

DOI: 10.1002/adma.200700911

High Photovoltaic Performance of Inkjet Printed Polymer:Fullerene Blends**

By Claudia N. Hoth, Stelios A. Choulis,* Pavel Schilinsky, and Christoph J. Brabec

During the past decade, there has been an intensive search for cost-effective photovoltaics.^[1] Among the alternative technologies to inorganic solar cells, polymer solar cells could provide the most significant cost reduction since their solution processability at low temperatures may ultimately allow for the printing of large area solar cells on flexible substrates with low fabrication cost.^[2]

At present bulk heterojunction structures, based on blends of polymer donors and highly soluble fullerene-derivative acceptors, are the material systems with the highest published power conversion efficiencies (PCE)^[3]. Konarka Technologies have recently demonstrated a 5.21 % PCE plastic solar cell with an active area of 1.024 cm² (NREL certificate for Konarka solar cell from 11-20-2006). The demonstration of higher than 5 % PCE solar cells under calibrated (AM) 1.5 conditions demonstrates the potential of the technology. The identification of suitable printing methods for the production of organic solar cells is regarded as the next important milestone.

In this contribution we demonstrate the use of inkjet printing technology as a fabrication tool for highly efficient polymer:fullerene bulk heterojunction solar cells. Inkjet printing is a commonly used technique for controlled deposition of solutions of functional materials in specific locations on a substrate and can provide easy and fast deposition of polymer films over large area. From this point of view, it can be a suitable technology for large scale production of organic solar cells. In addition, inkjet printing is very promising because the polymer devices can be fabricated very easily because of the compatibility with various substrates and need of no addi-

tional patterning. Inkjet printing has been extensively used in the field of polymer light emitting diodes and thin film transistors.^[4] Fundamental characterization of the optical properties of inkjet printed polymer:fullerene blends^[5] and device performance of screen printed bulk heterojunction solar cells have already been published in the literature.^[6] The performance of inkjet printed bulk heterojunction solar cells as efficient solar cell devices has not yet been reported. The only previously published data reported inkjet printed bulk heterojunction organic solar cells with a PCE of 0.000333 % and short circuit current densities of 0.004835 mA cm⁻².^[7]

In this Communication we discuss and analyze the performance of highly efficient inkjet printed organic bulk heterojunction solar cells. We will demonstrate that the morphological and interfacial properties of the inkjet printed polymer:fullerene blend photoactive layer can be favorably determined by a suitable solvent formulation. In detail, we show that a mixture of high and low boiling solvent, in our case 68 % of ortho-dichlorobenzene (oDCB) and 32 % of 1,3,5-trimethylbenzene (mesitylene) respectively, allows us to produce inkjet printed organic solar cells with AM 1.5 calibrated power conversion efficiency in the range of 3 %. Figure 1a shows a schematic representation of an organic film formation by inkjet printing. The spreading and wetting of the liquid on the substrate and the drying behavior of the printed film are controlled by the solvent formulation and the temperature of the inkjet printing table.

More details of how the oDCB:mesitylene formulation was developed are included later in the text. The concentration of the oDCB:mesitylene mixture was chosen by investigating the droplet formation properties in terms of drop volume, velocity and angularity on the inkjet printhead. The best droplet formation was achieved by adding 32 % mesitylene to pure oDCB. Our results based on droplet formation were confirmed by the inkjet printed layer. We observed that a mesitylene concentration less than 32 % in the solvent mixture resulted in poor wetting and spreading of the solution, while mesitylene concentrations higher than 32 % in the solvent mixture result in lower solubility of the materials and reduced reliability of firing of the printhead nozzles owing to the lowered surface tension of the solution. During the drying process and subsequent annealing, the suggested oDCB:mesitylene solvent mixture leads to an optimum phase separation network of the polymer donor and fullerene acceptor and therefore strongly enhanced device performance. The results from the device with the suggested solvent mixture are compared with inkjet printed samples prepared from a pristine solvent

[*] Dr. S. A. Choulis, C. N. Hoth, Dr. P. Schilinsky
Konarka Technologies GmbH
Landgrabenstr. 94, 90443 Nürnberg (Germany)
E-mail: schoulis@konarka.com

C. N. Hoth
Department of Energy and Semiconductor Research
University of Oldenburg
26129 Oldenburg (Germany)

Dr. C. J. Brabec
Konarka Technologies Inc.
Boott Mill South, 3rd Floor
116 John Street, Suite 12, Lowell, MA 01852 (USA)

[**] We would like to acknowledge Professor Jürgen Parisi for valuable discussions.

