SUPPLEMENTAL INFORMATION

Stable large area drop-on-demand deposition of a conductive polymer ink for 3D-printed electronics, enabled by bio-renewable co-solvents

Geoffrey Rivers[1], Jonathan S. Austin[1], Yinfeng He[1], Adam Thompson[2], Negar Gilani[1], Nathan Roberts[2], Peng Zhao[1], Christopher J. Tuck[1], Richard J.M. Hague[1], Ricky D. Wildman[1] and Lyudmila Turyanska[1]**

[1]Centre for Additive Manufacturing, Faculty of Engineering, University of Nottingham, Nottingham, NG8 1BB, UK

[2] Manufacturing Metrology Team, Faculty of Engineering, University of Nottingham, Nottingham, NG8 1BB, UK

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*Corresponding Authors: Lyudmila.Turyanska@nottingham.ac.uk and Geoffrey.Rivers@nottingham.ac.uk

SI1 Preliminary ink formulation development

Prior to the use of Ink_{DMSO} or Ink_{CG}, a variety of PEDOT:PSS ink formulations were investigated for jettability indicators (*Oh*), storage stability, inkjet reliability, and electrical conductivity. These preliminary inks utilised the following materials in addition to those in the main text: commercial PEDOT:PSS ink (0.8 wt% in H_2O PEDOT:PSS, 739316, Sigma Aldrich), pH neutral PEDOT:PSS (1.1% in H2O, neutral pH, high-conductivity grade, 739324, Sigma Aldrich), concentrated PEDOT:PSS (3.0-4.0% in H2O, high-conductivity grade, 655201, Sigma Aldrich), ethanol, butanol, pentanol, 2-propanol, ethylene glycol, glycerol, sodium dodecylbenzene sulfonate (SDBS), dimethylformamide (DMF), tannic acid, acetic acid, 1-Ethyl-3-methylimidazolium ethyl sulfate (EMIM ESO_4), polysorbate 20, diethylphthalate (DEP). These additives were selected based on literature sources that noted their beneficial improvement of the conductivity of PEDOT:PSS.

Formulations were prepared by diluting the PEDOT:PSS stock to inkjet-compatible viscosities with a combination of deionized water and the additives, with a maximum additive content of 5 wt% of the total mixture. In the formulations investigated, the typical trends of conductivity improvement were observed, accompanied by a decrease in ink stability either in storage, or in the jetting process, leading to poor control of the printed patterns, or clogging of the nozzle leading to loss of jetting.

Of those investigated, Ink_{DMSO} was the formulation that best balance of stability and conductivity, and thus was used as control in the study of Ink_{CG}. However, the stability was limited, and after either 5 hours at room temperature or 12 hours at 4°C would no longer be jettable, even after restirring. This was true when prepared with or without GOPS.

SI2 Development of Ink_{CG}

While developing Ink_{CG}, seven inks based on cyrene and glycerol carbonate were produced with different concentrations of the components (Table S1). All formulations were printable with $1 < Z < 10$. The first, Ink_{CG}-4.9, was produced with 4.9 wt% of both cyrene and GC and had stable jetting, however, the pores and incomplete lines are observed (Figure S1a and b). The formation of pores is likely due to high surface tension or the gelation of the PEDOT:PSS in the presence of high concentrations of additives. To counteract these effects, the formulation was diluted with water, reducing cyrene and GC each to 4.3 wt%, and the amount of surfactant was increased to form Ink_{CG}-4.3. The quality of printed lines was slightly improved, though small pores were still observed at the edges (Figure S1c). It was found that during drying at 45°C, drop cast mixtures containing only PEDOT:PSS dispersion and 5 wt% GC underwent gelation and contraction (Figure S2a), while those composed of PEDOT:PSS with 5 wt% cyrene did not (Figure S2b). Thus, additional inks were formulated based on Ink_{CG}-4.3, in a range of GC concentrations between 4.3 and 0 wt%. The dried drop cast specimens of all inks with GC concentration higher than Ink_{CG}-0.85 (Figure S2c-h) had morphology similar to that of Ink_{CG}-4.9 and Ink_{CG}-4.3. The Ink_{CG}-0.85 (from now Ink_{CG}) had good jetting and print quality, hence was used for further studies. It was also found that with decreasing GC concentration the sheet resistance was increased (Figure S3).

