only the addition of the Capstone surfactant (*i.e.* 18 mN/m). It has to be noted that the alcohols are added in higher concentrations than the surfactants as the alcohols will evaporate during drying of the PEDOT:PSS layer. As the surfactants don't evaporate they are used in low concentrations such that their presence does not adversely affect the PEDOT:PSS layer performance, although a higher concentration could lead to a faster reduction in surface tension. In Figure S1 an example is shown that a higher concentration (2%) of the 1-pentanol can create a larger decrease in surface tension. This larger decrease in surface tension will be beneficial for a better wetting of the PEDOT:PSS solution on
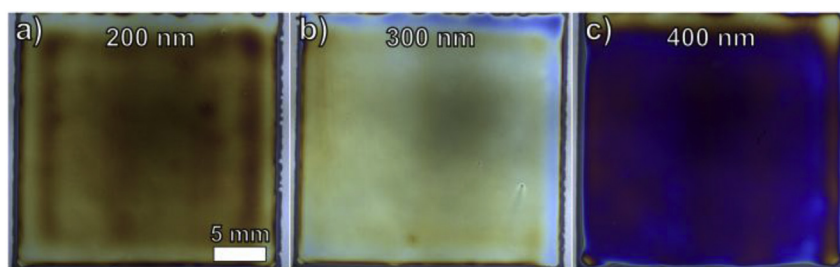
Fig. 6. Inkjet printed layers of two-fold diluted CH8000 + 0.1 wt% Capstone FS-3100 + 2 wt% 1-pentanol. The layers are inkjet printed with dotpitches of DP = 31 μm (a), 21 μm (b), 15 μm (c). The corresponding layer thicknesses are indicated.
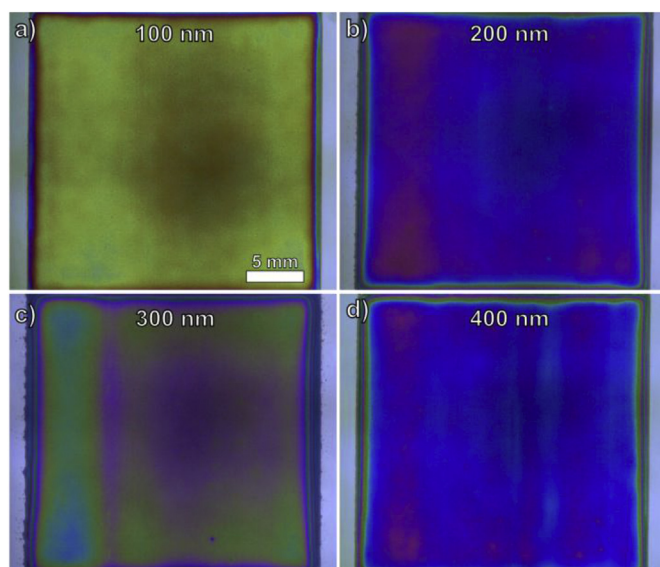

Fig. 7. Inkjet printed layers of high conductivity AGFA HILHC5i + 0.1 wt% Capstone FS-3100 + 2 wt% 1-pentanol. The layers were printed with dotpitches of (a) DP = 40 μm, (b) DP = 20 μm, (c) DP = 13 μm and (d) DP = 10 μm. The corresponding dry layer thicknesses are indicated.

the P3HT/PCBM surface, however the concentration cannot be increased further as this is already the solubility limit of 1-pentanol [32]. This makes the combination of the speed of 1-pentanol and the strength of the Capstone FS-3100 on the surface tension on the PEDOT:PSS such an elegant solution.

To study the influence of the different ink components, we studied the behavior of individual inkjet printed droplets using high speed camera imaging. The relevance of droplet impact, dynamic wetting and spreading behavior for inkjet of organic electronics is highlighted by the review from Caironi et al. [33] To examine the effect of the added Capstone FS-3100 and 2 wt% 1-pentanol on the time evolution of the contact angle, individual 10 pL ink droplets of these formulations were jetted onto a spin coated P3HT/PCBM layer and imaged over time with a high speed camera. Images were obtained at a frame rate of 15000 frames per second. Some characteristic frames at different delay times after the landing of the droplet are shown in Fig. 3.

The contact angles of the landed droplets as a function of time are plotted in Fig. 4.