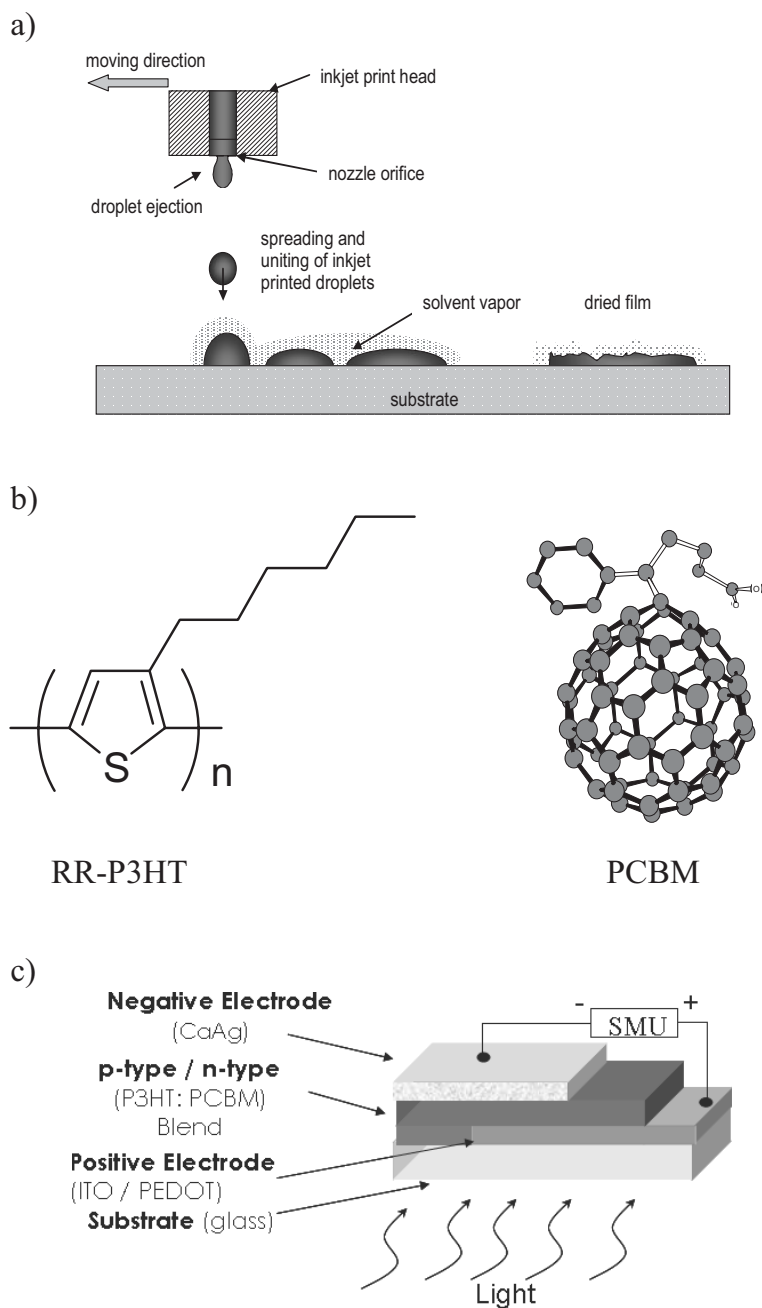


Figure 1. a) Schematic organic film formation by inkjet printing. b) Chemical structure of the regioregular P3HT polymer donor and PCBM acceptor used to print the photoactive layer. c) The device structure of the Glass/ITO/PEDOT:PSS/P3HT:PCBM/CaAg solar cells.

such as tetrahydronaphthalene (Tetralene). We note that the solvents used in this study (pristine oDCB, pristine Tetralene and the oDCB:mesitylene mixture) are excellent representatives for the inkjet printing technology and will be discussed in more details later in the text.

The devices were built on transparent indium tin oxide (ITO) coated glass substrates. A thin layer of poly(3,4-ethylenedioxythiophene) doped with polystyrene sulphonic acid

(PEDOT:PSS) was deposited by doctor blading on top of the ITO bottom electrode. After the PEDOT:PSS doctor blading step, the samples were placed 1 mm below the inkjet printhead for the coating of the photoactive layer by a commercial piezoelectric driven inkjet printing tool (from Fujifilm Dimatix, Inc.). The photoactive layer consists of regioregular poly(3-hexylthiophene) (P3HT) blended with fullerene [6,6]-phenyl C61 butyric acid methyl ester (PCBM) and dissolved in a Tetralene and oDCB:mesitylene solvent mixture. The chemical structure of the P3HT and PCBM materials is shown in Figure 1b and the device structure (Glass/ITO/PEDOT:PSS/P3HT:PCBM/CaAg) used in our studies is presented in Figure 1c.