Table S1. Compositions of PEDOT:PSS inks developed during optimization of ink formulation.

	PEDOT:PSS stock mixture	Water	Cyrene	GC	Tween80	GOPS	Printability	1 < Z < 10	Notes
	wt%	wt%	wt%	wt%	wt%	wt%			
Ink_{CG}-4.9	44	45	4.9	4.9	0.7	0.5	✓		Clogged nozzles, pores
Ink_{CG}-4.3	38.43	51.7	4.3	4.31	0.81	0.42	✓		Pores, jetting instability
Ink_{CG}-3.5	38.4	55.2	4.3	3.5	0.8	0.45	✓		coffee stain
Ink_{CG}-2.6	38.4	55.2	4.3	2.6	0.8	0.45	✓		coffee stain
Ink_{CG}-1.7	38.4	55.2	4.3	1.7	0.8	0.45	✓		coffee stain
Ink_{CG}-0.85 (Ink_{CG})	38.4	55.2	4.3	0.85	0.8	0.45	✓		Stable, good print quality
Ink_{CG}-0	38.4	55.2	4.3	0	0.8	0.45	✓		---

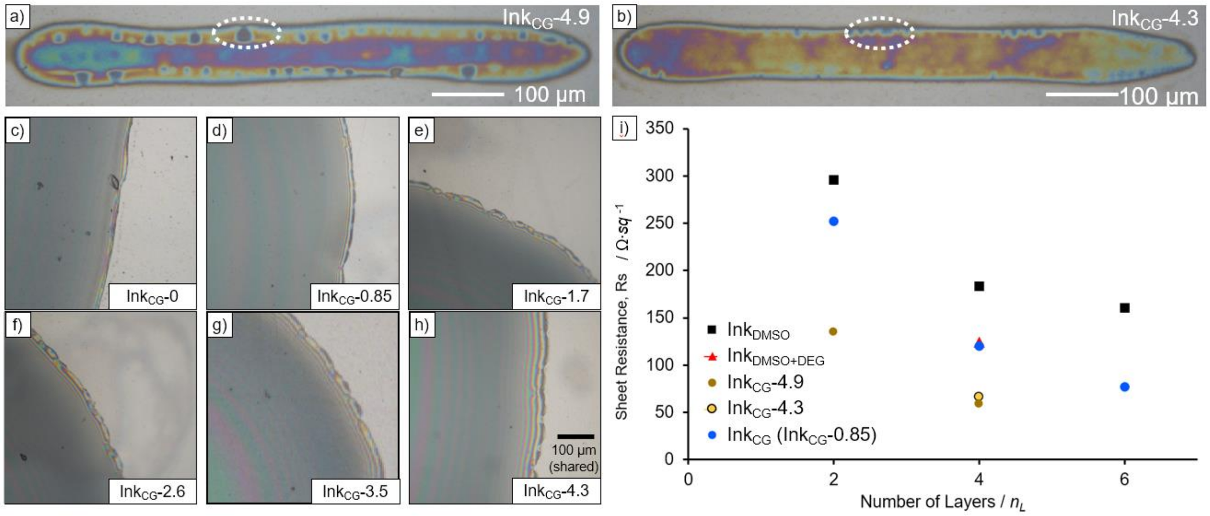

Figure S1. Optical images of inkjet printed lines of **a)** Ink_{CG}-4.9 and **b)** Ink_{CG}-4.3, displaying pock marks correlating with concentration of additives; **c-h)** Micrographs of drop cast specimens (2 µL each) dried at 45°C, demonstrating variation in edge pockmarks as GC is increased, **i)** Dependence of sheet resistance of PEDOT:PSS films on the number of printed layers.

SI3 Electrical characterisation details

Electrical measurements made by Van der Pauw (vdP) method utilised printed square specimens, with 1.24 mm edge length, with silver paste contacts applied (Figure S2). These contacts and specimen would be rejected if they did not comply with a contact size being smaller than ¼ the edge length.

