Supplementary Information

A Self-Correcting Inking Strategy for Cantilever Arrays Addressed by an Inkjet Printer and Used for Dip-Pen Nanolithography

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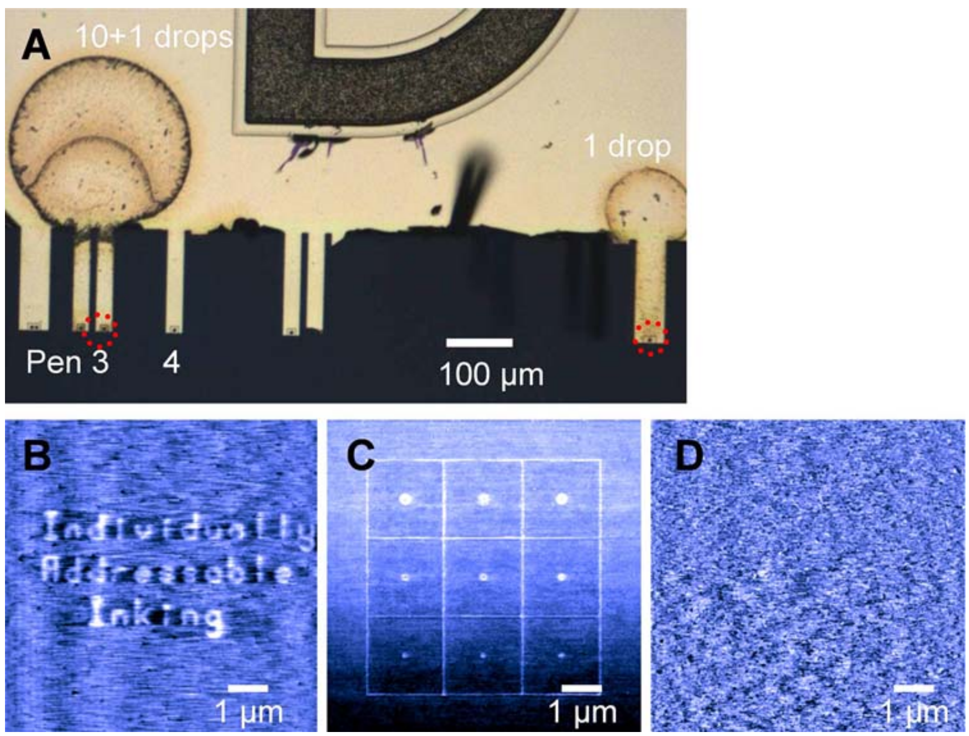

Figure S1. Inkjet printing of MHA (saturated solution in acetonitrile) on a custom pen array with different pen-to-pen spacings. (A) An optical microscopy image of an inked pen array. (B, C) Lateral force microscopy images showing that pen 3 (inked) was effective for DPN (ink diffusion rate of 0.015 µm^2 sec^{-1}). (D) Pen 4 (uninked control) did not produce patterns. DPN was carried out at a relative humidity of 49%.