Immediately after the impact phase both the unmodified CH8000 (blue) and the CH8000 containing 0.1 wt% Capstone (red) have initial contact angles of 100°. The former has these high values until the end of the measurement at 750 m s, while the latter starts a slow decline to contact angles below 30° after about 80 m s. The influence of the 1-pentanol on early stage wetting is clear from the initial contact angle of the CH8000 containing 2 wt% 1-pentanol (green, "1-pentanol") and the CH8000 containing 0.1 wt% Capstone and 2 wt% 1-pentanol (black, "Capstone + 1-pentanol") which are both 80° ± 3°. The onset of the
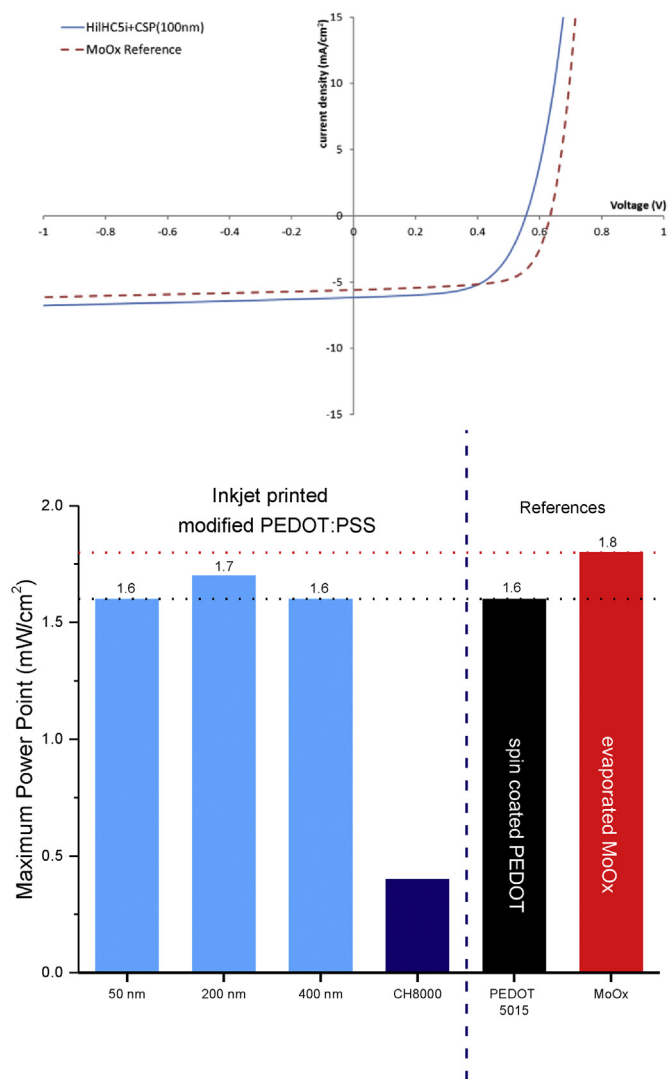
Fig. 8. (A) J-V curves for a device with a 100 nm inkjet printed modified HILHC5i PEDOT:PSS layer on top of a spin coated P3HT/PCBM layer (blue solid line) and a reference with an evaporated MoOx hole transport layer (red dashed line). (b) An overview of the maximum power points for devices with inkjet printed PEDOT:PSS layers of HILHC5i + 0.1 wt% Capstone + 2 wt% 1-pentanol at thicknesses of 50, 200 and 400 nm (light blue) where the number of cells (n) = 2, 11 and 8, respectively. For a device with a 300 nm inkjet printed layer of CH8000 + 0.1 wt% Capstone + 2 wt% 1-pentanol (dark blue, n = 4). And for a device with a spin coated layer of PEDOT Orgacon 5015 (black, n = 4) and a device with an evaporated MoOx layer (red, n = 4). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 1

Overview of the performance of OPV devices fabricated with the newly developed PEDOT:PSS ink formulations. The CH8000 formulation containing 0.1 wt% Capstone and 2 wt% pentanol is abbreviated as CSP. Values in brackets are standard deviations. Yield indicates the ratio between functional devices and the total fabricated devices.