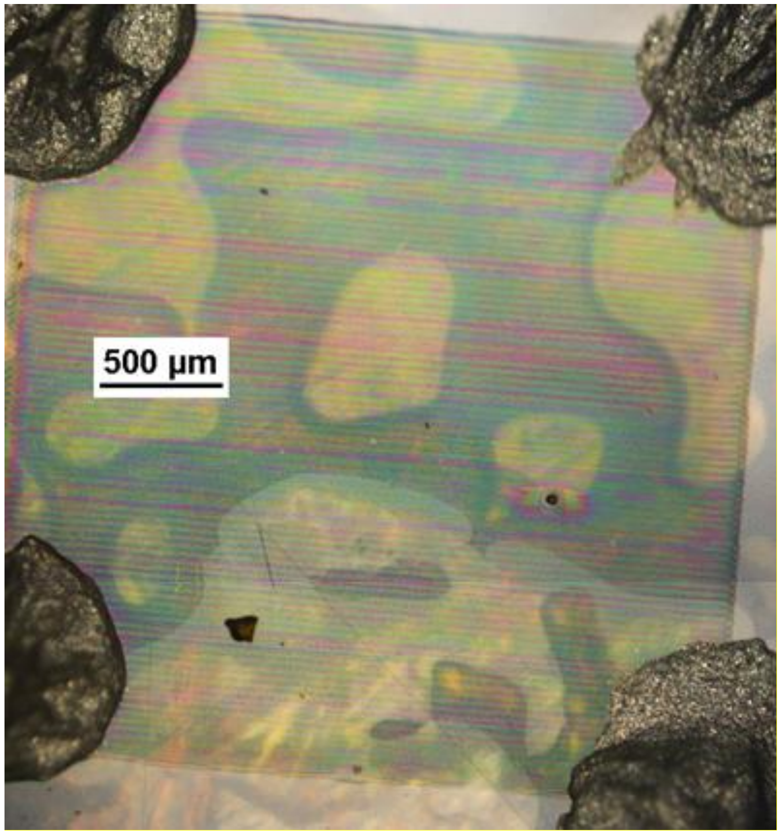

Figure S2. Optical microscopy image of typical vdP specimen, demonstrating acceptable dimensions of silver paste electrical contacts.

SI4 Topography of InkCG printed by varying print strategies

Three different printing strategies were explored for Ink_{CG}, and their corresponding height maps acquired using coherence scanning interferometry (CSI) and optical images are shown in Figure S3. Small surface pitting has formed in the aligned printing strategy, which does not appear in the other strategies (Figure S3 d-e, and main text Figure 3).

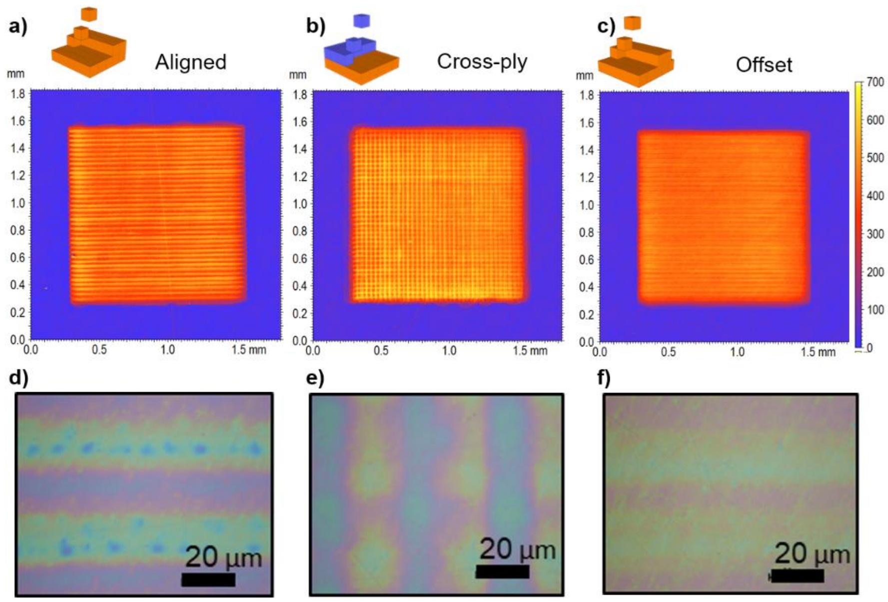

Figure S3. Height maps acquired using optical interferometry method for 4-layer PEDOT:PSS films printed using **a)** aligned, **b)** cross-ply and **c)** offset print strategies. Insets present a voxel-based schematic of the print strategy; and **d-f)** optical microscopy images of the same films, respectively.

