Fully Inkjet-Printed, Ultrathin And Conformable Organic Photovoltaics As Power Source Based On Cross-Linked PEDOT:PSS Electrodes

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Ultra-lightweight solar cells have attracted enormous attention due to their ultra-conformability, flexibility, and compatibility with applications including electronic skin or miniaturized electronics for biological applications. With the latest advancements in printing technologies, printing ultrathin electronics is becoming now a reality.

This work offers an easy path to fabricate ITO-free ultra-lightweight organic solar cells through inkjet-printing while preserving high efficiencies. A method consisting of the modification of a poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) ink with a methoxysilane-based cross-linker (3-glycidyloxypropyl)trimethoxysilane (GOPS)) is presented to chemically modify the structure of the electrode layer. Combined with plasma and solvent post-treatments, this approach prevents shunts and ensures precise patterning of solar cells. By using poly(3-hexylthiophene) along rhodanine-benzothiadiazole-coupled indacenodithiophene (P3HT:O-IDTBR), the power conversion efficiency (PCE) of the fully printed solar cells is boosted up to 4.73% and fill factors approaching 65%. All inkjet-printed

ultrathin solar cells on a 1.7 μm thick biocompatible parylene substrate are fabricated with PCE reaching up to 3.6% and high power-per-weight values of 6.3 W g^{-1} . After encapsulation, the cells retain their performance after being exposed for 6 hours to aqueous environments such as water, seawater, or phosphate buffered saline, paving the way for their integration in more complex circuits for biological systems.

Organic functional materials present undeniable advantages over inorganic analogues such as their soft nature, reduced cost of manufacturing, and low-temperature processing, rendering them convenient for roll-to-roll processes such as blade coating, slot-die coating, or printing techniques.^[1,2] Organic materials are the choice for the fabrication of a new generation of ultralight organic photovoltaics (OPV) that could be used as power sources for low-energy-density applications such as micro-drones or other flying devices.^[3,4] OPV stand as a promising alternative for powering miniaturized devices for e-skin applications or in the biomedical arena for biosensors.^[5,6] Their potential was featured with the development of solar-powered ultra-flexible electronic devices, for instance, integrated with organic electrochemical transistors for the detection of electrophysiological signals such as cardiac monitoring or combined with an organic electronic ion pump for electrophoretic ion transport.^[5,6] Photosensitive materials have also been lately studied for optoelectronic neurostimulation in novel retinal implants and prosthesis.^[7–9]

So far, ultrathin OPV have been fabricated via spin-coating or thermal evaporation techniques which are restricted in terms of geometry, freedom of design and viability.^[3–5] Inkjet printing, in this respect, has many advantages compared to other deposition techniques such as high versatility, easy customization, low material usage and, associated low cost of manufacturing. Yet, several challenges remain to efficiently produce all-printed miniature devices for ultralightweight applications. For instance translating the solution-processing of a highly conducting material on ultrathin substrate such as parylene is required to replace the traditionally used ‘Indium Tin Oxide (ITO)’ as a bottom transparent electrode, as well as to limit the diffusion of the top electrode into the active layer through the hole transport layer interface which can result in poor device performance.

Substitute candidates that have been investigated in the past include carbon nanotubes, metal nanowires, graphene, or conducting polymers.^[10–13] So far, the only conducting polymer that has been successfully used as a transparent alternative in ultrathin OPVs is poly(3,4-

ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS).^[3,14] Yet, there have been intrinsic difficulties in interfacing PEDOT:PSS with other materials. Indeed, PEDOT:PSS films alone are unstable in ambient conditions due to their high hygroscopicity, thus creating shunts and defects upon swelling, especially when used as electrode in solar cells as evidenced in literature.^[15,16] Inherent problems associated with inkjet-printing all layers include the creation of pinholes or poor uniformity in the film formation due to the inks energy mismatches, as well as limitations in terms of the rheological properties of the functional inks and solvent compatibilities.^[17]

Very few studies in the literature have reported the fabrication of all the layers through inkjet printing for OPV.^[18,19] The record performance for fully inkjet-printed OPV on glass (4.1% Power Conversion Efficiency (PCE)), was achieved by utilizing a commercially available ink PV2000, a high-efficiency polymer blend.^[19] P3HT is the reference donor material of choice for the fabrication of low-cost solar cells due its availability in abundant quantities making it a viable candidate for the commercialization of OPV. In most studies, P3HT has been used in conjunction with soluble fullerene derivatives such as PCBM or ICBA.^[19,20] However, recent efforts have been dedicated to the study of new non-fullerene acceptor (NFA) materials that outperform the intrinsic properties of bucky-ball based materials and boost the performance of the bulk heterojunction organic solar cells.^[21,22] One of the promising candidates is rhodanine-benzothiadiazole-coupled indacenodithiophene (O-IDTBR), a NFA derivative first introduced by Holliday et al.^[23–26] Recently, we demonstrated that we could fabricate highly efficient fullerene-free OPV in custom designs via inkjet-printing the P3HT:O-IDTBR active layer blend with a PCE of up to 6.47%.^[27] This performance puts inkjet printing alongside other traditional technologies such as spin coating and blade coating.