Spreading and wetting on the substrate and of course the drying behavior of the inkjet printed films are, among other parameters, influenced by the inkjet table temperature. Importantly the substrates were heated to 40 °C during the deposition of the active layer by inkjet printing. We found that platen temperatures above 40 °C can result in the accumulation of the P3HT:PCBM in the center of the substrate. This can cause strong thickness variations in the active layer, resulting in a very thick layer in the middle and a pile-up of very low concentrated formulation at the edges resulting in an ultrathin layer at the edges. Thus, an inkjet platen temperature of 40 °C results in a uniform film and reliable printing with respect to the spreading and film formation. More details for the device fabrication can be found in the Experimental section of this paper and elsewhere.^[8,11]

The vapor pressure, boiling point, and surface tension of the solvents are critical parameters for inkjet printing technology.^[9] Table 1 summarizes the vapor pressures, boiling points, and surface tensions for the solvents used in this study. For the solvents used in our studies higher vapor pressures at a defined temperature (20 °C) result in lower boiling points, as can be seen in Table 1. This indicates a more rapid vaporization of mesitylene owing to the higher vapor pressure and the lower boiling point in contrast to Tetralene, which vaporizes slowly. We show later in the text that solvent vapor pressure and boiling point properties strongly

Table 1. Vapor pressures and boiling points of the solvents used in this study.

Solvent	Vapor Pressure at 20 °C [mm Hg]	Boiling Point [°C]	Surface Tension [dynes/cm ⁻¹]
Tetralene	0.18	207	34.9
ortho-Dichlorobenzene	1.20	180	37.0
Mesitylene	1.86	165	28.8

affect the inkjet printed polymer:fullerene blend morphology.

We have observed that the use of high boiling solvents (b.p. $> 180^{\circ}\text{C}$) such as oDCB or Tetralene, is an essential part to develop an ink formulation for inkjet printing. Since the nozzle orifice is open to the atmosphere, when not printing the solvent will evaporate. This results in an increase in the viscosity at the nozzle orifice. The increased viscosity is affecting the characteristics of the inkjet droplets in terms of velocity, volume, and angle deviation (angularity). During the vaporization of the solvents at the nozzle orifice the solid blend materials precipitate in the jet and the nozzles can be clogged. A high-boiling solvent is used to prevent nozzle clogging of the printhead and ensure reliable printing.

Pristine oDCB is a high surface tension solvent (37 dynes cm^{-1}). Therefore, its use resulted in a suppressed film formation and therefore a non-uniform film with strong thickness variation in the micrometer scale within one printed area, showing a dewetting behavior. This could be due to the lower surface energy of the PEDOT:PSS underlayer. Therefore, the inkjet printed polymer:fullerene blend active layer from oDCB shows clear limitations regarding the wetting and spreading of the solution on the PEDOT:PSS layer used in this study. The above limitations can be overcome by using pristine Tetralene as a solvent. Tetralene is a high boiling solvent showing a lower surface tension of $34.9\text{ dynes cm}^{-1}$ compared to oDCB. The Tetralene formulation can provide reliable inkjet printing (prevent nozzle clogging) with uniform coating, but the resulting films suffer from poor morphology and significantly rough surfaces as demonstrated in the atomic force microscopy (AFM) images in Figure 2a. This is specific to our inkjet printed trials since doctor-bladed cells fabricated in our labs using Tetralene as a solvent produce high PCE (3.3 %) P3HT/PCBM solar cells.^[11]

The combination of oDCB:mesitylene, a higher/lower boiling solvent mixture, serves two purposes: a) the first component of the solvent mixture (oDCB with b.p. $= 180^{\circ}\text{C}$) can be used to prevent nozzle clogging and provide a reliable jetting of the printhead, b) the second component (mesitylene) of the solvent mixture, with a lower surface tension of $28.8\text{ dynes cm}^{-1}$, is used to achieve optimum wetting and spreading of the solution on the substrate. Furthermore, mesitylene has a higher vapor pressure of 1.86 mm Hg ($133.322\text{ mm Hg} = 1\text{ Pa}$) at 20°C and a lower boiling point of 165°C compared to oDCB and Tetralene. Therefore, it increases the drying rate of the solvent mixture, which is a critical parameter for morphology as we discuss later in the text.

