Digital inkjet printing of high efficiency large area nonfullerene organic solar cells

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Novel emerging materials for organic solar cells, such as non-fullerene acceptors, are paving the way for commercialization of organic photovoltaics. Their utilization in unconventional applications, such as conformable and disposable electronics, has turned the focus to inkjet printing as a fabrication method with advantages including low material usage, rapid digital design changes and high-resolution. In this work, we report for the first time the fabrication of efficient non-fullerene acceptor devices through inkjet printing for organic photovoltaic applications. The engineering of printable P3HT:O-IDTBR inks is centered on tuning the rheological properties for proper droplet ejection and the selection of solvents, including hydrocarbons, that meet solubility and volatility requirements to avoid common inkjet printing complications like nozzle clogging. The optimization of printing parameters including drop spacing and deposition temperatures resulted in homogeneous P3HT:O-IDTBR films with device efficiencies of up to 6.47% for small lab-scale devices (0.1cm²), comparable with that of spin-coating or blade-coating. A 2cm² inkjet-printed device is also shown to achieve a remarkable efficiency of 6%. To demonstrate their potential usage in customized applications, large area devices were fabricated in the shape of a

marine turtle with 4,76% efficiency, showcasing the versatility of the inkjet printing process for efficient organic photovoltaics.

1. Introduction

The sprout of the Internet of Things (IoT) has given rise to novel technological applications with customized devices that can be integrated into a wide range of objects and locations. The need to power such devices is on the rise, and the use of organic photovoltaics as energy harvesting components is a natural approach in unconventional and custom shaped applications as they offer properties including flexibility, stretchability, compatibility of materials with specific environments, and the low-cost associated with solution processing.^[1] Continuous improvements in chemical design of organic semiconductor materials have paved the way for record-breaking power conversion efficiencies (PCE) of over 14% with the use of emerging nonfullerene acceptors (NFA).^[2-5] However, fully exploiting the advantages of organic solar cells (OSCs) requires overcoming scale-up and manufacturing challenges including the availability and accessibility of materials^[5], compatibility with fabrication processes^[6], and overall costs for transitioning from laboratory-made devices into industrial and consumer ready scale.^[7] Moreover, the transition from halogenated solvents that pose risks to health and the environment to safer alternatives is required for their application in high-throughput large-scale production.^[8-11]

The system composed of the well-known poly3-hexylthiophene (P3HT) with the NFA molecule O-IDTBR (rhodanine-benzothiadiazole-coupled indacenodithiophene) has been suggested as a great candidate for wide commercialization of OSCs due to the straightforward synthesis and availability in higher quantities of the components^[5, 12, 13], longer device stability^[12, 14, 15], compatibility with a wide range of solvents and fabrication techniques^[16, 17], as well as high power conversion efficiencies.^[12, 14-18] Since its introduction by Holliday *et al*^[12], there have been many

efforts to further push the P3HT:O-IDTBR system from low-throughput and material-wasting laboratory fabrication techniques such as spin-coating to other printing methods with higher throughput.^[16, 17] For instance, Gasparini *et al* fabricated devices by blade-coating the P3HT:O-IDTBR active layer, and both electron and hole transport layers, attaining efficiencies of over 6%.^[16] Strohm *et al* formulated an active layer ink from non-halogenated solvents, and through slot-die coating fabricated larger areas ($>60\text{cm}^2$) while retaining solar module efficiencies of over 4.5%.^[17] These techniques yield uniform high-quality films over larger areas at higher speeds than conventional methods and can easily be adapted for lower cost roll-to-roll fabrication of devices. However, the fabrication of microwatt power electronics requires further control over the size and shape of the modules through the utilization of high-resolution printing techniques.

