Supporting Information

From Chaos to Order: Evaporative Assembly and Collective Behavior in Drying Liquid Crystal Droplets

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1. Materials and Apparatus

All Chemicals were used as received without further purification. The nematic liquid crystal (LC) 4-cyano-4′-pentylbiphenyl (5CB, 98%) was purchased from Sigma Aldrich. The non-ionic Pluronic F127 (M_w=13000, 99%) and zwitterionic 3-(N, N-dimethyl-myristyl-ammonio) propane-sulfonate (DMAPS, ≥99%) were used as surfactant, and purchased from Sigma Aldrich. De-ionized water was obtained from the Millipore-purified water system.

Polarized optical microscopy (POM) image was conducted on Olympus BX51-P microscope with images taken by polarizers in a perpendicular arrangement to verify the anisotropy of the samples. Videos were taken by the same microscope with a motorized stage, and a high-resolution DP74 camera (Olympus, resolution of 5760×3600 pixels) were used to record the motion of individual liquid crystal droplet in suspension. Images were acquired with the frame rate up to 30 frames/s, at 200× magnification in cross-polarized light. Color video with the resolution 1920×1200 and the frame rate 30 frames/s and 100×magnifications were used to acquire large-scale patterns of collective motion. The acquired videos were converted into image sequences and processed in Matlab software.

2. Experimental Section

Preparation of liquid crystal droplet emulsion.

In a typical experiment, LC-in-water droplet emulsions were prepared by emulsifying 25 μL of 5CB in 10 mL of an aqueous phase of surfactant (DMAPS or Pluronic F127)

with the concentration of 0.5 wt%. By using sonicator (VCX-750, Sonics & Materials. Inc) for 60 s at the power input of 50%, we generated a white 5CB droplet suspension with the droplet size ranged from 2-10 μm. The resulting emulsions were preserved in glass vials for further use.

3. Supporting Movies

Supplementary Movie S1: The collective motion of 5CB droplets with bipolar configuration swimming from the droplet centre to the contact line, showing loosely packed deposition.

Supplementary Movie S2: The collective motion of 5CB droplets with radial configuration swimming from the droplet centre to the contact line, exhibiting densely packed quasi-static structures at the interface.

Supplementary Movie S3: The collective motion of LC-droplet colony swimming from the droplet edge to its centre. During the moving process, all the LC-droplets are swimming in the same direction with the inter-adjacent droplets in arrested structure and showing dynamic hexagonal patterns.

Supplementary Movie S4: The growth of LC-droplet colony during the collective motion. Individual LC-droplets are attracted and incorporated into the LC-droplet cluster and make the cluster grow bigger during the moving process.

Supplementary Movie S5: The merging process of two individual LC-droplet colonies into a big cluster during the collective motion. The velocity of individual droplet inside the colony changes (speed and orientation) with the decrease of

distance between two colonies which due to the intrinsic attractive forces in LC molecules.

Supplementary Movie S6: The collective behavior of LC-droplets schooling with bipolar configuration, showing a chaotic assembly and movement.

Supplementary Movie S7 and S8: The Brownian motion of LC-droplets with radial (Movie S7) and bipolar (Movie S8) configuration in suspension.

Supplementary Movie S9: The collective behaviour of 5CB droplets cluster moving from the drop edge to centre. The diameters of the droplets near the contact line are smaller than those in the centre.

Supplementary Movie S10: The formation and retaining of defects in the hexagonal LC-droplet colonies during collective motion.

Supplementary Movie S11: During collective motion, the droplets in LC cluster near defects disrupted their periodic ordering and rearranged into long-range dislocation line.

Note: All the videos are recorded and played at 30 fps.

4. Supporting Figures

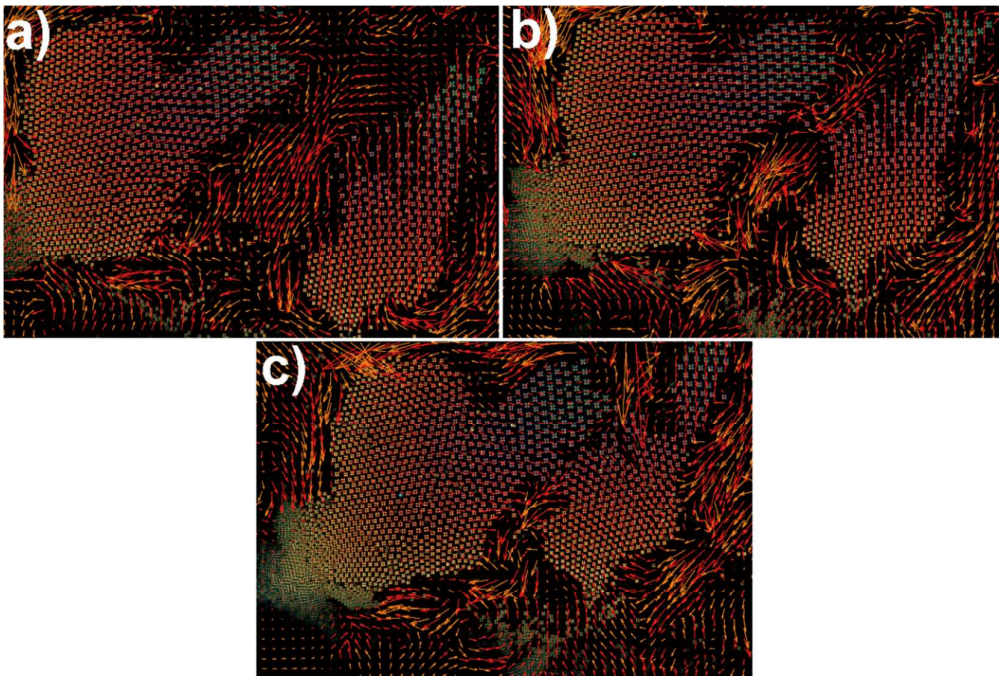

Figure S1 A sequence of POM images demonstrates the merging process of two individual LC-droplet colonies. During the merging evolution, the velocity speed and orientation of the LC-droplet changes all the time due to the attractive forces in 5CB molecules. Particle image velocimetry of the droplet flow and orientation was performed using the freely available Matlab-based package PIVlab.[1]