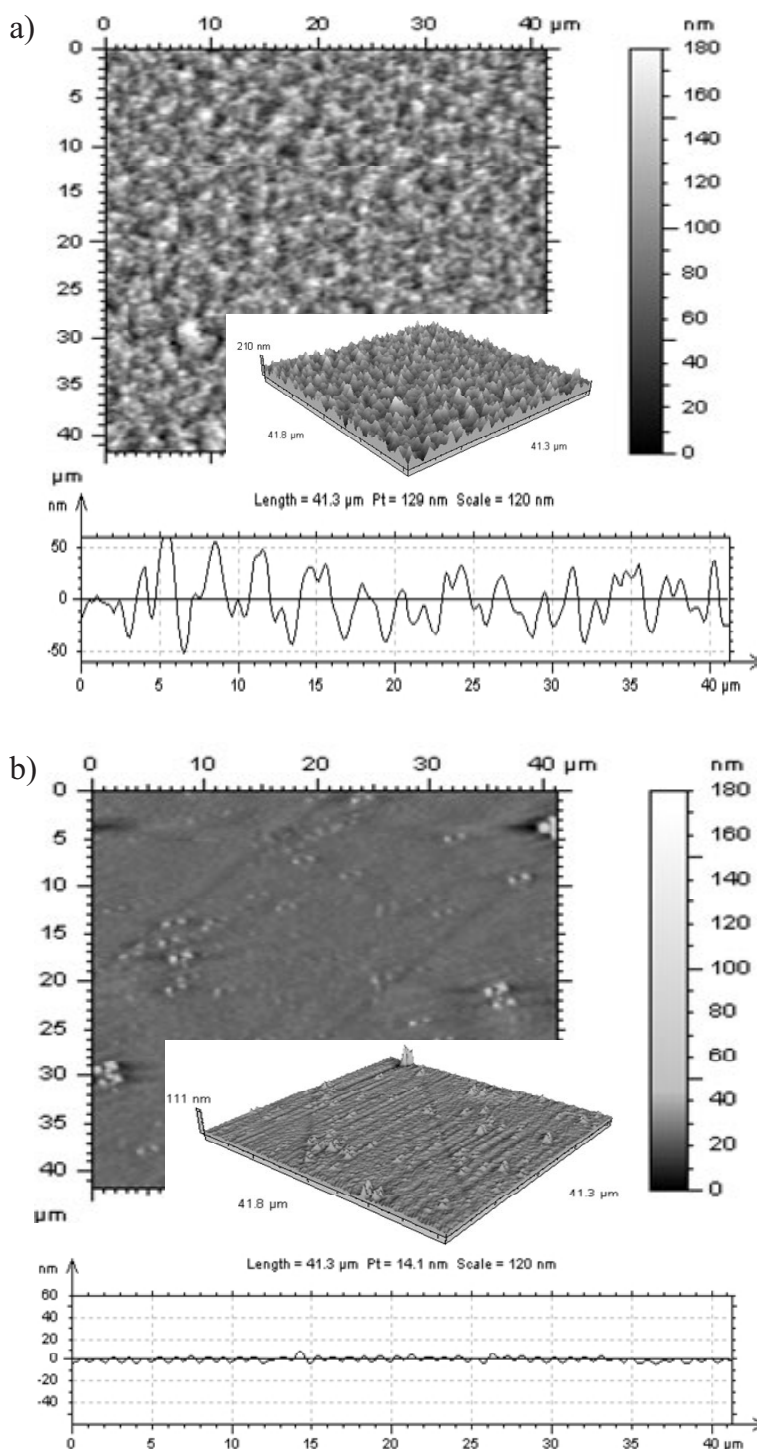


Figure 2. AFM images of P3HT/PCBM blend solution. a) Deposited from Tetralene formulation. b) Deposited from oDCB:mesitylene formulation by inkjet printing.