Drop-on-Demand (DoD) inkjet printing has many advantages over other fabrication methods including a contactless conformal deposition, compatibility of diverse substrates, lower material usage, and digital control over the design of resulting films with increased feature resolution.^[19-21] Since the first demonstration of inkjet-printed organic solar cells^[22], there have been continuous developments in ink engineering and the optimization of printing parameters.^[19, 23, 24] Aernouts *et al* explored the printability of P3HT:PCBM inks showing that the viscosity and surface tension of a solution must fall within specific ranges to overcome the forces at the printer nozzles and to form droplets with the right characteristics for proper ejection and deposition.^[25] The effect of printer parameters such as drop spacing, substrate temperature and printing height has been investigated by various groups to obtain homogeneous films for higher efficiency devices.^[26-28] Further optimization such as adjusting the regioregularity of P3HT, solvent mixing, and the use of additives, was performed by various groups pushing the efficiencies of P3HT based devices up to 3.7%.^[28-30] Furthermore, the use of new donor polymers have helped showcase the potential of

higher performing materials in closing the breach between inkjet printing and coating methods.^{[31,}

^{32]} There have been a few attempts to adapt non-halogenated solvent solutions to inkjet printing with promising results, however, they have mainly focused on inks based on fullerene derivatives.^[32, 33] Recent efforts to formulate NFA inks with based on hydrocarbon solvents have demonstrated spin-coated devices efficiencies are comparable to halogenated solvent based inks^{[8,}
^{34-36]}, however there is further need to adapt their rheological properties to ensure their compatibility with the inkjet printing process along with high efficiencies.

In this work, we report the adaptation of the P3HT:O-IDTBR system to the inkjet printing process, yielding solar cell device efficiencies of up to 6.47% and demonstrating the potential lab-to-fab transition through the formulation of inks based on hydrocarbon solvents and the fabrication of large area devices (2cm²). We tune the viscosity and surface tension of the inks beyond the printability threshold through manipulation of solvent composition and concentration, validating their compatibility with the DoD inkjet printing process. Through the modification of printing parameters including drop spacing and deposition temperature, we optimize the uniformity and homogeneity of the resulting P3HT:O-IDTBR films as well as the electrical characteristics of the completed solar cells, with performances matching those of coated devices. The characteristics of devices printed from ink systems composed from the hydrocarbons 1,2-xylene and tetralin are compared side to side with dichlorobenzene-based films to assess their feasibility as alternative solvents. Furthermore, the advantage of free-form printing is explored through the fabrication of P3HT:O-IDTBR solar cell in the shape of a marine turtle.

2. Results & Discussion

2.1. Ink Adaptation Process

The molecular structures of the active layer materials and solvents used are shown in **Figure 1a**, the well-known P3HT acts as the donor unit, while O-IDTBR acts as the non-fullerene acceptor in the bulk heterojunction (BHJ) film. The photoactive layer components are dissolved in 1,2-dichlorobenzene (oDCB), 1,2-xylene or tetralin to formulate inks which are deposited through DoD inkjet printing. **Figure 1b** illustrates how the printer head moves side-to-side, jetting droplets as dictated by the software, depositing the ink and constructing the final film in a line-by-line manner. The adaptation of solutions normally used in laboratory deposition techniques such as spin-coating to inks used for printing is not straightforward, as there are many property requirements and optimization steps to obtain continuous functional films. Most solutions optimized for spin-coating use highly volatile low viscosity solvents, including chlorobenzene and chloroform, to achieve a good spread over substrates with a fast evaporation, however they rarely match the requirements for inkjet printing. The formulation of an ink for inkjet printing requires:

- i) The accurate ejection of droplets from the printer head for a repeatable process,
- ii) The compatibility with the underlying layers, and
- iii) the proper evaporation of the solvent to obtain functional films.

The first step of inkjet process concerns the formation and ejection of satellite-free droplets (e.g. consisting in a round body with a short ligament). Many parameters need to be adjusted, including the waveform and voltage applied to the piezoelectric actuators at the nozzles to achieve stable droplet jetting. We select and tune materials according to volatility and ink rheological properties to overcome the surface tension forces at the nozzles. We investigate the change in both dynamic viscosity η and surface tension γ by adjusting the concentration of a oDCB-based ink,

demonstrating a linear increase for both properties (**Figure 1c**). By using cartridges with 9 μm diameter nozzles, fixing the droplet velocity at 6m/s, and using the measured values for the rheological properties, we constructed the printability chart in **Figure 1d** based on the flow properties of the ink. The Z number (**Equation 1**), as proposed by Ohnesorge and Fromm, denotes the ratio between the Reynolds Re and the Webber number We , where a is the nozzle diameter and ρ is the density of the solution.^[20, 37, 38]

