Supporting Material

Solvent Vapour Mediated Spontaneous Healing of Self-Organized Defects of Liquid Crystal Films

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Figure S1. (A) Change in film thickness (**h**) after spin coating with concentration (**C** in % w/v) of 5CB in different solvents. (B)The circular symbols denote the rate of change of mass of the solvent (**m**_S) with time (t – bottom y-coordinate) when the volume of the solvent (**V**) at the source was kept constant at 100 μ L. The hollow square symbols show the rate of evaporation of solvents ($\Delta m_S/\Delta t$) with the change in the volume of the solvent (**V** – top y-coordinate). The joining of the data points act as a guide only. (C) Change in film thickness (**h**) with concentration (**C** in % w/v) of the nematic and isotropic films before and after the N-I or I-N phase transition. (D) Change in the surface roughness (**R**) with time during N-I and I-N transitions for a film of thickness, **h** = 53.3 ± 0.2 nm.

In the experiments, 5CB nematic films were spin coated from a solution of 5CB, either in toluene or in n-hexane, on square ($\sim 1 \text{ cm} \times \sim 1 \text{ cm}$) and thoroughly cleaned pieces of silicon wafer. The coated samples were vacuum dried at ambient condition to remove any excess residual solvent. The thicknesses of the films were measured using an imaging Ellipsometer. **Figure S1A** shows the variations in the film thicknesses (*h*) with the variation in the concentration of 5CB (C%) in toluene and n-hexane. The figure

indicates that the 5CB film thicknesses at different concentration (w/v) of solute in the different solvents.¹ The figure clearly shows that the same concentration (w/v) of 5CB in n-hexane and toluene could lead to two different thicknesses after the coating was completed. The difference in the casted film thicknesses in different solvents could be attributed to the solubility of the 5CB in the solvent together with the viscosity of the solvents. **Figure S1B shows** the temporal variation in the mass of the solvent (m_s) and subsequent rate of evaporation ($\Delta m_s/\Delta t$) from the sources with the change in the volume of solvent (V) inside the sources. **Figure S1C** indicates that during the N–I the film swelled significantly as the solvent molecules diffuse into the film matrix. Ellipsometric measurement of the surface roughness (R) in **Figure S1D** shows that during the N-I and I-N transitions the surface roughness initially increased to a maximum value before reducing to near zero roughness in the nematic or isotropic phase. **Figure S1D** confirms that the film did not dewet on the substrate during the N–I transition because the amplitudes of the surface undulations were much lower than the film thickness.

Supplementary video 1: The video shows the nematic to isotropic (N–I) phase transition of a liquid crystal film ($h = 43.8 \pm 0.9$ nm) upon short time solvent vapour annealing. The nematic 5CB film with flat surface was exposed to the toluene vapour and after sometime the spatial patterns appeared on the surface. The spots grew with time as more solvent vapour adsorbed on the surface and coalesced to form a bi-continuous pattern. The completion of the N–I phase-transition was indicated by the reappearance of the flat surface.

Supplementary video 2: The video shows the reverse isotropic to nematic (I–N) phase transition of a liquid crystal film ($h = 43.8 \pm 0.9$ nm) upon removal of the solvent vapour exposure after the completion of the N–I phase transition. In this situation, a reverse cycle of the I–N phase transition was observed when the solvent vapour exposure was removed. The I–N phase transition initiated with the appearance of the darker circular spots indicating the sites with nematic phase as the solvent diffused out of the film matrix. These spots grew to form the bi-continuous pattern. Once the film matrix was free of the solvent molecules a flat nematic film was observed.

Supplementary video 3: This video shows the polarization microscopic images of the forward (N-I) and backward (I-N) phase transitions of a liquid crystal film ($h = 47.3 \pm 1.2$ nm) upon exposing and removal of solvent vapour, respectively. The nematic surface texture of the film started to disappear

with the progress in time and formed a flat surface after the N-I transition was complete. The video also shows that, after the N-I phase transition was complete and the solvent exposure was withdrawn from chamber, the textures reappeared on the surface before disappearing after the I-N transition was complete.

Supplementary video 4: The video shows surface morphologies of a nematic film ($h = 47.3 \pm 1.2$ nm) when the experimental chamber was kept partly open to maintain a nearly constant partial pressure of the solvent vapour on the film. The video suggests that during the N-I phase transition the patterns could be retained for a longer duration.

Supplementary video 5: The video shows surface morphologies of a nematic film ($h = 64.4 \pm 0.55$ nm), when the experimental chamber was kept partly open to maintain a nearly constant partial pressure of the solvent vapour surrounding on the film. The video suggests that although the surface patterns during the N-I phase transition could be retained for longer duration by tuning the partial pressure on the film.

Supplementary video 6: The video shows that when a liquid crystal film ($h = 72.9 \pm 0.2$ nm) was under long-time exposure of the solvent vapour, the N–I phase transition took place after ~90 s. Following this, the isotropic film started dewetting the silicon wafer after ~548 s, as circular holes appeared on the film surface. The holes grew with time to achieve equilibrium contact angle and after ~708 s the solvent vapour exposure was removed. Consequently, the hole stopped growing and the contact line became unstable. At this stage, the film surface showed an I–N transition at ~755 s. Thereafter, the nematic fingers started growing towards the centre of the holes at ~760 s. The fingers almost healed up the entire dewetted region after ~1462 s. The fingers showed secondary contact line instabilities as branching patterns while healing the dewetted zone.

Supplementary video 7: The video shows the reversibility of the fingers growth upon periodic exposure and removal of the solvent source. After the fingers were grown, if the film ($h = 72.9 \pm 0.2$ nm) was again exposed to solvent vapour exposure, N–I phase transition was observed after ~21 s. A prolonged solvent exposure again led to dewetting with disappearance of the fingers after ~ 294 s. After ~350s, when the solvent vapour exposure was removed, the nematic fingers were formed followed by an I–N transition ~399 s. Later the fingers grew to nearly heal the dewetted zone after ~ 457 s.

Supplementary video 8: The video shows that when the liquid crystal film ($h = 53.3 \pm 0.2$ nm) film was exposed to solvent vapour exposure for a prolonged duration, holes appeared randomly across the space. The holes grew with time and coalesced. At this stage, when the solvent exposure was removed then the nematic fingers started to grow with time and nearly self-heal the dewetted region.

References:

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