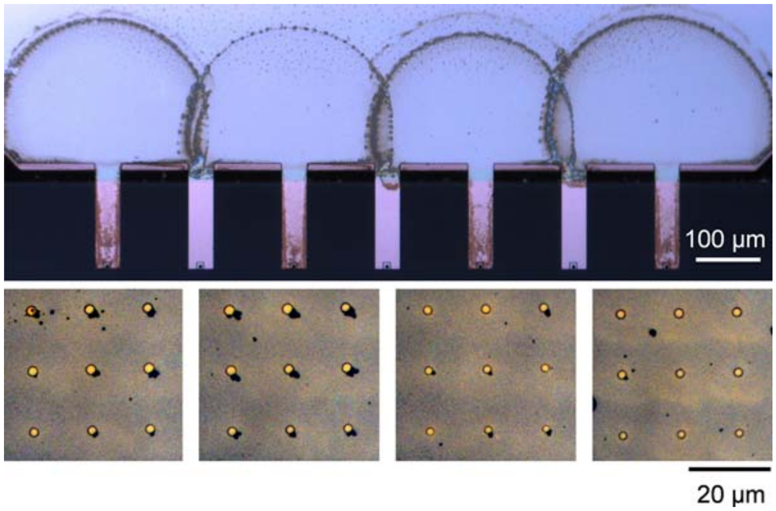

Figure S2. Pattern uniformity of inkjetted pen arrays. Two drops of an MHA-ethanol solution (10 mM, 320 pL/drop) were inkjetted on alternating pens. The DPN was carried out at a relative humidity of 40%, and the dwell time per dot is 360 seconds. The standard deviation of the gold patterns generated by pens in the same array is 4.4 ± 1.4%, and increases to 4.8 ± 0.7% when comparing three different pen arrays.

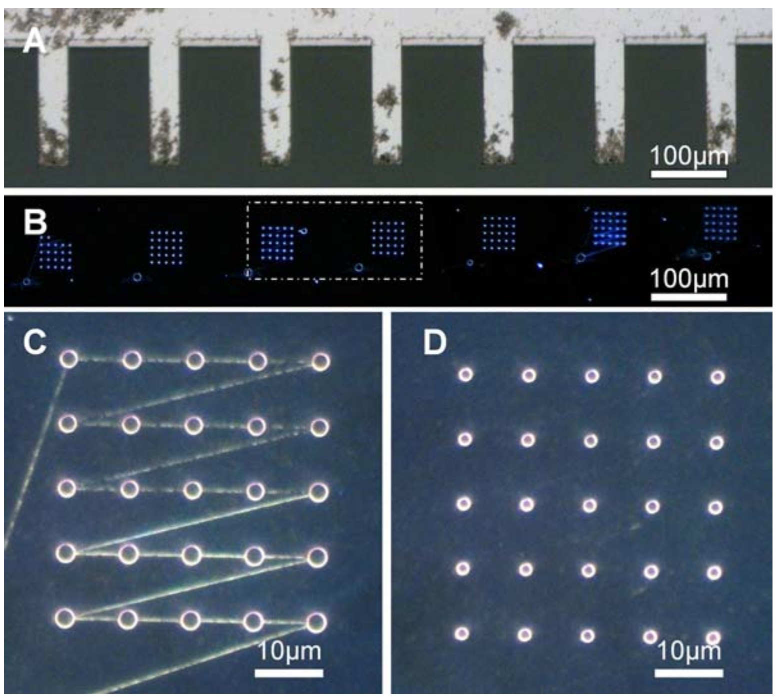

Figure S3. Pattern size variation of pen arrays inked by dip coating. The cantilevers were dipped into a saturated MHA-acetonitrile solution for 20-25 seconds and blown dry with a stream of N_2 from the cantilevers towards the tips. Subsequently, the cantilevers were dipped into ethanol briefly and brown dry with N_2. (A) Optical microscopy image of dip-coated pen array. (B) Dark field microscopy image of raised gold features generated by the pen array in "A". (C, D) Higher magnification of patterns boxed in (B). The standard deviation of dots created by different pens in the same array was at least 9.9%. Both inks (2 mM MHA-ethanol solution, results not shown, and saturated MHA-acetonitrile solution) showed similar standard deviations. In this particular example, DPN was carried out at a relative humidity of 50%, and the dwell time for each dot was 30 seconds. Note that the lines in "C" connecting the dots are present because the pen was not completely removed from contact with the surface.