	Device	Yield	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	MPP (mW/cm^2)/Efficiency (%)
Inkjet Printed	HilHC5i + CSP* 50 nm	2/4	564.5 (6.4)	4.9 (0.2)	58.0 (3.0)	1.6 (0.06)
	HilHC5i + CSP 100 nm	12/12	560.7 (5.8)	5.6 (0.4)	60.3 (1.6)	1.9 (0.13)
	HilHC5i + CSP 200 nm	11/12	551.5 (8.4)	5.2 (0.2)	58.0 (1.8)	1.7 (0.19)
	HilHC5i + CSP 400 nm	8/8	556.00 (10.7)	5.1 (0.3)	56.9 (2.4)	1.6 (0.19)
	Clevios CH8000 + CSP	4/8	489.4 (15.0)	2.4 (0.8)	31.8 (4.9)	0.36 (0.08)
SC	Spincoated PEDOT Orgacon 5015	4/4	545.9 (6.2)	5.3 (0.3)	55.1 (0.8)	1.6 (0.08)
Evap	Evaporated MoOx	4/4	563.6 (8.6)	5.0 (0.4)	64.6 (1.2)	1.8 (0.18)

reduction in surface tension and resulting decrease in contact angle caused by the FS-3100 does not seem affected by the presence of the 1-pentanol. The contact angle of the formulation containing both additives is at all measurement times lower than that of the formulation containing only one of them.

In contrast to the surface tension obtained in the bubble tensiometer measurements, the contact angle of the CH8000 with added 1-pentanol reverts to the values obtained for the pure CH8000 after about 200 m s. This is most likely due to the much higher surface area and smaller volume of a single 10 pL droplet compared to the 10 mL volume on which the bubble tensiometer measurements were performed: during the high speed camera measurements the composition of the droplet changes due to the evaporation of the solvents, while in the bubble tensiometer the composition is expected to remain constant for the duration of the experiment. The drying effect on the jetted droplets will also cause the surfactant concentration to increase over time, as the 1-pentanol and water evaporate. The same effect will occur during the drying of actual printed layers.

The CH8000 formulation containing 0.1 wt% Capstone FS-3100 and 2 wt% 1-pentanol was inkjet printed on spin coated P3HT/PCBM samples at with several dotpitches to obtain different dry layer thicknesses. The results are shown in Fig. 5.

Here, it can be observed that PEDOT:PSS layers with a dotpitch of 41 and 31 μm can be inkjet printed from the modified formulation to obtain layers of approximately 300 and 400 nm thickness. To further optimize layer formation the PEDOT:PSS was diluted with demineralized water in a 1:1 v/v ratio prior to the addition of the surfactant and alcohol. The latter where both added to yield the same concentration as in the undiluted mixture. The effect of the two-fold dilution is that a twice as large wet layer thickness must be applied to obtain the same dry layer thickness. This facilitates the formation of a closed, uniform wet film. The effect of a two-fold dilution of the CH8000 with demineralized water and subsequent addition of 0.1 wt% Capstone and 2 wt% 1-pentanol can be seen in Fig. 6. A two-fold thicker wet layer must be inkjet printed to yield the same device layer thickness as for the undiluted ink, this leads to a closed dry layer already at a calculated thickness of 200 nm dry (Fig. 6a) instead of at a calculated dry layer thickness of 400 nm (Fig. 5b).

The advantage of the CH8000 PEDOT:PSS dispersion we used so far, is that it is a very simple formulation as it contains no solvent other than water, no surfactants and is a very stable dispersion because of its high PSS:PEDOT ratio of 20:1. With a resistivity of 3·10^3 Ωm it is, however, not a suitable material for large area transparent electrodes. Therefore, the same chemistry has been tested on a highly conductive PEDOT and OPV cells have been made to evaluate their properties. The formulation of highly conductive AGFA Orgacon HILHC5i was therefore also modified by the addition of the same amounts of 0.1 wt% Capstone FS-3100 and 2 wt% 1-pentanol. Layers with thicknesses between 100 nm and 400 nm of this materials could also be inkjet printed on the same P3HT/PCBM photoactive layer (Fig. 7).

The influence of the formulation on the performance of the layers was evaluated by fabricating solar cells in which the top PEDOT:PSS layer was inkjet printed using the new formulation and the other layers were applied using spin coating or thermal evaporation. The results are shown in Fig. 8 and Table 1.