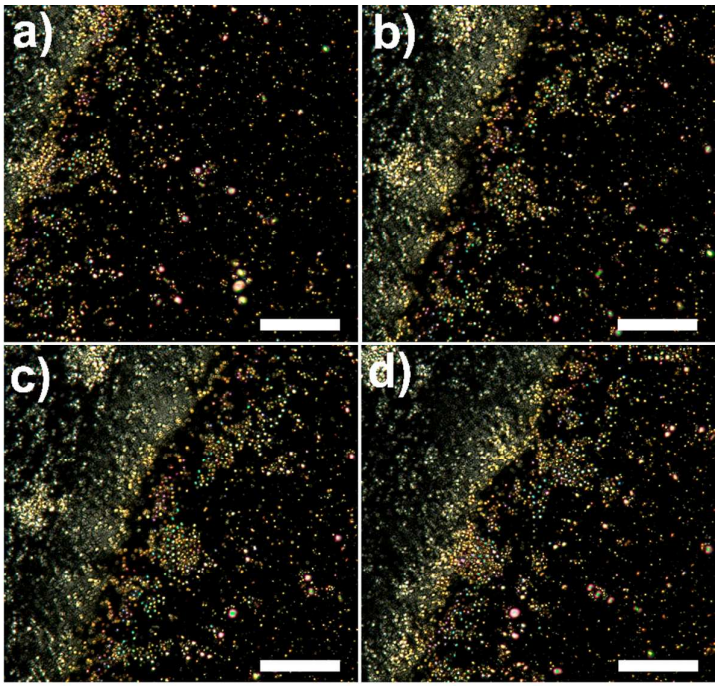

Figure S2 a)-(d) A sequence of POM images demonstrates the collective behaviour of 5CB droplets with bipolar configuration during the evaporation. Time interval: 5s. Scale bars: 50 μm.

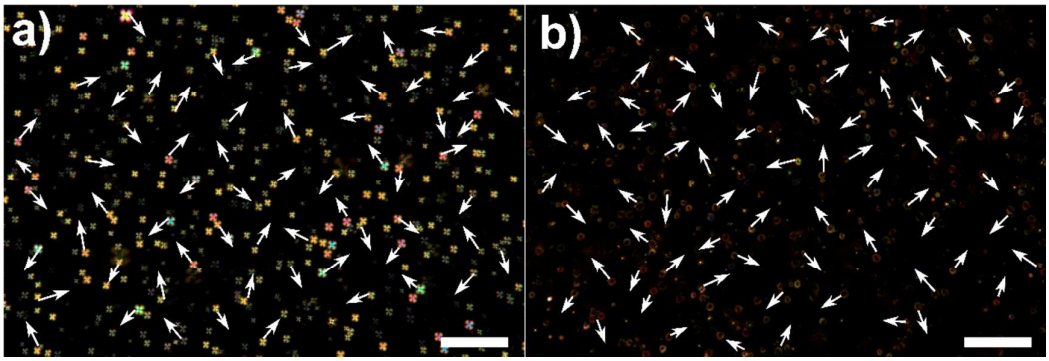

Figure S3 POM images showing the collective behaviours (Brownian motion) 5CB droplets in water with radial (a) and bipolar (b) configurations, respectively. Arrows at the droplets indicate their transient direction of motion. Scale bars: 20 μm.

Details for the derivation of the number of accumulated droplets at contact line.

During evaporation, we assume that the drying droplet keeps a spherical cap with volume V_p and diameter R_p from the center when the contact line is pinned at a position. The height of the droplet cap is h_p. Before evaporation, the initial droplet volume, diameter and height is V_0 R_0 and h_0, respectively. Thus, on the base of the geometric analysis, the corresponding droplet volume can be expressed as: $V_0 = \frac{\pi h_0}{6}(3R_0^2 + h_0^2)$ and $V_p = \frac{\pi h_p}{6}\left(3R_p^2 + h_p^2\right)$, respectively. The total number of droplets that are transported to the contact line can be given by $N = (V_0 - V_p)\rho_n$, where ρ_n is the density of droplets in emulsion. We also assumed that the droplets form a circular ring (outer radius R_p, inner radius r_p) at the contact line, thus, the occupied area of the droplets can be given by $\pi\left(R_p^2 - r_p^2\right) = (V_0 - V_p)\rho_n \pi a^2$ (a is the diameter of the droplet). Then, based on the equation above, we can conclude that the average number of droplets in the radial droplet cluster is given by $N = \frac{R_p - r_p}{2a} = \frac{R_p - \sqrt{R_p^2 - (V_0 - V_p)\rho_n a^2}}{2a}$.

REFERENCE:

(1) Thielicke, W.; Stamhuis, E., Pivlab–Towards User-Friendly, Affordable and Accurate Digital Particle Image Velocimetry in Matlab. *J. Open Res. Software* **2014**, *2,* e30.