Electronic Supplementary Material (ESI) for Materials Horizons.

Supporting Information

Direct-writing microporous polymer architectures - print, capture and release

Qingxin Zhang, Niamh Willis-Fox, Clare Conboy, and Ronan Daly

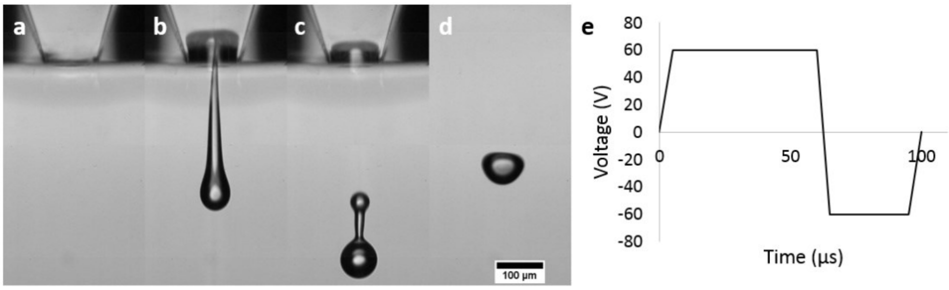

Figure S1. Visualisation of inkjet printing with a single piezoelectric printhead and a typical printing waveform. **(a)** Resting condition of the nozzle. **(b)** Drop ejected from the nozzle with an elongated ligament, and the meniscus sucked back due to negative pressure. **(c)** Drop break-up and travel away from the nozzle. **(d)** One single drop formed and imaged in flight. **(e)** The waveform used for single drop generation.

S2. Studying printed droplet self-organisation on liquid surfaces.

In the Breath Figure method, droplets self-organise through convection set up by the temperature gradient during rapid solvent evaporation. With the PDMS noted in the main text, we provided heat to the bottom of the sample to induce convection in the system and drive self-organisation. Droplets was printed at a significant distance away from each other and driven closer by self-organisation into hexagonal arrays. Droplets were generated by the Dimatix Materials Printer 2850, and the convection was captured by the convection and imaging system noted in Figure S2-1.

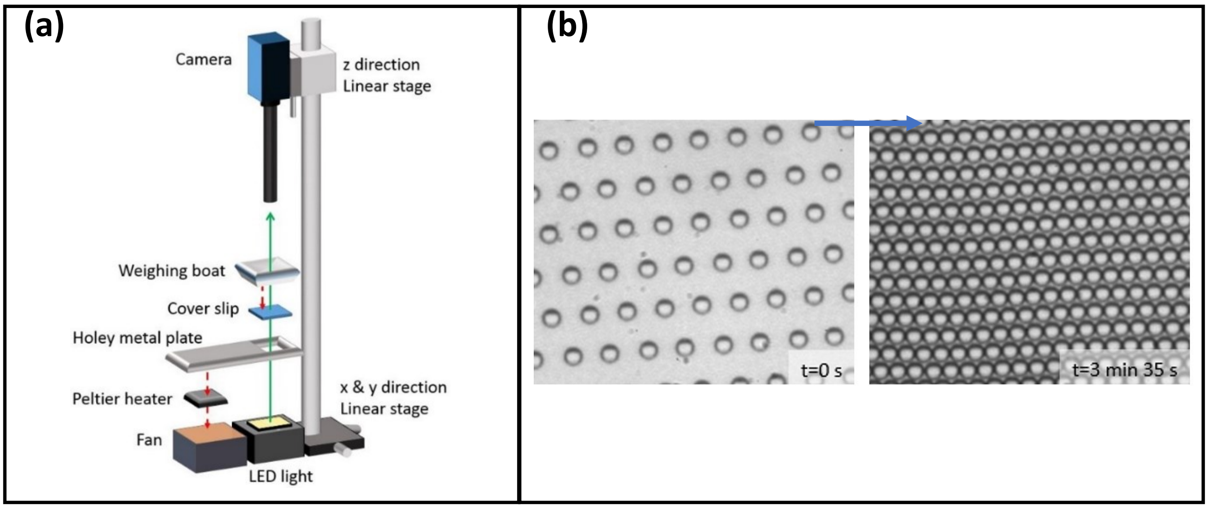

Figure S2-1: (a) Convection visualisation using optical setup with temperature control and transmission imaging. (b) Example image of printed droplets of water/glycerol solutions on PDMS surface before and after self-organisation.

To study the convection current, solvent blue 35 was used to dye a separate supply of PDMS. This dyed solution was deposited manually with an ultra-sharp syringe tip to the surface of PDMS in a range of patterns, to help track surface movement and identify when convection has occurred. The PDMS was poured into plastic weighing boats (Sigma-Aldrich), with dimensions of 43 mm × 43 mm × 9 mm. The weighing boats was filled with approximately 5 ml of PDMS and degassed with a vacuum pump. As an example, shown in Figure S2-2 (a-f), a diamond pattern, approximately 20 mm in diameter was deposited. Upon application of heat from below, these panels show the flow moving equally from the outside towards the centre over the course of 4.5 minutes. The dyed PDMS is miscible and much larger than the microdroplets, and so it experiences laminar flow, observed as streaking.