The best performance was obtained for the devices with inkjet printed modified HILHC5i thickness of 100 nm for which the maximum power point (MPP) was 1.9 mW/cm^2, which was approximately the same as the value of 1.8 mW/cm^2 obtained for cells with an evaporated Molybdenum oxide (MoOx) topelectrode. The effect of the layer thickness of the printed PEDOT:PSS layer is not very large as cells with layer thicknesses between 50 nm and 400 nm all have MPPs between 1.5 mW/cm^2 and 1.9 mW/cm^2, see supplementary information. The same holds for the open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor (FF) which are all without clear trends as function of the layer thickness within the investigated range.

The overall yield of devices with an inkjet printed layer of modified HilHC5i was over 90%, as 40 out of 44 devices were functional (see supplementary information). Devices in which modified CH8000 PEDOT:PSS was printed instead of HILHC5i had a much lower output of MPP = 0.36 mW/cm^2 which was attributed to the much lower conductivity of the former.

4. Conclusion

A sufficient and sufficiently fast surface tension reduction of aqueous PEDOT:PSS dispersions is required for inkjet printing this transparent conductor on a hydrophobic P3HT/PCBM photoactive layer. Addition of a combination of a moderately miscible alcohol, i.e. 1-pentanol, in combination with a fluorosurfactant, i.e. Capstone FS-3100, resulted in uniform inkjet printed device layers. Both the instantaneous but moderate reduction in surface tension caused by the alcohols and the large but slow effect of the fluorosurfactant can clearly be observed in measurements of the dynamic surface tension of the inks and the evolution of the contact angle of single inkjet printed ink droplets. The use of these additives was found to have no negative effect on the performance of organic photovoltaic devices since devices with a 100 nm thick inkjet printed PEDOT:PSS layer had a MPP of 1.9 mW/cm^2 compared to an MPP of 1.8 mW/cm^2 obtained for reference devices with an evaporated top electrode. As we have shown that the formulation is transferable among different PEDOT:PSS dispersions and many organic photoactive materials have comparable surface energies to P3HT/PCBM we expect that this formulation strategy can also be applied for different OPV device stacks.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding sources

Supporting information

Table with the properties of all fabricated devices.

Notes

The authors declare no competing financial interest.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.orgel.2018.06.004.

References

[1] F.C. Krebs, S.A. Gevorgyan, J. Alstrup, A roll-to-roll process to flexible polymer solar cells: model studies, manufacture and operational stability studies, J. Mater. Chem. 19 (2009) 5442, http://dx.doi.org/10.1039/b823001c.

[2] C.N. Hoth, P. Schilinsky, S.A. Choulis, S. Balasubramanian, C.J. Brabec, Solution-processed Organic Photovoltaics, in: Appl. Org. Print. Electron., Springer US, Boston, MA, 2013, pp. 27–56, http://dx.doi.org/10.1007/978-1-4614-3160-2_2.

[3] F. Machui, L. Lucera, G.D. Spyropoulos, J. Cordero, A.S. Ali, P. Kubis, T. Ameri, M.M. Voigt, C.J. Brabec, Large area slot-die coated organic solar cells on flexible substrates with non-halogenated solution formulations, Sol. Energy Mater. Sol. Cells 128 (2014) 441–446, http://dx.doi.org/10.1016/j.solmat.2014.06.017.

[4] M.M. Voigt, R.C.I. Mackenzie, S.P. King, C.P. Yau, P. Atienzar, J. Dane, P.E. Keivanidis, I. Zadrazil, D.D.C. Bradley, J. Nelson, Gravure printing inverted organic solar cells: the influence of ink properties on film quality and device performance, Sol. Energy Mater. Sol. Cells 105 (2012) 77–85, http://dx.doi.org/10.1016/j.solmat.2012.04.025.

[5] F.C. Krebs, Fabrication and processing of polymer solar cells: a review of printing and coating techniques, Sol. Energy Mater. Sol. Cells 93 (2009) 394–412, http://dx.doi.org/10.1016/j.solmat.2008.10.004.

[6] R. Abbel, I. de Vries, A. Langen, G. Kirchner, H. T'Mannetje, H. Gorter, J. Wilson, P. Groen, Toward high volume solution based roll-to-roll processing of OLEDs, J. Mater. Res. 32 (2017) 2219–2229, http://dx.doi.org/10.1557/jmr.2017.204.