$$Z = Oh^{-1} = (\gamma \rho a)^{1/2} / \eta \quad (1)$$

They suggest that inks with Z values in the range $1 < Z < 10$ form stable droplets and can be successfully used for inkjet printing.^[37, 39-41] With surface tension values between 20-50 dynes/cm, inks based on common organic solvents require a minimum viscosity of 1.2 cP to sit at the edge of the printable region. A zoomed-in view of the region of interest delineated by the dotted rectangle is shown in **Figure 1e**. The pure solvents chlorobenzene, dichlorobenzene and xylene have Z values ranging between 15.9 and 22.6, in the satellite droplet region, confirming the practical observations of dripping as they overcome the surface tension forces too easily. Pure tetralin falls in the printable range with a Z value of 8.76. The chlorobenzene-based ink with a concentration of 24 mg/ml normally used for spin-coating^[12] has a Z-value of 12.1, meaning it cannot directly be used for inkjet printing. Increasing the concentration of oDCB-based inks above 15 mg/ml push the Z values into the printable fluid region, meaning that stable droplets could be formed by carefully adjusting the printing parameters. **Figure 1f** displays the contrast between normal jetting and jetting through a clogged nozzle. While inks with higher concentrations seem to be more adequate for jetting, they are prone to clogging due to the localized increased concentration induced by solvent evaporation at the nozzles, resulting in misfiring, satellite droplets, and ultimately affecting the resolution of the print (**Figure S1**). We formulated printable inks from

different solvent systems with z values ranging from 3.6 to 7.9 by fixing the concentration at 25mg/ml. Nozzle clogging was minimized by adjusting the waveform and the firing voltage. Moreover, we reduced the possibility of resolution defects by adopting a band printing strategy (**Figure S2**).

2.2. Effect of printing parameters on P3HT:O-IDTBR film formation

The second and third requirements of inkjet printing go hand-in-hand with forming uniform homogeneous functional films. Unlike spin-coating and blade-coating where the film forms radially or uni-directionally through a fast deposition and evaporation, the film formation in inkjet printing occurs through the evaporation at the edges of each deposited line and the internal flows of the deposited wet layer (commonly known as coffee-ring effect).^[42, 43] Ideally, the drying behavior of inkjet printing should resemble that of blade-coating.^[44] Obtaining uniform films requires controlling the evaporation behavior of the deposited wet film through the properties of the ink^[45], the separation between each deposited line, and the substrate temperature.

The table of micrographs in **Figure 2** displays the effect of the variation in drop spacing (DS) and temperature on the homogeneity of the resulting films. Printing with a DS below 10 μ m lead to the formation of continuous films at all temperatures, minimizing potential electrical shorts due to the pinholes coming from misfiring nozzles. Higher temperatures lead to the formation of overlaps, as each printed line dries before connecting to the next. The effect is evidenced by the presence of the peaks and valleys in films printed with a DS higher than 15 μ m at temperatures higher than 50°C. A closer look at the higher resolution micrographs (**Figure S3**) suggests that the most uniform surfaces are obtained when printing with a DS of 10 μ m in a range between 40 and 50°C.

We used atomic force microscopy (AFM) to analyze the topography and roughness of P3HT:O-IDTBR films (**Figure S4**). Higher surface roughness RMS values of 19.9nm and 16.9nm are obtained for P3HT:O-IDTBR films at room temperature and 30°C respectively, with the values decreasing to 10.6nm as the temperature approaches 50°C. While overlaps and some discontinuities were present, printing at 60°C resulted in an RMS value of 9.84nm.

Perhaps, one of the main advantages of the P3HT:O-IDTBR blend is that it has long diffusion lengths and good charge transport and therefore the active layer is not required to be within the 100nm thickness limit which is the case with most photoactive materials for OSCs.^[14, 16, 17] To evaluate the influence of the DS and temperature on the thickness of the films we performed profile measurements (**Figure S5**). Temperature plays a critical role in the uniformity of the films, as the evaporation of the solvent determines the drying behavior and internal flows in the wet layer (**Figure S6**). The wavefront effect is greatly reduced with the utilization of deposition temperatures above 40°C, as the wet film dries proportionally to the newly deposited lines. Printing with a DS of 10µm with at temperatures above 40°C resulted film thicknesses between 400 and 500 nm.