In this work, we report fully inkjet-printed ultrathin and conformable OPV that can potentially be used as a power source for biological applications. We achieve shunt free devices with efficiencies of up to 3.6% on a 1.7 μm thick parylene substrate and 4.73% PCE on glass. The combination of the cross-linked PEDOT:PSS electrode with O_2 plasma treatment and a solvent post-treatment enables the creation of fully printed organic electronics that can be used for the manufacturing of fully inkjet-printed, metal-free OPV. We measured the performance of the devices after exposing them up to 6 hours to various aqueous media to assess their utilization in moist environments. The cells exhibited a limited loss of performance inferior to 18% (of PCE) in deionized water, 27% in phosphate buffered saline (PBS) solution, and 22% in seawater. This is the first time that ultrathin non-fullerene

solar cells are integrally printed and evaluated in aqueous media, making them adaptable for manufacturing in large quantities.

A schematic of all the layers of the inkjet-printed OPV on a conformable parylene substrate is presented in **Figure 1a**. The cathode electrode is composed of a highly conductive PEDOT:PSS layer (PEDOT_A), a Zinc Oxide (ZnO) layer deposited on top is used for electron transport layer (ETL) while a bulk heterojunction (BHJ) composed of P3HT:O-IDTBR is used as the photo-active layer. For charge extraction, a different formulated ink of PEDOT:PSS (PEDOT_B) is deposited on top of the active layer to ensure surface energy compatibility. Owing to the high conductivity of the ink ($295 \pm 10 \text{ S cm}^{-1}$), PEDOT_B is used as both the transport layer and the anode without the support of a metallic electrode for the current collection. Printed silver side-contact pads were added to prevent damage to the polymer layer and ensure good contact with external electronics used for support and measurements. An ultra-thin and ultra-lightweight fully organic and inkjet-printed OPV draping on a soap bubble is shown in **Figure 1b**. The total weight of one solar cell (0.1 cm^2) is 0.057 mg. As presented in the supplementary video, the ultra-lightweight solar cell can adhere to the surface of a bubble demonstrating its potential implementation in airborne applications. The typical current density-voltage characteristic under light and dark conditions for ultrathin fully printed solar cells on parylene is represented **Figure 1c**. These solar cells exhibited short circuit current densities (J_{sc}) around $8.5\text{-}9.6 \text{ mA cm}^{-2}$, an open-circuit voltage (V_{oc}) of $0.71\text{-}0.74\text{V}$, fill factors around $50\text{-}53\%$, and a PCE around 3.0% , the champion device PCE being 3.6% . The printed solar cells exhibited a power-per-weight of 6.3 W g^{-1} , comparable to previously reported values in literature of state-of-the-art ultrathin devices fabricated through other fabrication processes such as vapor deposition and spin-coating.^[3] A comparison of the power-per-weight values of different technologies alongside our ultrathin printed solar cell is given in **Figure 1d**.

Before transitioning to a conductive polymer bottom electrode, we optimized the inkjet process conditions on ITO-coated glass layer by layer (**Figure 2a**). Adjusting the rheological properties of the ink such as viscosity, surface tension, the surface energy components and volatility of the solvents used plays a vital role in proper jetting and uniform drying of the deposited wet films.^[28] The optimized printing parameters for each layer (ZnO, AL, PEDOT_B and Silver contact pads) are described in **Table S1**. The cells characteristics are summarized in Table 1. The maximum PCE value measured for solar cells in which all layers were printed onto ITO coated glass was 5.76% . The photo-active area is semitransparent, as well as the

bottom and top electrodes, and the light could be collected from both sides of the device. We compared the performance of these ITO-based semi-transparent devices under illumination from the cathode and the anode sides (**Figure 2b**) and observed a slight decrease in PCE (from 5.14% to 5.06%). Indeed, when illuminated from the ITO side the device PCE is slightly higher than to the one where the light was shone from the PEDOT:PSS top electrode instead. This decrease in performance was mainly attributed to the reduction in the J_{SC} from 12.81 mA cm^{-2} to 11.05 mA cm^{-2} resulting from the absorbance of PEDOT:PSS in the visible light region, as shown in **Figure S1**.