[7] F.C. Krebs, Polymer solar cell modules prepared using roll-to-roll methods: knife-over-edge coating, slot-die coating and screen printing, Sol. Energy Mater. Sol. Cells 93 (2009) 465–475, http://dx.doi.org/10.1016/j.solmat.2008.12.012.

[8] Y. Galagan, I.G. de Vries, A.P. Langen, R. Andriessen, W.J.H. Verhees, S.C. Veenstra, J.M. Kroon, Technology development for roll-to-roll production of organic photovoltaics, Chem. Eng. Process. Process Intensif 50 (2011) 454–461, http://dx.doi.org/10.1016/j.cep.2010.07.012.

[9] M.M. Voigt, R.C.I. Mackenzie, C.P. Yau, P. Atienzar, J. Dane, P.E. Keivanidis, D.D.C. Bradley, J. Nelson, Gravure printing for three subsequent solar cell layers of inverted structures on flexible substrates, Sol. Energy Mater. Sol. Cells 95 (2011) 731–734, http://dx.doi.org/10.1016/j.solmat.2010.10.013.

[10] T.M. Eggenhuisen, M.J.J. Coenen, M.W.L. Slaats, W.A. Groen, Large area inkjet printing for organic photovoltaics and organic light emitting diodes using non-halogenated ink formulations, J. Imag. Sci. Technol. 58 (2014) 404021–404026, http://dx.doi.org/10.2352/J.ImagingSci.Technol.2014.58.4.040402.

[11] T.M. Eggenhuisen, Y. Galagan, E.W.C. Coenen, W.P. Voorthuijzen, M.W.L. Slaats, S.A. Kommeren, S. Shanmuganam, M.J.J. Coenen, R. Andriessen, W.A. Groen, Digital fabrication of organic solar cells by Inkjet printing using non-halogenated solvents, Sol. Energy Mater. Sol. Cells 134 (2015), http://dx.doi.org/10.1016/j.solmat.2014.12.014.

[12] C.A. Lamont, T.M. Eggenhuisen, M.J.J. Coenen, T.W.L. Slaats, R. Andriessen, P. Groen, Tuning the viscosity of halogen free bulk heterojunction inks for inkjet

[13] printed organic solar cells, Org. Electron. 17 (2015) 107–114, http://dx.doi.org/10.1016/j.orgel.2014.10.052.

[13] O. Ostroverkhova, Handbook of Organic Materials for Optical and (Opto)electronic Devices ;: Properties and Applications, Woodhead Publishing Ltd, 2013.

[14] F.J. Lim, K. Ananthanarayanan, J. Luther, G.W. Ho, Influence of a novel fluorosurfactant modified PEDOT: PSS hole transport layer on the performance of inverted organic solar cells, J. Mater. Chem. 22 (2012) 25057, http://dx.doi.org/10.1039/c2jm35646e.

[15] B. Meng, Y. Fu, Z. Xie, J. Liu, L. Wang, Phosphonate-functionalized donor polymer as an underlying interlayer to improve active layer morphology in polymer solar cells, Macromolecules 47 (2014) 6246–6251, http://dx.doi.org/10.1021/ma5008754.

[16] N. Perinka, C.H. Kim, M. Kaplanova, Y. Bonnassieux, Preparation and characterization of thin conductive polymer films on the base of PEDOT: PSS by ink-jet printing, Phys. Procedia 44 (2013) 120–129, http://dx.doi.org/10.1016/j.phpro.2013.04.016.

[17] D. Hegemann, H. Brunner, C. Oehr, Plasma treatment of polymers for surface and adhesion improvement, Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. Atoms 208 (2003) 281–286, http://dx.doi.org/10.1016/S0168-583X(03)00644-X.

[18] J. Weickert, H. Sun, C. Palumbiny, H.C. Hesse, L. Schmidt-Mende, Spray-deposited PEDOT: PSS for inverted organic solar cells, Sol. Energy Mater. Sol. Cells 94 (2010) 2371–2374, http://dx.doi.org/10.1016/j.solmat.2010.08.018.

[19] D. Angmo, M. Hösel, F.C. Krebs, All solution processing of ITO-free organic solar cell modules directly on barrier foil, Sol. Energy Mater. Sol. Cells 107 (2012) 329–336, http://dx.doi.org/10.1016/j.solmat.2012.07.004.