2.3. Effect of printing parameters on device performance

The organic solar cells are fabricated with an inverted architecture (**Figure 3a**), where the inkjet-printed P3HT:O-IDTBR BHJ active layer is sandwiched between a coated electron transport layer, and evaporated hole transport layer and silver top electrode. The current density-voltage (J - V) curves in **Figure 3b** shows that the performance of optimized inkjet-printed devices is comparable to that of coated devices, which can reach short-circuit current densities (J_{sc}) of over 13 mA cm⁻², an open-circuit voltage (V_{oc}) of 0.71 V, and fill factors (FF) over 60%.

In adherence to our film homogeneity observations and to previous reports with an oDCB based P3HT:PCBM ink^[26], our optimization approach focused on varying the DS at fixed deposition temperature (42°C). The characteristic *J-V* curves under AM 1.5 G illumination in **Figure 3c** display the overall performance of the corresponding printed solar cells. The pinholes and discontinuous films when printing with a DS of 20 µm yielded devices with low V_{oc} and electrical shorts, while printing with a DS of 5 µm resulted in low J_{sc} values due to the poor charge collection associated with thicker layers. At a DS of 10 µm, the devices presented improved J_{sc} and FF values of 12.76 mA/cm⁻² and 64% respectively, resulting in power conversion efficiencies (PCE) over 5.5%. **Figure 3d** shows the *J-V* characteristics of the best performing devices printed with a fixed drop spacing of 10 µm while changing the deposition temperature. When printing at room temperature and at 50°C, the J_{sc} values surpass the 14 mA cm⁻² mark, while the FF reaches up to 62%, with the drawback of reduced V_{oc} values below 0.7V. Our champion device was obtained using oDCB ink with a deposition temperature of 60°C yielding a film thickness of 343 nm and resulting in a 67.2% FF and a PCE of 6.47%. The resulting parameters for all *J-V* curves with varying DS and deposition temperature are summarized in Table 1, while the dark curves are shown in **Figure S7**.

To analyze the influence of the DS and deposition temperature in a broader spectrum, we fabricated devices with a drop spacing ranging from 5µm up to 20µm at temperatures scaling from 23°C up to 60°C. The maps of the average FF and PCEs of the resulting cells are represented in **Figure 3e and f**, respectively. Optimal conditions are observed in the area delimited by a DS between 8 and 15 µm at temperatures above 50 °C, where the smooth topography (Figure S4) and correct thickness resulted in J_{sc} values above 14 mA cm⁻², FF over 60%, and efficiencies surpassing the 5.9% mark. Interestingly, high FF values are achieved with thinner layers at high DS and lower

temperatures, however the J_{sc} values do not surpass the 10 mA/cm² mark. As demonstrated in previous NFA studies^[46-48], we performed ellipsometry measurements and calculated the transfer matrix optical model (**Figure S8**) further confirming that thicknesses above 300nm are ideal for efficient current generation regardless of deposition temperatures. Moreover, low deposition temperatures lead to the apparition of an unwanted wave front (Figure S6). Temperature plays a significant role on the crystallization of the materials in the bulk heterojunction.^[17, 49] The crystallization of both P3HT and O-IDTBR compete with each other during film formation.^[14] A double hump in the average efficiency map occurs with films printed with a DS of 10 μ m, with higher efficiencies sitting above 50°C and at room temperature, with a valley occurring around 40°C. We performed UV-vis absorption spectroscopy on the films to compare the crystallization of the films at different drying temperatures after annealing at 140°C for 10 minutes (**Figure S9**).