SI5 Dependence of morphology on the number of printed layers for a commercial ink formulation

To investigate whether the presence of DEG in the commercial inks increases printing stability and quality, a PEDOT:PSS ink was prepared without DEG. The commercial ink (0.8 wt% in H_2O PEDOT:PSS, 739316, Sigma Aldrich) was prepared with 5 wt% DMSO, and 0.14 wt% sodium dodecylbenzenesulfonate (SDBS) surfactant (Ink_{Comm}) and was modified with 5 wt% DEG ($Ink_{Comm+DEG}$). When printed on PEN at substrate temperature of 45°C, a microporous surface was formed for Ink_{Comm} with the number of printed layers n_L = 2 (Figure S4). With increasing n_L the voids were filled. The $Ink_{Comm+DEG}$ displayed a wavy surface for all n_L investigated. This is likely due to slower gelation of $Ink_{Comm+DEG}$ when drying, which allows further the spreading of the ink. Electrical conductivity of Ink_{Comm} increases with increasing n_L, while no significant change is observed for $Ink_{Comm+DEG}$. Hence, the improved jetting stability due to DEG was not sufficient to enable large-area printing, with clogging observed for printing over 1 cm × 1 cm area or larger.

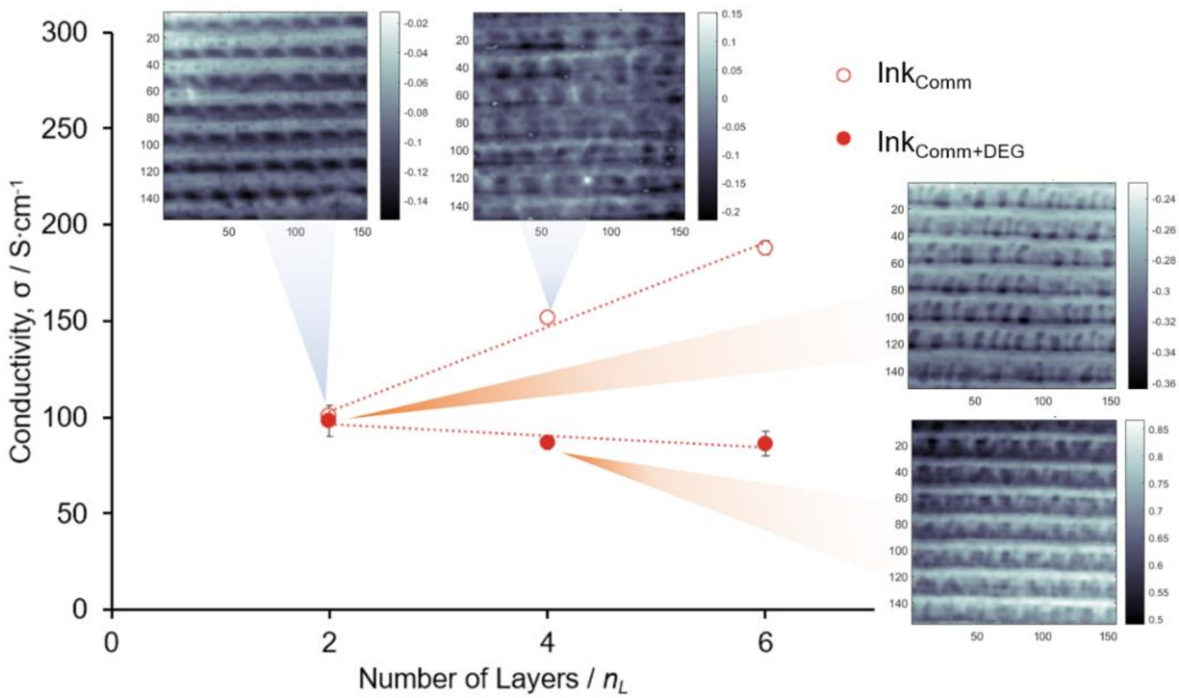

Figure S4. Conductivity of commercial PEDOT:PSS inkjet formulation, with and without 5 wt% DEG, printed onto PEN at n_L = 2, 4, 6. Insets display CSI topography of representative specimens for indicated numbers of layers, highlighting the changing topography in the Commercial ink, and the self-similar topography of the Ink$_{Comm+DEG}$ ink.

SI6 Stability of electrical properties of PEDOT:PSS

Stability of the PEDOT:PSS layers produced using Ink$_{CG}$ with respect to electrical properties was studied under exposure to UV illumination (Figure S5a) and during storage in ambient conditions (Figure S5b). Electrical contacts were made using silver paste. Cyanoacrylate glue (Loctite 1608412) was used as a protective layer (Figure S5c). The uncapped specimens degraded more rapidly in both cases, confirming that oxygen and/or moisture affect the ink stability, likely contributing to the degradation of Ink$_{CG}$. After 3 months of storage in ambient conditions, the resistance of the layer increased by a factor of about 2.5 to R = 9.6 kΩ. Thermal treatment at T_{ann} = 140°C for 18 hours partially restored the electrical properties, with resistance decreasing by 40% (Figure S5d). Optical microscopy images of printed InkCG specimens subjected to cyclic bending (2000 cycles) revealed no morphological change in the PEDOT:PSS lines (Figure S6).