To move away from glass and use the ultrathin parylene as a substrate, we replaced ITO as the bottom electrode. We selected a highly conductive PEDOT:PSS ink (464 S cm^{-1}) (PEDOT_A) matching the rheological requirements for printability as well as the work function required to be used as a cathode (approx. -4.8 to -5 eV) and similar to that of ITO (-4.7 eV). One advantage is that the ITO-free printed electrodes do not suffer from the loss that is caused by the waveguiding effect of the glass/ITO interface. The printed PEDOT:PSS film was found to be highly hydrophilic with a surface energy around 55.5 mN m^{-1} (Table 2), allowing the deposition of a uniform layer of ZnO on top of it, however, most of the devices were shunted. To overcome this challenge, we introduced a cross-linking agent into the PEDOT:PSS solution, namely GOPS. The amount of cross-linker was carefully chosen to ensure a dense network while keeping a high conductivity (360 S cm^{-1}) as well as to avoid delamination when exposed to other solvents^[29]. The side effect of the modification of the ink formulation was an increased polar component of the printed film with a total surface energy of 62 mN m^{-1} . The ZnO ink surface energy was, on the other hand, measured to be around 30.5 mN m^{-1} . This surface energy mismatch can prove difficult when depositing already developed inks on top, as the difference in the components of their surface tension can cause issues with wetting and film formation.^[30] The difference between the surface energy of PEDOT:PSS and the surface tension of the ZnO ink caused under-wetting upon deposition, for which a uniform layer could not be formed as is (**Figure S2**). We explored the utilization of an oxygen plasma surface treatment combined with a solvent post-treatment (methanol) to optimize the wetting of the ZnO ink on the surface of the PEDOT:PSS electrode layer (**Figure 2c**). It is demonstrated in literature that short exposure to oxygen plasma positively impacts the wettability of PEDOT:PSS; however exposure times longer than 5 minutes may affect the surface roughness.^[31]

We compared the sheet resistance of PEDOT:PSS layers (cathode) exposed to plasma treatment of different durations and demonstrated that up to 5 minutes of plasma treatment has almost no effect on its sheet resistance (**Figure S3a**). By fixing the plasma exposure at 1 minute combined with a methanol post-treatment, the polar component of the surface energy decreased from 28 mN m^{-1} to 22 mN m^{-1} (**Figure 2c, d**), turning the surface more hydrophilic and improving the wettability of the ZnO ink while keeping the surface roughness at 15.2 nm (**Figure S4**). Interestingly combining plasma and solvent post-treatments with the cross-linking of the electrode enabled to prevent the shunts present in the fabricated ITO-free solar cells. (**Figure S5**). Although, some studies addressing solution-processed devices attribute shunts to the roughness of the resulting layers, the electrodes, as well as the formation of defects or pinholes in the active layer.^[1,32] **Figure S6** displays the resulting films after these each layer is deposited. The morphologies of the different layers printed on parylene are represented in **Figure S7** while the RMS of the different layers ($<15 \text{ nm}$) are consistent with the presence of shunts in a few of the devices. We attributed the formation of the pinholes to the contrast of surface energies between the ZnO layer and the PEDOT layer underneath, i.e. the active layer ink wets ZnO but does not wet PEDOT:PSS, and if the ZnO layer is not uniform, then the active layer will not be uniform either. Another issue to be addressed in PEDOT:PSS optoelectronic devices is the relationship between the thickness of the PEDOT:PSS electrodes, their sheet resistance, and their light transmittance. While a lower sheet resistance is critical for the collection of charges and can be obtained by increasing the thickness of the PEDOT:PSS layers, it is countered by the decrease in transmittance leading to a reduced generation of charges in the active layer. Thus, a trade-off exists for optimizing both transmittance and electrical conductivity of the semi-transparent electrode (**Figure S8a & b**). We investigated the relationship of the thickness of PEDOT:PSS on the performance of the solar cells and correlated to the findings with the transmittance of the films (**Figure 3a & S8c**). The best PCE on parylene substrates, 3.6 %, is achieved when printing 2 layers of PEDOT:PSS (cathode) with a resulting thickness of $1 \text{ }\mu\text{m}$. At $27 \text{ }\Omega/\text{square}$, the sheet resistance of the bottom electrode is comparable to that of ITO at $10 \text{ }\Omega/\text{square}$, and the use of an assisting silver grid is not mandatory. Despite the improvement in conductivity, printing 2 layers reduces the transmittance in the 300-700 nm spectra to a range between 50-70 %, and the resulting J_{SC} is reduced to 7.5 mA cm^{-2} when illuminated from cathode side (bottom). Interestingly, when the light is absorbed on the anode side, i.e. the top side, the cells exhibit higher PCE values. The higher transmittance of the top PEDOT:PSS layer at 70-80 % correlates with the lower thickness of 330nm and improves the generation of charges in the

active layer, which is reflected with a J_{SC} value of 10 mA cm^{-2} . The total thickness of the ultrathin printed solar cell including the parylene substrate is $3.6 \text{ }\mu\text{m}$, translating to a power-per-weight of 6.3 W g^{-1} . We compared the J_{SC} of the best-performing devices on glass and parylene substrates under the same illumination (1 sun) from both bottom side and top side (**Figure 3b**). As expected, we observed the same trend on both types of substrates: higher efficiency when illumination comes from the anode side. The highest PCE measured for all printed layers on a glass substrate is 4.73 %. The series resistance of the fully printed solar cells is higher in comparison to ITO-based devices ($9.4 \text{ }\Omega$ vs $4.3 \text{ }\Omega$), affecting the current collection at the bottom electrode and translating into a slightly lower PCE.