Figure 2 shows the AFM images of the P3HT/PCBM blend films inkjet printed using either Tetralene (Fig. 2a) or the mixture of oDCB:mesitylene (Fig. 2b). Because of the different solvent formulations, a significant distinction in the grain size and surface roughness between the inkjet printed layers is

visible. The AFM images of the inkjet printed Tetralene formulation display significantly rough surfaces for the inkjet printed active region. The mean roughness is calculated to be 21 nm for the inkjet printed P3HT/PCBM formulation with Tetralene, while the mean roughness for the oDCB:mesitylene mixture inkjet printed active layer was only 2.6 nm. A non-uniform surface roughness could affect the interfaces of the photoactive layer and therefore the performance of the inkjet printed device. The larger grain size of the P3HT:PCBM inkjet printed layer for the Tetralene formulation indicates morphological limitations. We interpret the poor morphology of the Tetralene inkjet printed P3HT/PCBM blend layer as a result of the low drying rate owing to the low vapor pressure leading to demixing of the polymer: fullerene within the inkjet printed blend. This is specifically related to our inkjet printed trials since, as reported by Li et al., low drying rate can produce highly efficient spin-coated solar cells.^[3c] Thus, the resulting morphology is dependent on the fabrication tool chosen for the deposition of the active layer.

In contrast the oDCB:mesitylene inkjet printed active layer shows a much more uniform mixing of the P3HT and PCBM

components within the blend. oDCB is a solvent able to achieve intimate morphology in the P3HT:PCBM blend, but as we discuss above, pristine oDCB formulation showed limitations in the spreading and wetting of the inkjet printed liquid on the substrate. To resolve this problem we have incorporated a second component in the solvent formulation, such as the mesitylene used in this study. Mesitylene is a solvent with lower boiling point (165 °C) and higher vapor pressure (1.86 mm Hg) than oDCB and thus, vaporizes first, increasing the concentration and viscosity of the deposited film. Because of the rising viscosity, the migration of the material close to the edges is decreased. Therefore, mesitylene is used to provide optimum spreading and wetting of the liquid bulk on the substrate while oDCB is used to achieve intimate morphology within the blend owing to the optimum solubility of the blended materials in chlorinated solvents.

To compare the impact of these different morphologies on the photovoltaic device performance, organic solar cells were fabricated in an identical manner except with either pristine Tetralene or a mixture of oDCB:mesitylene as the solvent used for the inkjet printed P3HT:PCBM active layer. Figure 3a shows the dark current density-voltage (J - V) log-linear