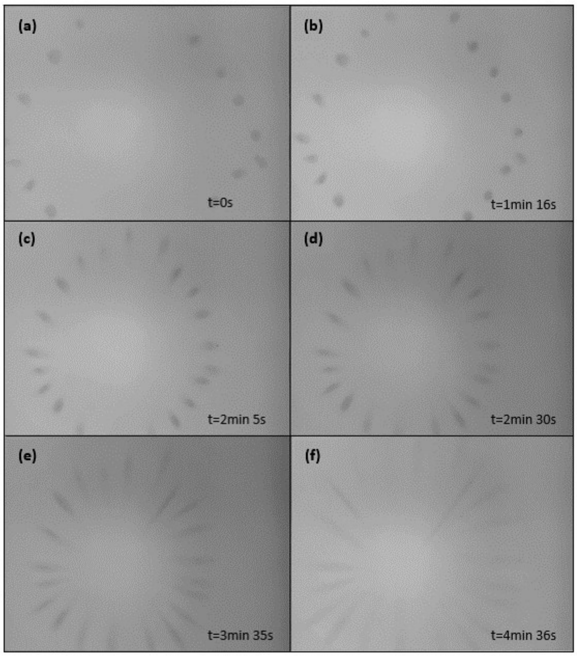

Figure S2-2: Convection visualisation for a diamond pattern by heating on hot plate at 80 °C, showing

A second example is shown in Figure S2-3 demonstrates the influence of convection on a dot array pattern over 1 minute, deposited with the same technique. The dots close to the centre move very little, whereas those further to the edge show the same streaking inwards as in Figure S1-2. This is a highly repeatable process and so there are clear flows towards the centre at the surface during convection.

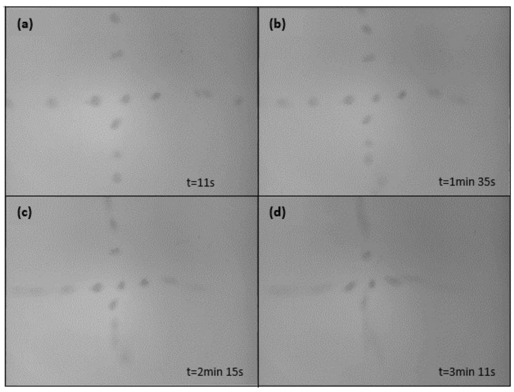

Figure S2-3: Convection visualisation for the cross pattern by heating on hot plate at 80 °C.

It has also been observed during convection studies with printed droplets, that when significant convection is driven, some drops can be pulled beneath the surface at the centre and brought down to the base of the weighing boat in a column. Together, these observations allow us to conclude that convection is occurring as indicated in Figure S2-4.

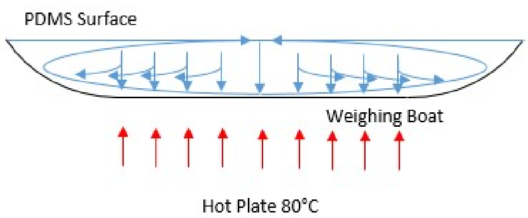

Figure S2-4: The cross-sectional schematic diagram of convection within the weighing boat containing PDMS, heated from below on a hotplate to 80 °C.

With the PDMS allowed to cure for 2 h prior to printing and self-organisation, the diameter of the final packed square pattern is ~3 mm. By allowing the curing to proceed for longer prior to printing and self-organisation, the reduction in convection means packing is stunted as viscosity increases. This is clearly seen by the decrease in packing from 2h cures to 10h cures, as shown in Figure S2-5.

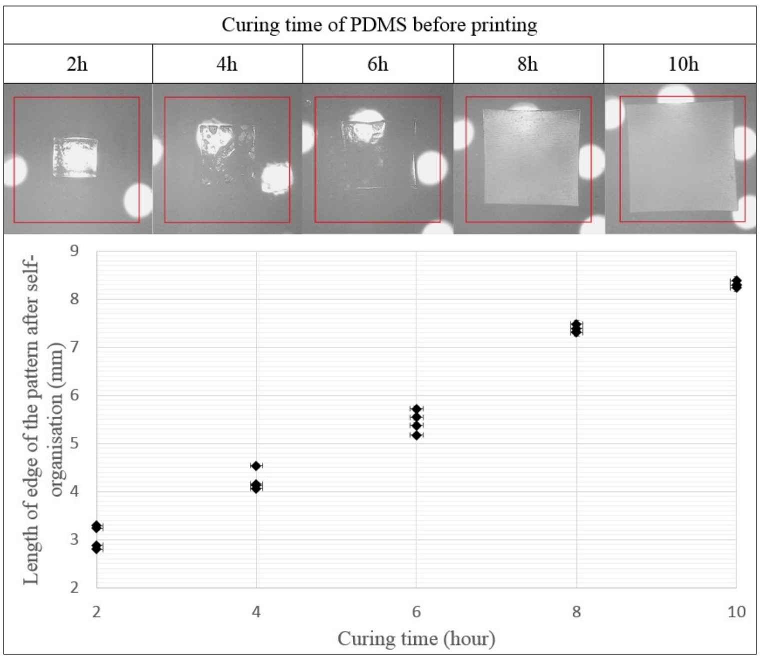

Figure S2-5: The dimensions of the packed pattern are observed to decrease to differing amounts, depending on the duration of curing allowed prior to printing. The red outline in each image indicates the original print area prior to self-organisation.