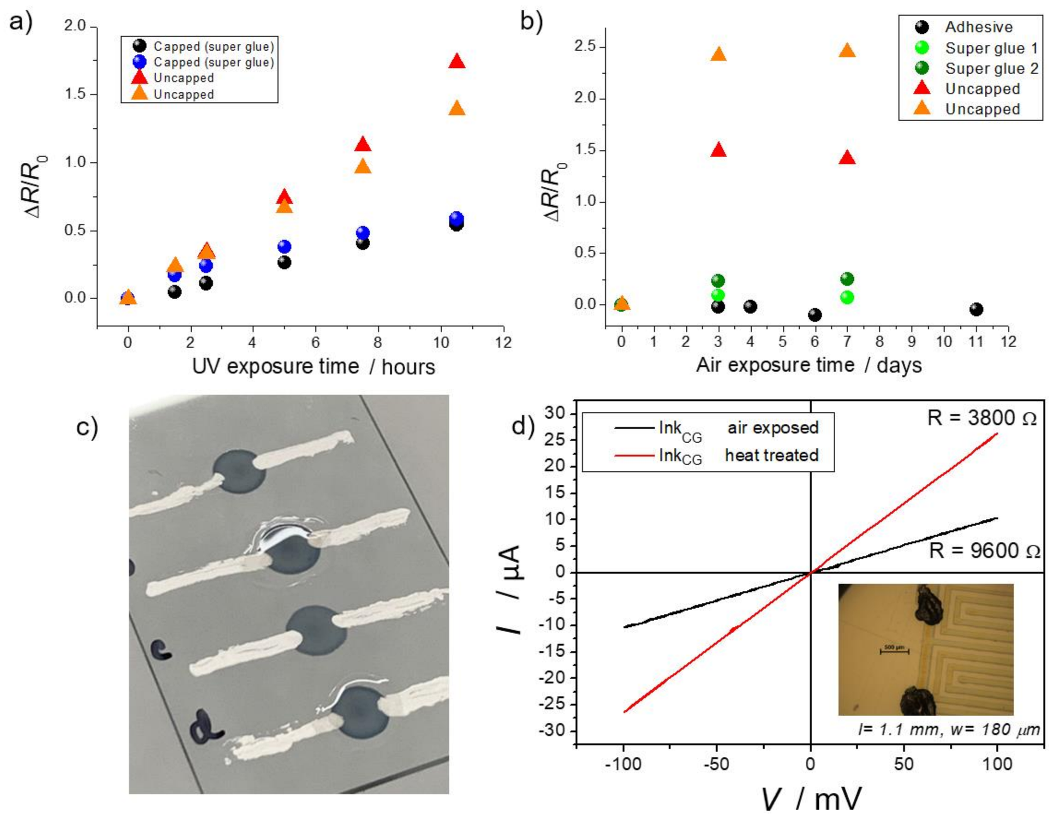

Figure S5. Relative resistance of capped and uncapped Ink_{CG} undergoing **a)** UV exposure and **b)** 3-month air exposure; **c)** A photograph of typical specimens used in this study; **d)** Current – voltage $I(V)$ characteristics of 2-layer printed Ink_{Cyr+GC} on PEN after exposure to air for 3 months and after annealing at T_{ann} = 140°C for 18 hours.

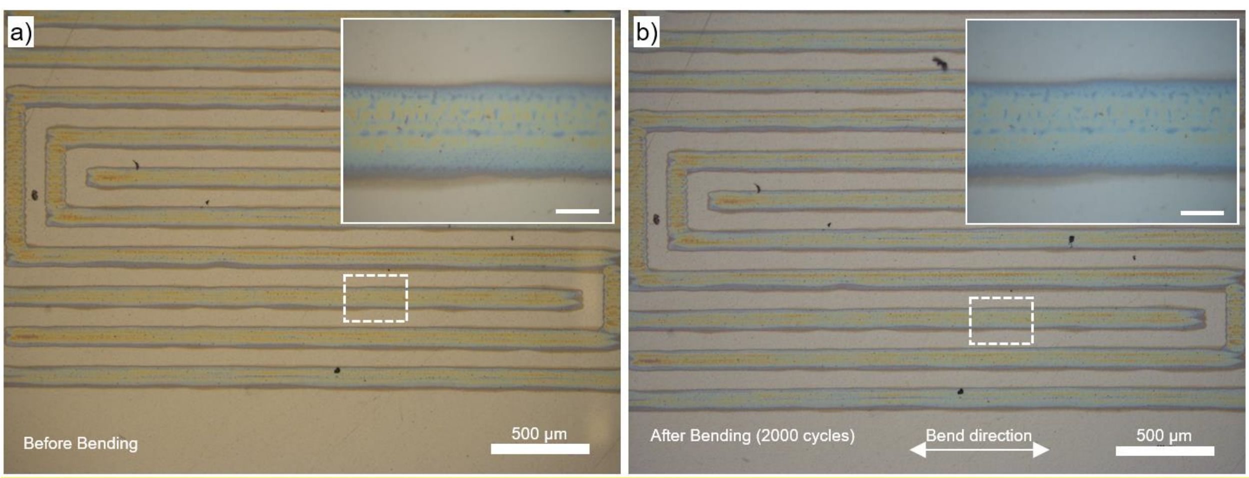

Figure S6. Representative optical microscopy images of printed InkCG patterns **a)** before and **b)** after 2000 bending, and (Insets) corresponding magnified images of areas indicated with white rectangles. Scale bar of insets is 50 µm.

SI7 PEDOT:PSS in heterostructures

Ink_{DMSO} was used in heterostructures with commercial inks of graphene and silver nanoparticles, (Figure S5a-c). Electrical measurements of these heterostructures reveal only a small increase of the PEDOT:PSS sheet resistance, which is independent of the position of PEDOT:PSS layer within the heterostructure (Figure S5d). Cross-section TEM images of PEDOT:PSS/graphene (Figure S5e), and corresponding EDX measurements (Figure S5f), indicate that the PEDOT:PSS layer is approximately 120 nm thick, which is thinner than that of individual PEDOT:PSS layer on PEN. Hence change in resistance can be attributed to intermixing between the layers in a heterostructure leading to decrease of effective thickness. InkCG printed onto inkjet printed graphene was investigated by cross-sectional SEM and EDX (Figure S8), demonstrating that a dense PEDOT:PSS layer has been printed without pores. Future studies will investigate similar heterostructures, utilising Ink_{CG} and the printing strategies for morphology control.