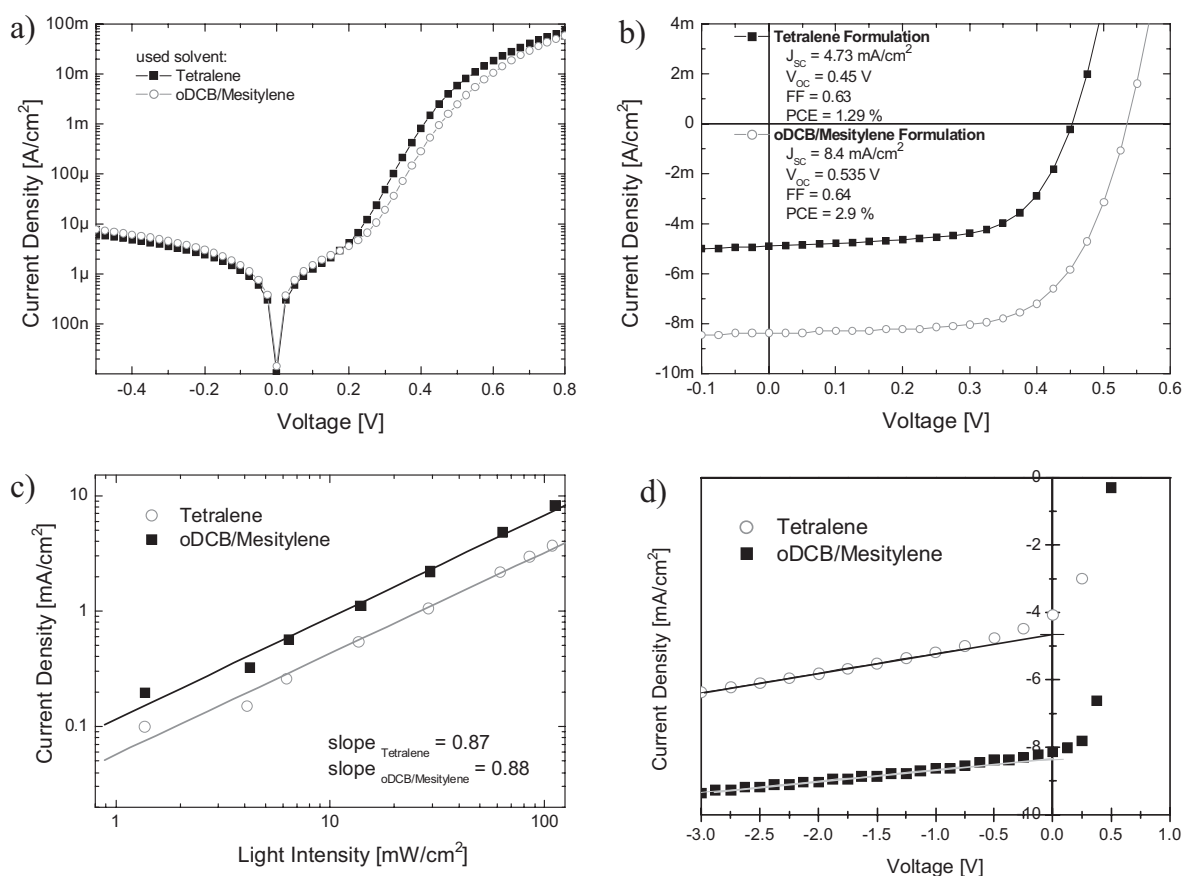


Figure 3. J - V curves for the inkjet printed solar cells processed using Tetralene as a solvent (solid squares) and oDCB:mesitylene (open circles). a) In the dark in a semi logarithmic representation. b) Under light in a linear representation. c) The light intensity dependence of the J_{sc} of the inkjet printed cells under study (black solid squares) in a double logarithmic representation. The lines present a linear fit to the experimental data. d) The voltage dependence of the illuminated photocurrent for extended reverse bias. The lines represent a linear fit of the J - V curves for the linear regime at negative voltages, where the J - V curves are dominated by the parallel resistance.

plot of the solar cell devices under study. The slope of the dark J - V curve between 0.2 V and 0.7 V represents the diode behaviour of the solar cells as governed by the diode ideality factor (n) and saturation current (J_0). We have previously shown, that for bulk heterojunction solar cells the ideality factor correlates with the number of distributed interfaces within the blend.^[10] However, both set of devices tested in our experiments show excellent rectification ratio and thus a good coverage for the PEDOT:PSS underlayer. According to the AFM images in Figure 2a and b, there is a clear difference in the ideality factor between the Tetralene and oDCB:mesitylene inkjet printed cells, which provide indications of different morphologies arising from the different solvent formulations. The morphological differences between the Tetralene and oDCB:mesitylene inkjet printed cells are reflected in the absolute values of n . The ideality is 1.6 and 1.3 for the oDCB:mesitylene and Tetralene inkjet printed samples, respectively. The difference in ideality between the Tetralene and oDCB:mesitylene inkjet printed cells under study gives an indication that there is difference in the molecular distribution of PCBM within the P3HT domains. The lower ideality factor for the Tetralene based inkjet printed cells indicates low intermixing of the P3HT:PCBM within the blend resulting in reduced bulk heterojunction interfaces and thus reduced charge-separation efficiency, which is expected to limit the J_{SC} of the Tetralene inkjet printed cells as shown in Figure 3b.

Figure 3b demonstrates the light current density-voltage (J - V) under AM 1.5 illumination with 100 mW cm^{-2} . The devices with an inkjet printed active layer based on pristine Tetralene formulation have a short-circuit current density (J_{SC}) of 4.7 mA cm^{-2} , an open-circuit voltage (V_{OC}) of 0.45 V, and a fill factor (FF) of 63 %. This corresponds to a PCE of 1.3 %. In contrast the devices with an inkjet printed active layer based on oDCB:mesitylene solvent mixture formulation have a significantly higher J_{SC} of 8.4 mA cm^{-2} , a V_{OC} of 0.54 V and a FF of 64 %, respectively. As a result the inkjet printed cells with the oDCB:mesitylene solvent mixture formulation obtain a PCE of 2.9 %.

The much higher values of J_{SC} (by 78 %) and V_{OC} (by 20 %) for the inkjet printed oDCB:mesitylene solvent mixture formulation are directly related to improved morphology and the smoother surface roughness profiles. We note that the drying behavior and the film uniformity of the inkjet printed layer are also influenced by the temperature of the inkjet table. As we discuss above, we have found that inkjet table temperatures of 40°C result in the most uniform film within one printed area and more reliable printing, with regard to the spreading and film formation, for both formulations studied. Higher table temperatures result in a suppressed film formation and therefore a dewetting of the inkjet printed layer owing to an unfavorable surface behavior of the substrate. The limitation in the performance of inkjet printed cells based on pristine solvent can be attributed to the low deposition temperatures (40°C) of the inkjet table for the comparatively high-boiling solvent, such as Tetralene, used in this study negatively affecting the P3HT:PCBM morphology and surface

roughness owing to demixing of the materials within the blend during the drying process.