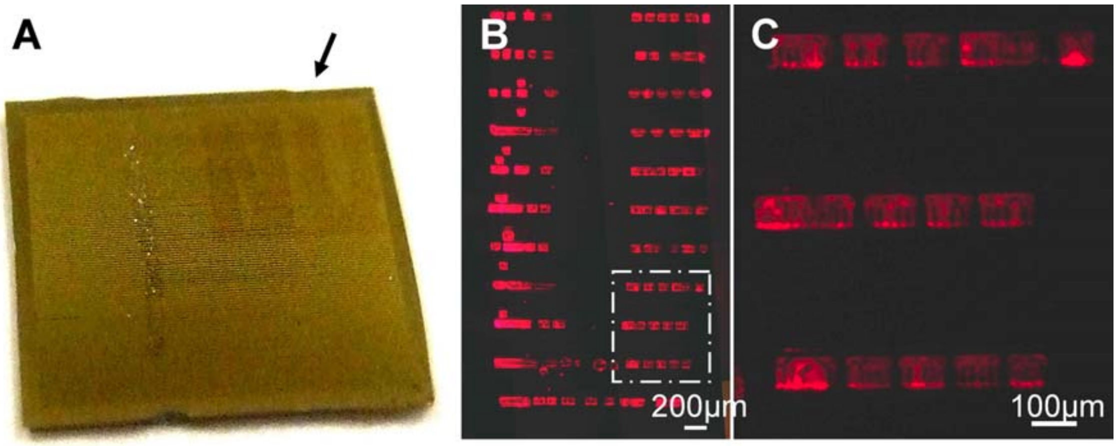

Figure S4. Phospholipids printed on a 55,000-pen 2D array with the pattern "NU". (A) Optical image. (B) Fluorescent microscopy images showing the rhodamine labeled DOPC ink making up the "U" pattern. Here the 2D pen array was on a SiO_2 support. The cantilevers were coated with titanium/gold and annealed to induce bending, following a published protocol.[1] The back sides of the cantilevers and SiO_2 support were functionalized with octyltrichlorosilane (OTS, 1 vol% in hexane for 30 minutes), while the front sides were functionalized with 11-amino-1-undecanethiol (AUT, 1 mM in ethanol for 20 minutes). This functionalization renders the back side of the cantilevers and the SiO_2 support hydrophobic, thereby preventing capillary action that causes the cantilevers to adhere to the SiO_2 support.

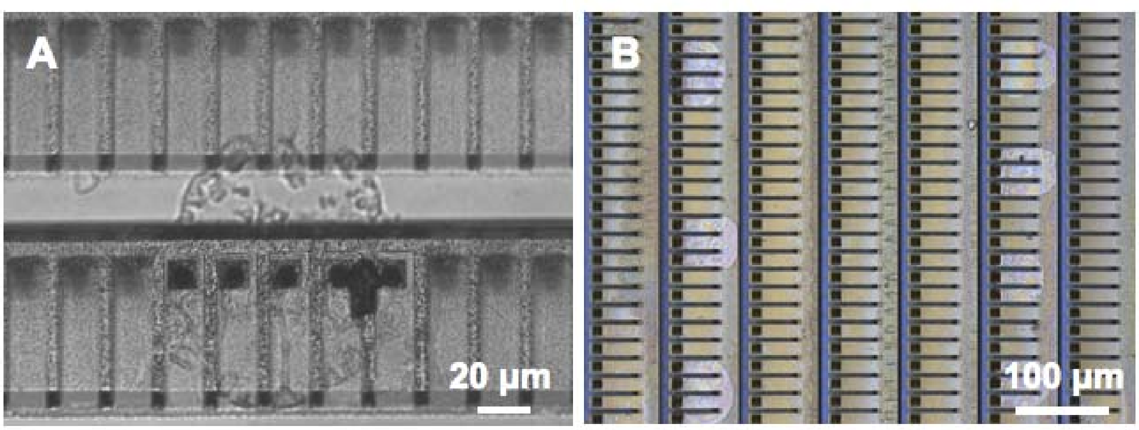

Figure S5. (A) DOPC ink droplets caused the cantilevers to stick to the support due to capillary action. The optical microscopy image shows that inked tips are in the focal plane of the SiO_2 support. (B) This stiction problem was eliminated by functionalizing the back sides of the cantilevers and the SiO_2 support with octadecyltrichlorosilane (OTS).