Many studies have demonstrated the use of parylene as a substrate and an insulation layer for skin-attached electronics or implantable devices because of its conformability, transparency biocompatibility, and low permeability to moisture and gases.^[5,33,34] Thus, we tested the encapsulation of the solar cells with a $1.7 \text{ }\mu\text{m}$ protective transparent layer of parylene to improve its stability and assess its utilization in aqueous environments. To assess the stability of the printed encapsulated in harsh environments, three biological liquids, i.e., deionized water, phosphate buffer saline (PBS) (pH 7.2, mimicking the ionic content of bodily fluids), and seawater, were selected as an array of biological fluids naturally present in different milieu. As evidenced in **Figure 3c**, the encapsulation process through parylene deposition does not cause any deterioration in the performance of the solar cell devices. First, we deposited a drop of deionized water on the active area of the solar cells to test their resistance to prolonged exposure to water. We tested the direct exposure of the devices to water for different periods and observed that short durations (up to 60 minutes) do not cause any deterioration. However, we did observe a small degradation of the efficiency of the cells after prolonged exposure to water (**Figure 3d**). Even after a 6-hour direct exposure to water, the cells preserved up to 84% of their initial performance while in air their performance was maintained around 96%, in accordance with the stability values reported by Holliday et al.^[35] for P3HT:O-IDTBR in air, and after 12 hours, this value was held at 70%. We repeated the same experiment using PBS as well as seawater. Likewise, short term exposures did not cause a significant drop in performance. However, we did observe that the solar cells similarly degraded after exposure to saline solution and seawater for 6 hours, conserving 73 % and 78 % of their original performance, respectively (**Figure S9**).

We introduced an easy, low cost, and scalable method to fabricate biocompatible, ultrathin and ultra-lightweight, all organic ITO-free solar cells with efficiencies

reaching up to 3.6 %. We fabricated ITO-free semi-transparent OPV devices through inkjet printing of highly conductive PEDOT:PSS without the need for a metal grid underneath and a reflective top electrode. We introduced a method enabling the cross-linking of the organic electrode preventing shunts as well as pinholes and we showed that the subsequent post-treatments enabled the control of the wettability of further layers on top of the PEDOT:PSS film, ensuring a precise patterning of the solar cells. The method implemented in this work for the bottom electrode can be further translated to other inks to limit the penetration of hole transport or electron transport layer inks into other photosensitive materials. The engineering of all-layers validates the successful deposition of all inkjet-printed OPV on glass with a PCE of 4.73%, demonstrating its potential as energy harvesting devices for a variety of applications. The encapsulation of ultrathin solar cells leads to compatibility with different aqueous environments with a minimal loss of performance for biological applications. Future studies will fully explore the stability, degradation processes and performance of these devices in real biological environments such as saliva or sweat. With the advantages of the inkjet-printing process, this work brings organic photovoltaics one-step closer to their integration in elaborate systems, such as stand-alone sustainable cutaneous or implanted biomedical devices.

Experimental section

Ink formulation: For the bottom electrode ink, we prepared a solution of PEDOT:PSS (Heraeus, CLEVIOS™ FHC) with 1 wt% glycidoxypolytrimethoxysilane (GOPS, Sigma Aldrich). We prepared ZnO ink by mixing 80mg of zinc acetate dehydrate in 21 μL of ethanolamine and 1 mL of 2-methoxyethanol solution. For the HTL and top electrode ink, we utilized a solution of PEDOT:PSS (Orgacon S315). Both PEDOT:PSS inks were sonicated 30 min in a ultrasonic bath and filtered through a 1.2 μm PTFE filter before cartridge preparation. The P3HT:O-IDTBR ink was prepared following the procedure described in our previous paper^[27]. To summarize, P3HT ($W = 40\text{k}/51\text{k}$ Pd = 2.1 Rieke Metals) and O-IDTBR (1-material) were dissolved in a dichlorobenzene solution (25 mg mL^{-1}). All solvents were purchased from Sigma-Aldrich and used as received. A silver nanoparticle ink ANP DGP HR was purchased from Anapro and used with no further modification for the fabrication of the metal contact pads. The surface tension experiments were carried using a pending drop technique on a drop shape analyzer (Kruss DSA100) at room temperature.