2.4. Towards Halogen-Free Solvent Fabrication

Moving one step further towards the development of inkjet printable eco-friendly inks, we then focused on the integration of hydrocarbon solvents with the P3HT:O-IDTBR system. A summary of the rheological properties and printability parameters of the chlorinated and hydrocarbon solvents used is provided in **Table S1**. The hydrocarbon 1,2-xylene provided a good base for the ink, as it has a similar solubility to chlorobenzene for both P3HT^[17] and O-IDTBR^[8, 12, 17], however its low viscosity (0.76 cP at room temperature) is not in the printable range. Despite possessing a lower solubility^[17], 1,2,3,4-tetrahydronaphthalene (tetralin) is a promising candidate to act as co-solvent, as it provides a viscosity around 2 cP and a higher boiling point of 207°C. We formulated 2 inks based on o-xylene:tetralin (1:1) and pure tetralin with identical P3HT:O-IDTBR (1:1,w:w)

blend concentration at 25mg/ml. The rheological properties and printability parameters of the hydrocarbon-based inks are shown in **Table S2**.

Based on the same methodology used for the optimization of the oDCB-based P3HT:O-IDTBR ink, we systematically varied parameters (waveform, applied voltages, drop spacing and bed temperature) of our hydrocarbon inks to obtain continuous homogeneous films. The best conditions were found with a DS of 10 μm for 1,2-xylene:tetralin and of 14 μm for pure tetralin with drying temperature of 60°C, yielding films with a thickness of 382nm and 260nm respectively. The J - V curve of each ink is shown in **Figure 4a**, and the results are summarized in **Table 2**. Tetralin, showed the best FF (63%) out of the inks tested with great reproducibility. The best efficiency was obtained with the 1,2-xylene:tetralin (1:1, v:v) solvent system, reaching out to 4.45% PCE, the highest achieved for an inkjet-printed hydrocarbon solvent ink OSC, so far. The UV-vis absorbance diagram in Fig S10 shows that in the tetralin based ink films, the absorbance of the P3HT is lowered at shorter wavelengths, while the O-IDTBR absorbance is pronounced when reaching the infrared wavelengths. In contrast, the 1,2-xylene:tetralin ink has a normalized absorbance comparable to that of oDCB. To verify the J_{sc} values obtained and further evaluate the light-to-current conversion of all the devices, we performed external quantum efficiency (EQE) measurements. **Figure 4b** shows the EQE spectra of the lab-scale devices fabricated from oDCB, tetralin, and 1,2-xylene:tetralin (1:1) solvents. The J_{sc} obtained from EQE differs between 5-10% to that extracted under AM1.5G for devices fabricated from all inks. The EQE of P3HT:O-IDTBR films obtained from the xylene:tetralin ink trails that of o-DCB by about 15%, however it opens the door for further optimization in terms of solvent mixing to completely match or surpass its performance.

2.5. Large area free-form device fabrication

One of the main benefits of using inkjet printing over other deposition techniques is the ability to digitally modify the design of the deposited droplets, enabling rapid prototyping of devices. We demonstrate a potential upscaling by inkjet printing P3HT:O-IDTBR solar cells over areas ranging from 0.033cm^2 up to 2cm^2 (**Figure 5a**) on pre-patterned ITO substrates. The performance of the devices over large areas is comparable to their small-scale counterparts, as the 6% PCE mark is sustained even at 2cm^2 . This advantage was taken into account for the fabrication of a freeform cell in the shape of a marine turtle (**Figure 5b**) with a total area of 2.2cm^2 . In here, the underlying ITO was patterned with a 60W ytterbium-fiber laser to define and separate the bottom electrodes. The ZnO ETL was coated by the same procedure as previously shown devices. The active layer was inkjet printed in specific areas to cover the bottom ITO electrode and complete the figure, while the HTL (MoO_3) and top electrode (Ag) were evaporated through a custom-made mask. Our custom turtle shaped solar cell resulted in a J_{sc} of 14.1 mA cm^{-2} , a V_{oc} of 0.72V , and despite having a FF of 47% which may be the result of laser patterning the ITO, demonstrated a remarkable 4.76% PCE.