To provide further indications that the main losses in the short-circuit current for the Tetralene formulation are due to reduced charge-separation efficiency, the inkjet printed devices were subjected to a light intensity and voltage dependence measurement to investigate the influence of recombination losses on the J_{SC} . The measurement of the light intensity dependence of the J_{SC} for both cells under study is presented in Figure 3c. The linear fits exhibit slopes of 0.87 and 0.88 for the inkjet printed cells with Tetralene and oDCB:mesitylene, respectively. This difference is within the experimental uncertainty of the measurement and therefore no difference in the bimolecular recombination for the two different cells can be detected. The fraction of second-order recombination is present to a similar extent for both devices and cannot be used to explain the lower J_{SC} for the Tetralene formulation.

The measurement of the voltage dependence of the current is presented in Figure 3d and used to investigate the influence of monomolecular recombination on the short-circuit current. Charges lost by monomolecular recombination can be extracted by a higher reverse voltage. Fitting the linear regime for negative voltages, where the sample is dominated by the parallel resistance, and extrapolating this regime to 0 V, the loss in the J_{SC} owing to monomolecular recombination can be evaluated.^[12] Considering the inkjet printed devices with Tetralene based formulation, 11 % of the losses in the J_{SC} can be related to a first-order recombination, whereas the oDCB:mesitylene inkjet printed cells displays a loss of 3 %. Thus, only a small fraction of the 78 % higher J_{SC} achieved with oDCB:mesitylene formulation can be explained by the reduced first-order recombination.

According to the above analysis, we argue that there are no dominant differences in recombination mechanisms between the cells fabricated with the two formulations under study and therefore we interpret the higher J_{SC} achieved for the oDCB:mesitylene formulation as mainly owing to improved charge-separation efficiency. This is discussed in more detail above from the ideality factor analysis included in the dark J - V data. Regarding the oDCB:mesitylene formulation, the higher V_{OC} might also be related to the improved morphology. In addition the ultrasmooth inkjet printed active layer (shown in Fig. 2b) creating an intimate interface with the CaAg and thus improving the contact quality of the top electrode could be influential.

In summary, we have shown that the boiling point and surface tension of the solvents are critical parameters to achieve a high-quality inkjet printed photoactive layer. The high boiling point and low surface tension values of the solvents are needed to achieve reliable inkjet firing and optimum wetting and spreading of the formulation on the substrate, respectively. Devices based on pristine solvents satisfying the above requirements, such as Tetralene, used in this study suffer from poor morphology and show limited PCE (in the range of 1.3 %), if the active layer is applied by inkjet printing.

We argue that the optimum inkjet formulation can be based on a higher- and lower-boiling solvent mixture such as

oDCB:mesitylene used in this study. The new proposed solvent mixture increases the photovoltaic performance of inkjet printed polymer:fullerene blends by four orders of magnitude in comparison to previously published literature^[7] and more than a factor of two in comparison to the pristine solvents used in this study. The proposed solvent formulation results in a reliable printhead firing with optimum wetting, spreading and drying rate of the formulation on the substrate and can provide an ultrasmooth 200 nm active layer with intimate morphology and interfaces offering high PCE inkjet printed cells. We believe that the above findings can be used as general specifications for the inkjet printing of polymer:fullerene blend solvent formulations. Based on the newly developed solvent mixture, we have demonstrated a 3 % PCE solar cell with inkjet printed polymer:fullerene blend photoactive layer. This high photovoltaic performance indicates the potential of inkjet printing for the mass production of organic photovoltaics.

Experimental

The devices were built on transparent indium tin oxide (ITO) coated glass substrates, purchased from TFD. The glass was cleaned for 10 min in acetone and another 10 min in isopropyl alcohol using an ultrasonic bath and finally with an ozone treatment lasting 10 min. A thin 60 nm layer of poly(3,4-ethylene dioxathiophene) doped with polystyrene sulphonic acid (PEDOT:PSS) was deposited by doctor blading on top of the ITO bottom electrode and the freshly coated layers were stored in a vacuum chamber for a couple of hours. The table temperature of the doctor blade was set to 40 °C and no additional annealing was performed for the PEDOT:PSS coating step on the anode interface. For our devices the Baytron PH, comprising a PEDOT:PSS ratio of 1:2.5 by weight, purchased from H. C. Starck was used.