Solar cell fabrication: The ITO-coated glass substrates were cleaned through sonication for 10 minutes in deionized water, acetone, and IPA. Then a 10 min O₂ plasma treatment was applied to further clean and improve the wettability of the substrates. For the reference samples, ZnO solution was spin-coated at 4000RPM for 30s, Inkjet printing of the active layer was performed as previously described and 10 nm of MoO₃ and 100 nm of Ag were deposited using thermal evaporation as the hole transport layer and top electrode respectively. A shadow mask was employed to define the area of the top electrode and the contact pad.

A Dimatix DMP-2800 inkjet printer was used for the optimization of each layer by itself, and the fabrication of fully inkjet-printed functional devices. The process parameters for each ink including Drop Spacing, Bed temperature, Drying temperature and duration are outlined in Table S1 of the supplementary information. One min of O₂ plasma treatment was applied on the printed PEDOT:PSS cathode using a Henniker plasma HPT-100 to improve wettability. After printing each layer, the samples were cured on a conventional hot plate. All the annealing steps were performed under ambient conditions except for the active layer, which was cured inside a glove box under nitrogen conditions. A Parylene C film was vaporized using a SCS Labcoater 2 and slowly deposited at room temperature on substrates using 3-(trimethoxysilyl)propyl methacrylate as an adhesion promoter to a final thickness of 1.7 μm .

Solar cell characterization: The current density-voltage (J–V) characteristics were obtained using a Keithley 2400 source meter under illumination of a 21 LED light engine at simulated AM 1.5 solar illumination (Wavelabs Sinus-70). The power per weight ratio is defined as the ratio between the device output power per unit area under 100mW cm⁻² (AM 1.5G) and the device weight per unit area. The weight of the device was measured using a Lab Analytical Balance Scale Precise Electronic Digital Scale Laboratory Weighing Balance. The power-per-weight was deduced from the ratio between the max device output power (per unit area) under 1 sun (AM 1.5G 100 mW cm⁻²) and the device weight per unit area. The solar cells weighted approximately 5.7g m⁻². The power output generated would be approximatively 35.9 W m⁻² for a specific weight of 6.3 W g⁻¹. The optimization of the process was realized for device area comprised between 0.033 cm² and 0.1 cm². The JV characterization of the ultrathin solar cells reported in this paper was performed with the parylene substrate still attached to a glass slide for ease of handling and to avoid damage while measuring. The transmittance spectra was obtained using a Perkin Elmer UV/VIS/NIR spectrometer. The sheet resistance of the films was determined with a Jandel 4-Point probe head unit (CMT-SR2000N) from Advanced

Instrument Technology on 1cm² printed squares and the thickness with a Tencor mechanical profilometer. AFM images were captured using the solver-next SPM by NT-MDT equipped with an OTESPA cantilever by Bruker.

Supporting Information

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

Conflict of interest: A patent application about the solar cell fabrication and function was filed by KAUST with E.B. and D.C and D.B as the inventors where D.B. E.B. and D.C. contributed to the conception of the work.

The remaining authors declare no competing interests.

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References

- [1] F. C. Krebs, *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 394.
- [2] S.-H. Bae, H. Zhao, Y.-T. Hsieh, L. Zuo, N. De Marco, Y. S. Rim, G. Li, Y. Yang, *Chem* **2016**, *1*, 197.
- [3] M. Kaltenbrunner, M. S. White, E. D. Głowacki, T. Sekitani, T. Someya, N. S. Sariciftci, S. Bauer, *Nat. Commun.* **2012**, *3*, 770.
- [4] J. Jean, A. Wang, V. Bulović, *Org. Electron.* **2016**, *31*, 120.
- [5] S. Park, S. W. Heo, W. Lee, D. Inoue, Z. Jiang, K. Yu, H. Jinno, D. Hashizume, M. Sekino, T. Yokota, *Nature* **2018**, *561*, 516.
- [6] M. Jakešová, T. A. Sjöström, V. Đerek, D. Poxson, M. Berggren, E. D. Głowacki, D. T. Simon, *Npj Flex. Electron.* **2019**, *3*, 1.