3. Conclusion

With the adaptation of the commercially available P3HT along with NFA O-IDTBR, we demonstrate the inkjet printing of 6% efficient organic solar cells under ambient conditions with large area (2cm^2) and custom design. We engineered the printability of oDCB and hydrocarbon based inks through the rheological properties to achieve consistent jetting and optimized the printing parameters including the drop spacing and deposition temperature to form homogeneous active layer films. The synergy of the ink formulation with optimized process

parameters allows efficiencies of up to 6.47% with oDCB, and 4.43% with 1,2-xylene:tetraline (1:1). Additionally, we exploited one of the main advantages of inkjet printing by designing and digitally fabricating a 2.2 cm² solar cell in the form of a marine turtle, demonstrating its versatility for free-form manufacturing. With advantages including digital design, rapid prototyping, low material usage and integration with other additive manufacturing techniques, inkjet printing with non-fullerene acceptors is envisioned to produce highly efficient solar cells to integrate them in innovative applications.

4. Experimental Section

Materials: P3HT (MW=40k/51k Pd=2.1) was purchased from Rieke metals. O-IDTBR was purchased from 1-Material. Solvents and all other chemicals were purchased from Sigma-Aldrich and used as received.

Device Fabrication: The solar cells were fabricated with an inverted architecture (glass/ITO/ZnO/P3HT:O-IDTBR/MoO₃/Ag). First Indium Tin Oxide (ITO) covered glass substrates were cleaned through sonication in detergent, deionized water, acetone, and isopropanol. Then, an oxygen plasma treatment was used to further clean the surface and to increase the wettability. Zinc oxide deposition was done by spin-coating a sol-gel solution (zinc acetate dehydrate in 21μl ethanolamine/1 ml 2-methoxyethanol) (Sigma Aldrich) at 4000 rpm for 30s, followed by annealing at 200°C for 10 minutes. A 25mg/ml P3HT:O-IDTBR (1:1) solution is then inkjet-printed onto the desired area by using a Dimatix DMP 2800 printer with the conditions previously shown for each different solvent system resulting in active layer films with varying thicknesses. The printed films are then annealed at 140°C for 10 minutes in the glovebox. Lastly, 10nm of MoO₃ and 100nm of Ag were deposited via thermal evaporation

through a shadow mask to complete the top electrode as well as the contact pads. Devices with different areas (0.033 cm^2 - 2cm^2) were fabricated with the help of a custom made shadow mask. For the fabrication of the marine turtle solar cell, the $5\text{cm} \times 5\text{cm}$ ITO covered substrate was patterned through a 75W ytterbium-fiber laser system (Universal Laser System ILS 12.5) to obtain the required geometry. Zinc Oxide and Active layers were deposit as previously described. Custom made masks for the evaporation of subsequent layers were fabricated with acrylic through 30W CO_2 laser patterning (Universal Laser Systems VLS 3.6).

Measurements: To assess the printability of the solvents and solutions, the viscosity was obtained through a shear stress viscometer (RheoSense m-VROC) while the surface tension was measured through pending drop technique on a drop shape analyzer (Kruss DSA100) at room temperature. To evaluate the quality of the printed films the surface characteristics were obtained through the following methods under ambient conditions. The surface morphology of the resulting films was analyzed by using an optical microscope (Zeiss) as well as through atomic force microscopy (NT-MDT Solver Next). Film thicknesses were measured through a stylus profilometer (Tencor P-7) by applying a 0.5 mN force on the probing tip. The absorbance of the active layer films was measured through Ultraviolet-Visible spectrophotometry (Agilent Cary 5000). The refractive index (n) and extinction coefficient (k) of the active layer were obtained by printing the films onto silicon oxide substrates and measuring with an ellipsometer (JA Woollam M2000). The transfer matrix optical modelling was obtained through the matlab program published by the McGeehee group. To test the performance of the devices the electrical characterization was performed under nitrogen conditions inside the glovebox. The J-V curves were obtained by using a 21 LED light engine at simulated AM 1.5 solar illumination (Wavelabs