[20] D. Chi, B. Qi, J. Wang, S. Qu, Z. Wang, High-performance hybrid organic-inorganic solar cell based on planar n-type silicon, Appl. Phys. Lett. 104 (2014) 193903, http://dx.doi.org/10.1063/1.4875913.

[21] W.-H. Baek, M. Choi, T.-S. Yoon, H.H. Lee, Y.-S. Kim, Use of fluorine-doped tin oxide instead of indium tin oxide in highly efficient air-fabricated inverted polymer solar cells, Appl. Phys. Lett. 96 (2010) 133506, http://dx.doi.org/10.1063/1.3374406.

[22] M. Vosgueritchian, D.J. Lipomi, Z. Bao, Highly conductive and transparent PEDOT: PSS films with a fluorosurfactant for stretchable and flexible transparent electrodes, Adv. Funct. Mater. 22 (2012) 421–428, http://dx.doi.org/10.1002/adfm.201101775.

[23] S.H. Eom, S. Senthilarasu, P. Uthirakumar, S.C. Yoon, J. Lim, C. Lee, H.S. Lim, J. Lee, S.-H. Lee, Polymer solar cells based on inkjet-printed PEDOT: PSS layer, Org. Electron. 10 (2009) 536–542, http://dx.doi.org/10.1016/j.orgel.2009.01.015.

[24] D.J. Lipomi, B.C.-K. Tee, M. Vosgueritchian, Z. Bao, Stretchable organic solar cells, Adv. Mater. 23 (2011) 1771–1775, http://dx.doi.org/10.1002/adma.201004426.

[25] R. Xing, S. Wang, B. Zhang, X. Yu, J. Ding, L. Wang, Y. Han, Inkjet printed polystyrene sulfuric acid-doped poly(3,4-ethylenedioxythiophene) (PEDOT) uniform thickness films in confined grooves through decreasing the surface tension of PEDOT inks, RSC Adv. 7 (2017) 7725–7733, http://dx.doi.org/10.1039/C6RA27475G.

[26] S. Yoon, S. Sohn, J. Kwon, J.A. Park, S. Jung, Double-shot inkjet printing for high-conductivity polymer electrode, Thin Solid Films 607 (2016) 55–58, http://dx.doi.org/10.1016/j.tsf.2016.03.068.

[27] S. Jung, A. Sou, K. Banger, D.-H. Ko, P.C.Y. Chow, C.R. McNeill, H. Sirringhaus, All-inkjet-printed, all-air-processed solar cells, Adv. Energy Mater 4 (2014) 1400432, http://dx.doi.org/10.1002/aenm.201400432.

[28] F.C. Krebs, Y. Thomann, R. Thomann, J.W. Andreasen, A simple nanostructured polymer/ZnO hybrid solar cell—preparation and operation in air, Nanotechnology 19 (2008) 424013, http://dx.doi.org/10.1088/0957-4484/19/42/424013.

[29] H. Gorter, M.J.J. Coenen, M.W.L. Slaats, M. Ren, W. Lu, C.J. Kuijpers, W.A. Groen, Toward inkjet printing of small molecule organic light emitting diodes, Thin Solid Films 532 (2013) 11–15, http://dx.doi.org/10.1016/j.tsf.2013.01.041.

[30] N.M. Kovalchuk, A. Trybala, V. Starov, O. Matar, N. Ivanova, Fluoro- Vs hydrocarbon surfactants: why do they differ in wetting performance? Adv. Colloid Interface Sci. 210 (2014) 65–71, http://dx.doi.org/10.1016/j.cis.2014.04.003.

[31] J.U.U. Eastoe, J.S.S. Dalton, Dynamic surface tension and adsorption mechanisms of surfactants at the air - water interface, Adv. Colloid Interface Sci. 85 (2000) 103–144, http://dx.doi.org/10.1016/S0001-8686(99)00017-2.

[32] DOW, MSDS 1-Pentanol, (n.d.). http://msdssearch.dow.com/PublishedLiteratureDOWCOM/dh_0985/0901b803809853fb.pdf?filepath=oxysolvents/pdfs/noreg/327-00016.pdf&fromPage=GetDoc (accessed April 30, 2018).

[33] M. Caironi, Y.-Y. Noh, Large Area and Flexible Electronics, Wiley-VCH, 2015.