- [7] D. Rand, M. Jakešová, G. Lubin, I. Vébraité, M. David-Pur, V. Đerek, T. Cramer, N. S. Sariciftci, Y. Hanein, E. D. Głowacki, *Adv. Mater.* **2018**, *30*, 1707292.
- [8] M. Jakešová, M. S. Ejneby, V. Đerek, T. Schmidt, M. Gryszel, J. Brask, R. Schindl, D. T. Simon, M. Berggren, F. Elinder, E. D. Głowacki, *Sci. Adv.* **2019**, *5*, eaav5265.
- [9] K. Mathieson, J. Loudin, G. Goetz, P. Huie, L. Wang, T. I. Kamins, L. Galambos, R. Smith, J. S. Harris, A. Sher, D. Palanker, *Nat. Photonics* **2012**, *6*, 391.
- [10] A. D. Pasquier, H. E. Unalan, A. Kanwal, S. Miller, M. Chhowalla, *Appl. Phys. Lett.* **2005**, *87*, 203511.
- [11] M. W. Rowell, M. A. Topinka, M. D. McGehee, H.-J. Prall, G. Dennler, N. S. Sariciftci, L. Hu, G. Gruner, *Appl. Phys. Lett.* **2006**, *88*, 233506.
- [12] Y. Galagan, J.-E. J.M. Rubingh, R. Andriessen, C.-C. Fan, P. W.M. Blom, S. C. Veenstra, J. M. Kroon, *Sol. Energy Mater. Sol. Cells* **2011**, *95*, 1339.
- [13] Y. Altin, M. Tas, İ. Borazan, A. Demir, A. Bedeloglu, *Surf. Coat. Technol.* **2016**, *302*, 75.
- [14] M. Kaltenbrunner, G. Adam, E. D. Głowacki, M. Drack, R. Schwödiauer, L. Leonat, D. H. Apaydin, H. Groiss, M. C. Scharber, M. S. White, N. S. Sariciftci, S. Bauer, *Nat. Mater.* **2015**, *14*, 1032.
- [15] Y. H. Kim, C. Sachse, M. L. Machala, C. May, L. Müller-Meskamp, K. Leo, *Adv. Funct. Mater.* **2011**, *21*, 1076.
- [16] S. R. Ha, S. Park, J. T. Oh, D. H. Kim, S. Cho, S. Y. Bae, D.-W. Kang, J.-M. Kim, H. Choi, *Nanoscale* **2018**, *10*, 13187.
- [17] S. Sumaiya, A. El-Shahat, K. Kardel, **2017**.
- [18] S. Jung, A. Sou, K. Banger, D. Ko, P. C. Chow, C. R. McNeill, H. Sirringhaus, *Adv. Energy Mater.* **2014**, *4*, 1400432.
- [19] T. Eggenhuisen, Y. Galagan, A. Biezemans, T. Slaats, W. Voorthuijzen, S. Kommeren, S. Shanmugam, J. Teunissen, A. Hadipour, W. Verhees, *J. Mater. Chem. A* **2015**, *3*, 7255.
- [20] S. Ganesan, S. R. Gollu, J. Alam khan, A. Kushwaha, D. Gupta, *Opt. Mater.* **2019**, *94*, 430.
- [21] X. Guo, C. Cui, M. Zhang, L. Huo, Y. Huang, J. Hou, Y. Li, *Energy Environ. Sci.* **2012**, *5*, 7943.
- [22] S. Holliday, R. S. Ashraf, C. B. Nielsen, M. Kirkus, J. A. Röhr, C.-H. Tan, E. Collado-Fregoso, A.-C. Knall, J. R. Durrant, J. Nelson, *J. Am. Chem. Soc.* **2015**, *137*, 898.
- [23] S. Holliday, R. S. Ashraf, A. Wadsworth, D. Baran, S. A. Yousaf, C. B. Nielsen, C.-H. Tan, S. D. Dimitrov, Z. Shang, N. Gasparini, *Nat. Commun.* **2016**, *7*, 11585.
- [24] D. Baran, R. S. Ashraf, D. A. Hanifi, M. Abdelsamie, N. Gasparini, J. A. Röhr, S. Holliday, A. Wadsworth, S. Lockett, M. Neophytou, C. J. M. Emmott, J. Nelson, C. J. Brabec, A. Amassian, A. Salleo, T. Kirchartz, J. R. Durrant, I. McCulloch, *Nat. Mater.* **2017**, *16*, 363.
- [25] N. Gasparini, M. Salvador, T. Heumueller, M. Richter, A. Classen, S. Shrestha, G. J. Matt, S. Holliday, S. Strohm, H.-J. Egelhaaf, A. Wadsworth, D. Baran, I. McCulloch, C. J. Brabec, *Adv. Energy Mater.* **2017**, *7*, 1701561.
- [26] S. Strohm, F. Machui, S. Langner, P. Kubis, N. Gasparini, M. Salvador, I. McCulloch, H.-J. Egelhaaf, C. J. Brabec, *Energy Environ. Sci.* **2018**, *11*, 2225.
- [27] D. Corzo, K. Almasabi, E. Bihar, S. Macphree, D. Rosas-Villalva, N. Gasparini, S. Inal, D. Baran, *Adv. Mater. Technol.* **2019**, 1900040.
- [28] B. Derby, N. Reis, *MRS Bull.* **2003**, *28*, 815.
- [29] M. ElMahmoudy, S. Inal, A. Charrier, I. Uguz, G. G. Malliaras, S. Sanaur, *Macromol. Mater. Eng.* **2017**, *302*, 1600497.
- [30] M. M. Voigt, R. C. I. Mackenzie, C. P. Yau, P. Atienzar, J. Dane, P. E. Keivanidis, D. D. C. Bradley, J. Nelson, *Sol. Energy Mater. Sol. Cells* **2011**, *95*, 731.