After the PEDOT:PSS doctor blading step, the samples were placed 1 mm below the inkjet printhead for the coating of the photoactive layer by a commercial inkjet printing tool (from Fujifilm Dimatix, Inc.). The inkjet printing tool includes a piezoelectric-driven inkjet head with a motorized xyz stage, a fiducial camera for the substrate alignment and a drop watcher camera to control the drop shape. The photoactive layer consists of P3HT blended with fullerene PCBM in a 1:1 weight ratio were dissolved in Tetralene and oDCB/ mesitylene solvent mixtures. On top of the active layer, an additional CaAg top electrode was deposited by physical vapor deposition to complete the bulk heterojunction solar cell. Before the evaporation of the top electrode, the devices were subjected to a thermal treatment at 140 °C for 10 min.

For efficiency evaluation the device area was defined by the overlap between the underlying ITO and the top electrode. Solar cells with an active area of typically 20 mm² and up to 1 cm² were studied. The devices' current density-voltage (*J*-*V*) characteristics were assessed with a source measurement unit SMU 2400 from Keithley under nitrogen atmosphere. For illumination a Steuernagel Solarsimulator was used providing an AM 1.5G spectra at 0.1 W cm⁻². The high-resolution atomic force microscope consists of a cantilever with a sharp tip at its end to scan the surface of the sample. The probe was based on silicon nitride with a radius of curvature in the nanometer scale.

Received: April 17, 2007

Revised: July 10, 2007

Published online: October 26, 2007

- [1] a) N. S. Sariciftci, L. Smilowitz, A. J. Heeger, F. Wudl, *Science* **1992**, 258, 1474. b) J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti, A. B. Holmes, *Nature* **1995**, 376, 498. c) G. Yu, J. Gao, J. C. Hummelen, F. Wudl, A. J. Heeger, *Science* **1995**, 270, 1789.
- [2] C. J. Brabec, J. A. Hauch, P. Schilinsky, C. Waldauf, *MRS Bull.* **2005**, 30, 50.
- [3] a) Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. D. C. Bradley, M. Giles, I. McCulloch, C. S. Ha, M. Ree, *Nat. Mater.* **2006**, 5, 197. b) J. Y. Kim, S. H. Kim, H.-H. Lee, K. Lee, W. Ma, X. Gong, A. J. Heeger, *Adv. Mater.* **2006**, 18, 572. c) G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *Nat. Mater.* **2005**, 4, 864. d) S. Curran, D. L. Carroll, *Org. Lett.* **2005**, 7, 5749.
- [4] a) H. Sirringhaus, T. Kawase, R. H. Friend, T. Shimoda, M. Inbasekaran, W. Wu, E. P. Woo, *Science* **2000**, 290, 2133. b) H. Sirringhaus, T. Kawase, R. H. Friend, *Mater. Res. Bull.* **2001**, 26, 539. c) J. Bharathan, Y. Yang, *Appl. Phys. Lett.* **1998**, 72, 2660. d) C. Edwards, D. Albertalli, *SID Symposium Digest* **2001**, 32, 1049.
- [5] V. Marin, E. Holder, M. M. Wienk, E. Tekin, D. Kozodaev, U. Schubert, *Macromol Rapid Commun.* **2005**, 26, 319.
- [6] S. E. Shaheen, R. Radspinner, N. Peyghambarian, G. E. Jabbour, *Appl. Phys. Lett.* **2001**, 79, 18.
- [7] V. G. Shan and D. B. Wallace, *Proc. IMAPS 37th Annual International Symposium on Microelectronics, Long Beach, CA, November 14-18, 2004*, pp 1.
- [8] P. Schilinsky, C. Waldauf, C. J. Brabec, *Adv. Funct. Mater.* **2006**, 16, 1669.
- [9] T. Shimoda, K. Morii, S. Seki, H. Kiguchi, *MRS Bull.* **2003**, 28, 821.
- [10] C. Waldauf, M. C. Scharber, P. Schilinsky, J. A. Hauch, C. J. Brabec, *J. Appl. Phys.* **2006**, 99, 104503.
- [11] C. N. Hoth, P. Schilinsky, S. A. Choulis, C. J. Brabec, *Nat. Mater.*, in press.
- [12] P. Schilinsky, *Ph.D. Thesis*, University of Oldenburg, Germany **2005**.