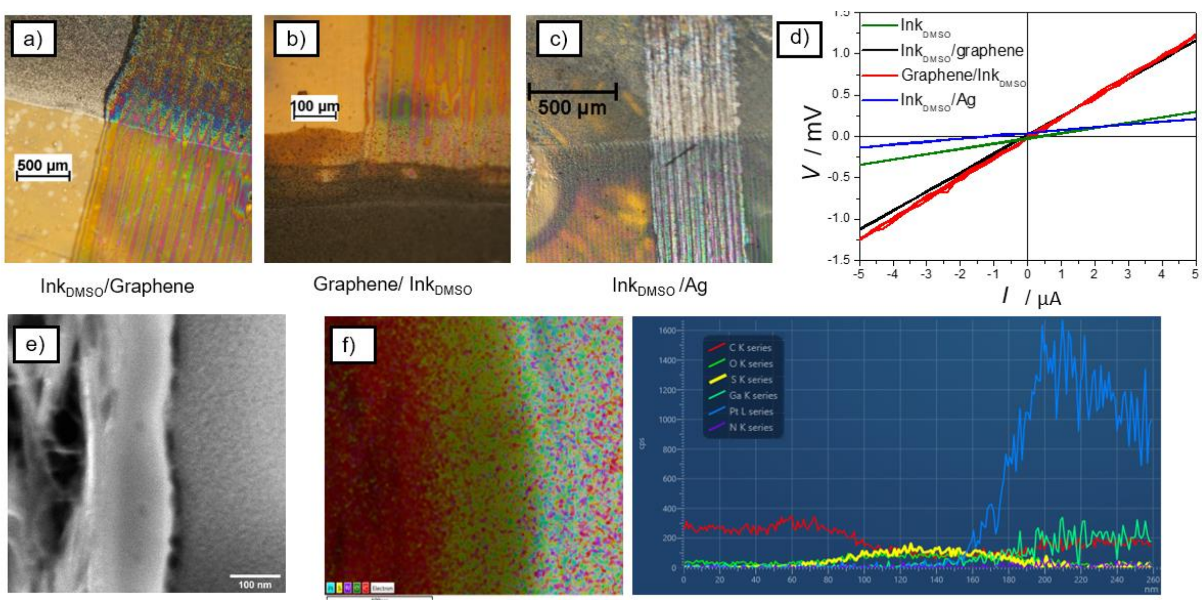

Figure S7. Optical photographs of 4-layer PEDOT:PSS (Ink_{DMSO}) in heterostructure **a)** above graphene (10 layers; T_{ann} = 250°C, 30 minutes); **b)** below graphene (10 layers, T_{ann} =150°C, 18 hours); and **c)** above Ag (4 layers, T_{ann} = 150°C, 35 minutes); **d)** Representative $I(V)$ characteristics of PEDOT:PSS in these heterostructures measured in van der Pauw configuration; **e)** Cross-section TEM images of PEDOT:PSS/graphene heterostructure and **f)** corresponding EDX elemental map and profiles.