- [31] Y. Zhou, Y. Yuan, L. Cao, J. Zhang, H. Pang, J. Lian, X. Zhou, *J. Lumin.* **2007**, 122–123, 602.
- [32] Y.-B. Cheng, A. Pascoe, F. Huang, Y. Peng, *Nature* **2016**, 539, 488.
- [33] D. Khodagholy, T. Doublet, P. Quilichini, M. Gurfinkel, P. Leleux, A. Ghestem, E. Ismailova, T. Hervé, S. Sanaur, C. Bernard, G. G. Malliaras, *Nat. Commun.* **2013**, 4, 1575.
- [34] A. Jonsson, S. Inal, I. Uguz, A. J. Williamson, L. Kergoat, J. Rivnay, D. Khodagholy, M. Berggren, C. Bernard, G. G. Malliaras, D. T. Simon, *Proc. Natl. Acad. Sci.* **2016**, 113, 9440.
- [35] S. Holliday, R. S. Ashraf, A. Wadsworth, D. Baran, S. A. Yousaf, C. B. Nielsen, C.-H. Tan, S. D. Dimitrov, Z. Shang, N. Gasparini, *Nat. Commun.* **2016**, 7, 11585.

Figure 1. (a) Schematic of layer-by-layer composition of the solar cells. (b) Photograph of the formation of ultralight inkjet-printed organic solar cells embedded in a soap bubble. (c) Current density-voltage curves of a fully inkjet-printed OPV on parylene under 1 sun illumination and dark condition. (d) Comparison of the power-per-weight values of different cell compositions and the printed OPV. The values have been obtained for comparison from reference^[3]

Figure 2. (a) Current density-voltage curves of solar cells comprising of 1 layer (Active layer e.g. P3HT:O-IDTBR), 2 layers (+ZnO), 3 layers (+PEDOT:PSS), 4 layers (+Ag), printed successively on ITO glass substrates. (b) Current density-voltage curves of optimized inkjet-printed solar glass on ITO substrate. (The light is coming respectively from the Bottom side (ITO) and the Top side (PEDOT_B)). The inset is a photograph of the semi-transparent solar cell printed on ITO coated substrate. (c) Polar component of surface tension (clear blue) vs the dispersive component (dark blue) before and after the application of 1min long plasma treatment on the PEDOT_A electrode, with and without GOPS, with and without MeOH treatment and d) wetting envelope before and after cross-linking the electrode (PEDOT_A) and after applying 1min of plasma treatment, and after MeOH treatment on the electrode.

Figure 3. (a) Comparison of transmittance of 1 layer of PEDOT_A, PEDOT_B, and ITO on glass substrate. (b) Current density-voltage curves of optimized inkjet-printed solar cells (2 layers of PEDOT_A) on parylene substrate and glass substrate. The light is coming respectively from the Bottom side (PEDOT_A) and the Top side (PEDOT_B). (c) Current density-voltage curves of fully inkjet-printed ultrathin solar cells before (yellow curve) and after encapsulation (red curve) with a second layer of parylene (1.7 μm) and (blue curve) after the encapsulated solar cells were exposed to an aqueous environment for 10 min. (d) Ratio $\frac{PCE}{PCE_0}$ as a function of the total exposition duration in aqueous environment (up to 12h) and in air for 6h. (PCE_0 is the initial power to conversion energy measured after encapsulation). The inset is a photograph of drops of water on top of the active area of the ultrathin solar cells.

Table 1.

Layers Printed	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF [%]	PCE [%]
Active layer (AL)	13.82	0.71	67.2	6.47
ZnO + AL	13.52	0.71	61.0	6.02
ZnO + AL + PEDOT _B	12.81	0.72	55.8	5.14
ZnO + AL + PEDOT _B + Ag	13.48	0.72	58.4	5.76
All printed on glass	10.39	0.71	64.4	4.73
All printed on parylene	9.65	0.74	50.8	3.61

Table 2.

Surface	R^2	Surface Energy (mN.m^{-1})		
		Dispersive	Polar	Total
No GOPS - No Plasma	0.89	27.51	28.01	55.51
No GOPS - Plasma	0.89	33.59	30.80	64.39
GOPS - No Plasma	0.89	28.03	34.34	62.37
GOPS - Plasma	0.90	31.56	32.17	63.72
No GOPS - No Plasma - Methanol	0.87	31.63	31.05	62.68
No GOPS - Plasma - Methanol	0.94	29.65	27.30	56.94
GOPS - No Plasma - Methanol	0.86	34.53	29.59	64.11
GOPS - Plasma - Methanol	0.88	32.39	22.64	55.03

The table of contents

Ultrathin and ultra-lightweight ITO-free organic solar cells are fabricated using inkjet-printing technology, with efficiencies reaching up to 3.6% and high power-per-weight values of 6.3W.g^{-1} . When encapsulated, the ultra-conformable solar cells are waterproof and continue generating power without a significant performance loss up to 12 hours of continuous exposure to various biological media.