Sinus-70) with the aid of a Keithley 2400 source meter. The External Quantum Efficiency was measured by using a 75W Xenon lamp along with a chopper and monochromator (Enlitech QE-R), the instrument was calibrated by using a silicon photodiode.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Figure 1. (a) molecular structures of components P3HT and O-IDTBR as well as the solvents oDCB, 1,2-xylene and tetralin (b) diagram showing the inkjet printing process (c) Surface tension and viscosity change of P3HT:O-IDTBR (1:1) ink based on oDCB as a function of concentration. (d) Printability chart based on the Ohnesorge number of pure solvents (circles) and inks based on different solvents with a fixed concentration at 25mg/ml (squares) (e) Zoomed in view of dashed area in in (d), showing the change from the satellite droplet region to the printable fluid region of the inks based on oDCB, tetralin, and 1,2-xylene:tetralin (1:1) (f) Droplet images taken with the Dimatix Drop Viewer Application, displaying the contrast between normal jetting and jetting through a clogged nozzle. The nozzles are pointed with red arrows the main droplets with black arrows, and the satellite droplet is pointed by the white arrow

Figure 2. Optical microscope images at 100x magnification displaying the effect of drop spacing and the bed temperature for deposition on the homogeneity and uniformity of the resulting P3HT:O-IDTBR films printed from a dichlorobenzene-based ink with 25mg/ml concentration.

Scale bar = 500μm

a

b

c

d

e

f

Figure 3. Electrical characterization of P3HT:O-IDTBR devices printed from a oDCB based ink.

The devices were fabricated using an inverted architecture (a). (b) J - V curves comparing the performance of inkjet-printed devices to blade coating and spin-coating. (c) J - V curves of cells printed at different drop spacing (DS) at a constant bed temperature of 42°C. (d) J - V curves of cells printed with fixed drop spacing of 10 μm and varying bed temperature. Performance maps showing the average fill factor (a) and power conversion efficiency (b) of films printed at varying drop spacing and bed temperature.

Figure 4. Comparison of J - V curves (a) and External Quantum Efficiency (b) of devices fabricated from inks based on 1,2-xylene:tetralin(1:1), tetralin, and oDCB.

Figure 5. (a) The performance of P3HT:O-IDTBR devices as a function of cell area and (b) J-V of free-form inkjet-printed solar cell in the shape of a marine turtle on top of ITO glass.

Table 1. Summary of photovoltaic parameters of P3HT:O-IDTBR devices at different bed temperatures with a constant drop spacing of 10 μm . The values are the average representation of 12 devices.

Drop Spacing ^a	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE_{av} [%]	PCE_{max} [%]
5 μm	4.6	0.58	30.6	0.86	1.47
10 μm	12.8	0.71	64.4	4.81	5.09
15 μm	8.0	0.75	53.2	2.12	3.15
20 μm	7.3	0.28	42.6	0.40	1.14

^a) Constant Bed Temperature = 42°C

Temperature ^b	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE_{av} [%]	PCE_{max} [%]
23°C	14.8	0.67	54.7	4.98	5.35
30°C	14.6	0.68	57.8	5.59	5.72
40 °C	13.2	0.71	66.0	5.67	6.17
50 °C	14.7	0.69	61.9	5.99	6.25
60 °C	13.8	0.71	67.2	6.11	6.47

^b) Constant Drop Spacing = 10 μm

Table 2. Summary of photovoltaic parameters of P3HT:O-IDTBR devices fabricated from different solvents systems. The values are representation of average of 12 devices.

Solvent	J_{sc} [mA cm ⁻²]	V_{oc} [V]	FF [%]	PCE _{av} [%]	PCE _{max} [%]
Dichlorobenzene	13.8	0.71	67.2	6.11	6.47
Tetralin	8.3	0.746	63	3.72	3.91
Xylene:Tetralin (1:1)	11.5	0.72	55	3.92	4.46

6% Large Area P3HT:O-IDTBR solar cells are fabricated through Inkjet-printing, matching the performance of coated devices. The optimization and control over the printing process enables the deposition of custom-shaped 2.2 cm² area devices with 4.7% PCE. The competitive efficiencies obtained through the engineering of inks with hydrocarbon solvents shows the potential for a more environmentally friendly industrial scale-up.