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[1] K. Salaita, Y. Wang, J. Fragala, R. A. Vega, C. Liu, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2006**, *45*, 7220-7223.

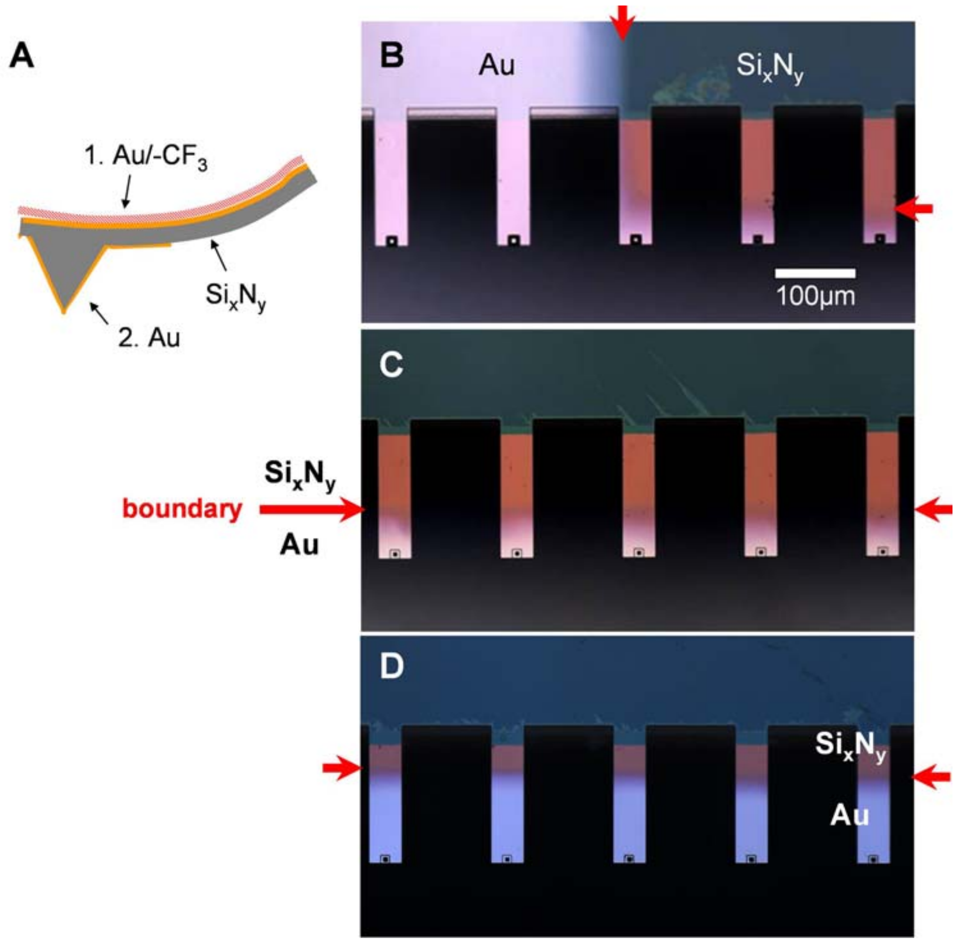

Figure S6. Anisotropically structured pens fabricated by shadow mask deposition of gold. A glass cover slide was used as a mask to expose select areas of the cantilevers for gold deposition. (A) Functionalization scheme. (B–D) Optical microscopy images showing cantilevers with varying areas coated with gold. The gold areas are brighter due to enhanced reflection. The arrows dictate the Si_xN_y-Au boundary.

Movie: Drying of a 0.2 µL droplet of 2 mM MHA-ethanol solution on an anisotropically functionalized 7-pen array. The movie is at a speed of 1 frame sec^{-1} with each frame taken at 5 second intervals.