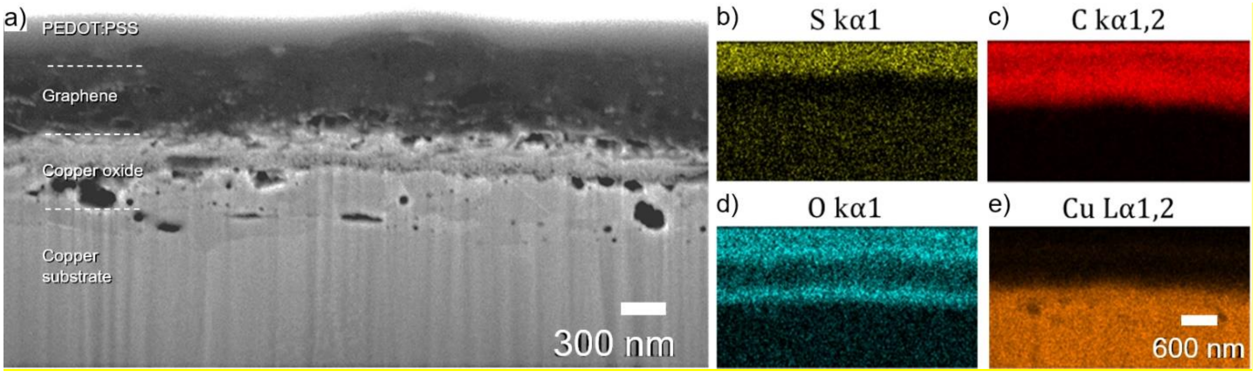

Figure S8. a) FIB-SEM images of the cross-section of PEDOT: PSS deposited on inkjet-printed graphene, corresponding EDX maps confirm the presence of (b) sulphur, (c) carbon, (d) oxygen, and (e) copper.

SI8 Printing stability of Ink$_{DMSO}$

The jetting stability of a PEDOT:PSS ink is necessary for reliable printing of electronic devices with precise features and over large areas. Unlike the new Ink$_{CG}$, Ink$_{DMSO}$ was found to be unreliable when printing a conductive strain sensor pattern with 2 layers of Ink$_{DMSO}$, and with dimensions of 1.5 cm × 1.1 cm onto PEN (Figure S9a). Five replicates were printed, one at a time: three were inoperable, with short-circuited paths due to misplaced droplets, or with incomplete open circuits due to clogging or misaligned swaths. The two operable replicates also contained misplaced droplets and missing or misaligned swaths; however, in these replicates these defects did not result in short circuits or incomplete traces, and thus the devices were operable. An example of one of these operable Ink$_{DMSO}$ specimens, with a representative region displaying the observed printing defects, is presented in Figure S9b.

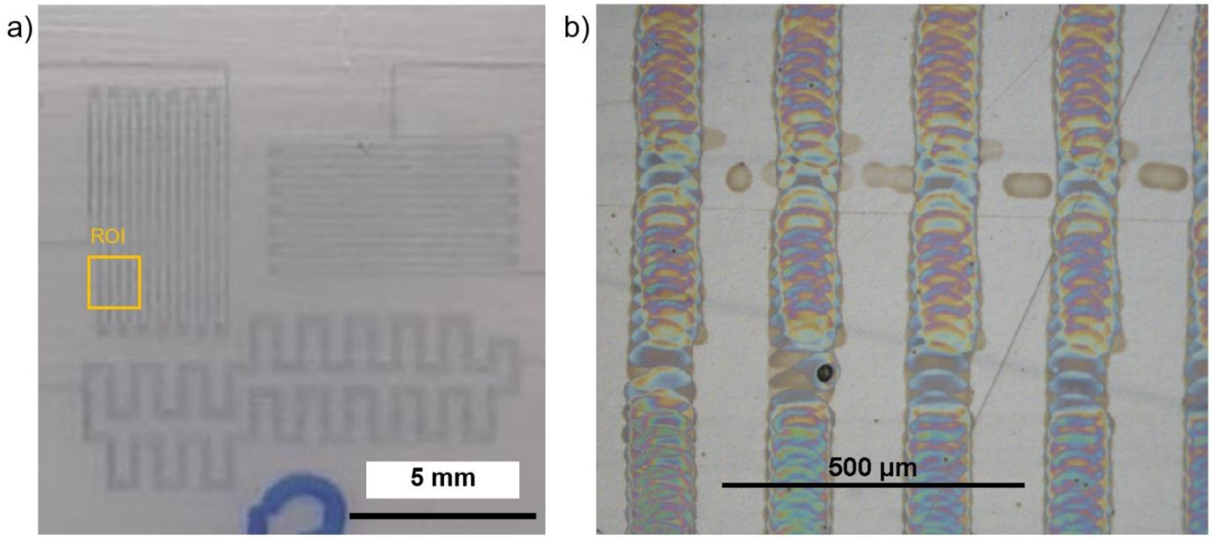

Figure S9. a) Photograph of two layers of Ink_{DMSO}, inkjet printed in a strain sensor conductive pattern on PEN; **b)** Representative optical microscopy image of Ink_{DMSO} printed strain sensor, displaying defects in the form of misplaced droplets, misaligned swaths, and missing swaths.