Organic solar cells

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Digital inkjet printing of high efficiency large area nonfullerene organic solar cells

Supporting Information

Digital inkjet printing of high efficiency large area nonfullerene organic solar cells

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Figure S1. Printing defects resulting from misfiring and clogged nozzles. Both pinholes and skipped lines can be observed in the normal light (a) and reflected light (b) images of printed

films. The printing resolution defects can be attenuated by optimizing the jetting parameters and smooth homogeneous films are obtained. The normal light (c) and reflected light (d) images show uniform surfaces with no defects.

Figure S2. Band Printing Strategy. The Dimatix printer is set up to deposit droplets in an even manner ($ds_x = ds_y$) in the horizontal and vertical direction by controlling the jetting frequency and the motion of the stage respectively. The band printing strategy involved fixing the vertical drop spacing by setting the cartridge angle at 0.3° , while controlling the horizontal drop spacing (ds_y) and the distance between each band (B_y) through the Dimatix software ($ds_x = B_y \neq ds_y$).

Figure S3. Optical microscope images of films at 500x Magnification. Scale bar = 250μm

Figure S4. Atomic Force Microscopy topography images of a 20 by 20 μm area scan for P3HT:O-IDTBR films obtained from a dichlorobenzene-based ink by inkjet printing with a bed temperature of a) 23°C, b) 30°C, c) 40°C, d) 50°C, and e) 60°C. The resolution is set at 120 nm height scale up to 40°C, and then it is set at 60 nm for the films at 50°C and 60°C to achieve contrast with the improved uniformity.

Figure S5. Thickness vs Drop Spacing of P3HT:O-IDTBR films obtained from a DCB based ink. The films were printed employing a band printing strategy with drop spacing of 5, 8, 10, 12, 15 and 20 μm .

Figure S6. Drying behavior of printed films. (a) The diagram shows the drop by drop deposition in the direction of the red lines, which connect to the previously deposited lines to create a wet film. (b) as the solvent evaporates the internal flows push the solution towards the newly deposited wet areas (c) The result is a bulging area with a greater thickness towards the end of the print (wavefront) (d) Fiducial camera sequential images of the drying process (e) light reflection images showing the resulting wavefront with different deposition temperatures.

Figure S7. JV curve of inkjet-printed P3HT:oIDTBR based devices under dark conditions with a) bed temperature fixed at 42°C and varying drop spacing, b) Drop spacing fixed at 10 μm and varying bed temperature

Figure S8. Transfer Matrix optical modeling calculated by inputting the n and k values of the P3HT:O-IDTBR films through ellipsometry and running a simulation based on the methodology explained by Burkhard et al.^[1] Assuming a 100% IQE, the thickness of the films affect the generated current density. The ideal thickness for the inkjet-printed P3HT:IDTBR films at all temperatures is of over 300nm, when the current density stabilizes.

Figure S9. Normalized absorbance of P3HT:O-IDTBR films inkjet-printed at different drying temperatures and annealed at 140°C.

a

b

Figure S10. (a) Image of resulting film printed from a xylene:tetralin (1:1) ink. (b) Normalized Absorbance measurements of the P3HT:O-IDTBR films printed from inks based on different solvents.

Solvent	Density [g/ml]	Viscosity [cP]	Surface Tension [mN.m]	Z-number	Boiling Point [°C]
Chlorobenzene	1.1	0.8	33.5	22.65	180.1
1,2- Dichlorobenzene	1.3	1.3	36.6	15.91	180.1
1,2-xylene	0.88	0.76	29.76	20.2	144.5
Tetralin	0.973	2.02	35.5	8.76	207

Table S1. Table of rheological properties of hydrocarbon solvents compared to the conventionally used chlorobenzene and dichlorobenzene.

Ink Solvent System	Viscosity [cP]	Surface Tension [mN.m]	Oh-number	Z-number
1,2- Dichlorobenzene	2.69	39.5	0.125	7.98
1,2-xylene:Tetralin (1:1)	2.71	27.1	0.181	5.53
Tetralin	4.4	29.7	0.273	3.66

Table S2. Table of rheological properties and printability parameters of P3HT:O-IDTBR inks with a concentration of 25mg/ml.

[1] G. F. Burkhard, E. T. Hoke, M. D. McGehee, *Adv. Mater.* **2010**, 22, 3293.