Keyword: Inkjet-printing ultrathin solar cells

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Fully Inkjet-Printed, Ultrathin And Conformable Organic Photovoltaics As Power Source Based On Cross-Linked PEDOT:PSS Electrodes

Supporting Information

Fully Inkjet-Printed, Ultrathin And Conformable Organic Photovoltaics As Power Source Based On Cross-Linked PEDOT:PSS Electrodes

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Figure S1. (a) Absorbance (uncorrected for reflection) of ITO electrode and PEDOT_B electrodes on glass substrates (b) Sheet resistance of the printed film of PEDOT_A (1 cm^2) prepared with 0, 0.7% and 1.4% of GOPS

Figure S2. Photograph of printed ZnO electron transport layer on PEDOT_A before and after plasma treatment

Figure S3. Ratio of the sheet resistance of the printed electrode (PEDOT_A) before and after the application 1, 2 and 5 min of O_2 plasma ($n=3$)

Figure S4. AFM images of (a) PEDOT:PSS (PEDOT_A), (b), PEDOT_A +0.7% of GOPS, (c) PEDOT_A +1.4% of GOPS, and (e) PEDOT_A +0.7% of GOPS+ MeOH and O_2 plasma treatment on glass substrate

Figure S5. (a,b) Current-voltage curve statistic for solar cells comprising PEDOT layers prepared without and with GOPS (combined with Plasma/solvent post-treatments) (J_{sc} and V_{oc} are compared from 6 pixels)

Figure S6. Photographs of the layers printed successively on glass substrate, left to right: 1) PEDOT_A, 2) + ZnO, 3) + P3HT:O-IDTBR, 4) + PEDOT_B, 5) + Ag

Figure S7. AFM images of (a) the substrate, parylene, (b), the bottom electrode, the printed PEDOT:PSS layer (PEDOT_A), (c) ZnO (d) the active layer P3HT:O-IDTBR, and (e) the top electrode PEDOT:PSS (PEDOT_B)

Figure S8. (a) Variation of the thickness and sheet resistance of the printed cathode (PEDOT_A) within 1-3 layers printed ($n=3$), (b) Transmittance of the PEDOT:PSS electrodes :1-3 layers of PEDOT_A and 1 layer of PEDOT_B, and 2 layers of PEDOT_A +ZnO) (c) Current density-voltage curves of fully inkjet-printed solar cells on 1.7 μm parylene substrate with 1 layer (red), 2 layers (blue), and 3 layers (yellow) of PEDOT:PSS (PEDOT_A) (without ITO electrode) illuminated from the Top (straight line) and Bottom (dash line) sides

Figure S9. Variation of the Ratio $\frac{PCE}{PCE_0}$ of solar cells exposed to different liquids: deionized water, seawater and PBS for 10 min, 1h and 6h and in air for 6 hours. ($n=3$)

Table S1. Optimization of the printing parameters

Inks	Bed Temperature (°C)	Drop (um)	SpacingDrying temperature (°C)	Drying time (min)
PEDOT _A	50	15	140	10
ZnO	T _{room}	30-70	150	15
AL	50	10	140	10
PEDOT _B	T _{room}	15	140	5
Ag	40	20	140	10

In accordance with our previous study, solar cell devices with an inkjet-printed P3HT:O-IDTBR active layer, spin-coated ZnO ETL, and evaporated MoO₃ hole transport layer (HTL) and silver electrode exhibited a maximum efficiency of 6.47% with a high fill factor of 67.2% (**Table 1**).^[27] In order to start replacing the fabrication method of the supporting layers, we started by printing layers of around 24nm from ZnO ink. With this change, the PCE was slightly reduced to 6.02%, with a decrease in the fill factor to 61.1 %, mainly due to a drop in the shunt resistance (R_{shunt}) from 1580 to 983 Ω . Switching the evaporated MoO₃ layer to a solution based PEDOT:PSS ink (3 layers printed: ZnO, P3HT:O-IDTBR, PEDOT:PSS) further reduced the PCE to an average of 5.14%. The drop in efficiency is mainly attributed to the loss in charge collection when only a PEDOT:PSS film is used as both the hole transporting layer and the anode. This assumption is confirmed by the decrease in J_{SC} from 13.92 mA.cm⁻² to 12.68 mA.cm⁻² while R_{shunt} drops from 983 Ω to 837 Ω and the series resistance increases slightly from 4.17 to 6.08 Ω . Printing an additional reflective silver coating on top of the PEDOT:PSS hole transport layer increases the value of the R_{shunt} to 965 Ω further improving the collection of charges and increasing the J_{SC} to 13.45 mA.cm⁻², similar to the values measured with evaporated silver.