Electronic Supplementary Material (ESI) for Soft Matter

Influence of droplet size, pH and ionic strength on endotoxin-triggered ordering transitions in liquid crystalline droplets

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Electronic Supplementary Information (ESI)

Size distribution of LC droplets

We quantified the size distribution of the 5CB droplets used to obtain the results shown in Fig. 3 by creating a histogram of the percentage of the droplets appearing in each size range (Fig. S1). The average diameter of the LC droplets was determined from our experiments to be 5.9 ± 0.4 μm. To calculate the average number of endotoxin molecules per LC droplet, we assumed a LC droplet diameter of 6μm.

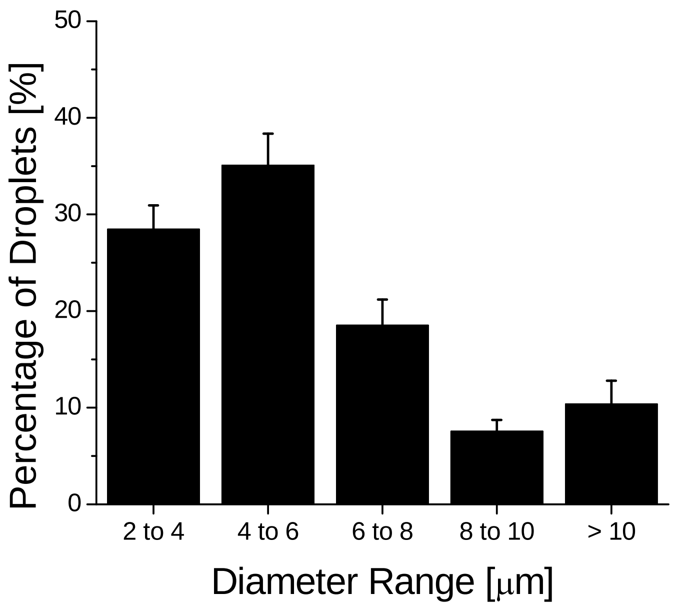

Fig. S1 Size distribution of the 5CB droplets used to obtain the results shown in Fig. 3 of the main text. The droplets were dispersed in PBS buffer, pH = 7.2.

Size-dependent changes in the configurations of LC droplets induced by endotoxin

Although LC droplets with diameters less than 10 μm exhibited configurations that were close to radial (outside of the central defect region that could not be imaged) in presence of endotoxin, we also observed the precise ordering of the droplets to depart from an exact radial configuration. For example, Fig. S2 shows polarized light micrographs of 5CB droplets with different diameters in the presence of 100 pg/mL endotoxin in a phosphate buffered saline solution (PBS buffer) with an ionic strength of 90 mM and pH 7.2. Radial droplets with diameters as large as ~5 μm (Figs. S2A and B) yielded polarized light micrographs with extinction bands approximately in line with the orientation of the crossed-polars mounted on the microscope, suggesting radial symmetry of the LC confined within the droplets. However, the droplets with diameters above 5 μm gave rise to polarized light micrographs with extinction bands that were twisted with respect to the crossed-polars, indicating the presence of a slightly twisted, radial configuration (Fig. S2C and D). When the diameters of the droplets were above 7 μm, polarized light micrographs of droplets revealed the formation of a small (~2 μm) region surrounding the core of the droplet with extinction bands that were twisted relative to the crossed-polars (again indicating a twisting of the LC within this region) (Fig. S2E). Outside of this small region containing LC in a twisted configuration, the extinction bands in the polarized light micrographs were in line with the crossed-polars, consistent with a radial symmetry of the LC within this region. The optical texture of the droplet displayed in Fig. S2E is similar to a texture reported in a study conducted by Lavrentovich and Terent'ev for a LC droplet suspended in a glycerin matrix containing 10 wt% lecithin.[1] We also note that the optical appearance of the larger droplets is influenced by the relative location of the focal plane and the equatorial plane of the droplets (the two are slightly displaced in D and E below). We refer the reader to references [1-8] for additional past studies of LC droplets.

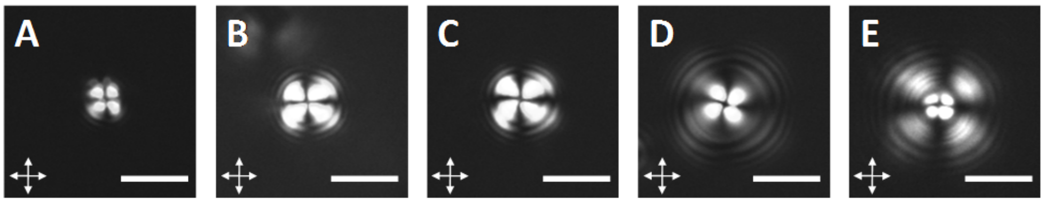

Fig. S2 Polarized light micrographs of radial 5CB droplets of different diameters in the presence of 100 pg/mL endotoxin in PBS buffer, pH = 7.2. The diameters of the droplets are: (A) 2.6 µm, (B) 4.4 µm, (C) 5.2 µm, (D) 7.0 µm, and (E) 8.1 µm. The double-headed arrows indicate the orientation of the crossed-polars. Scale bars, 5 µm.

Characterization of the ordering within LC droplets dispersed in a 100 pg/mL endotoxin solution

Previously, we demonstrated that both preradial and escaped-radial director configurations are observed transiently during the transition of a 5CB droplet from a bipolar to a radial configuration in the presence of pg/mL concentrations of endotoxin in solution.[5] Fig. S3 reports the percentages of droplets exhibiting the bipolar, transitional (either preradial or escaped-radial), or radial configurations in the presence of 100 pg/mL endotoxin in PBS buffer with an ionic strength of 90 mM and pH 7.2 for the five diameter ranges presented in Fig. 3 of the main text. The data presented in Fig. S3 corresponds directly to the solid black bars in Fig. 3 of the main text. A majority of the droplets in each diameter range existed in either a bipolar or a radial configuration. Less than 20 % of the droplets in each size range were observed to exist in the transition states (preradial or escaped-radial configuration). This result is consistent with our previous study and confirms that the preradial and escaped-radial configurations are indeed transient intermediate states.[5]

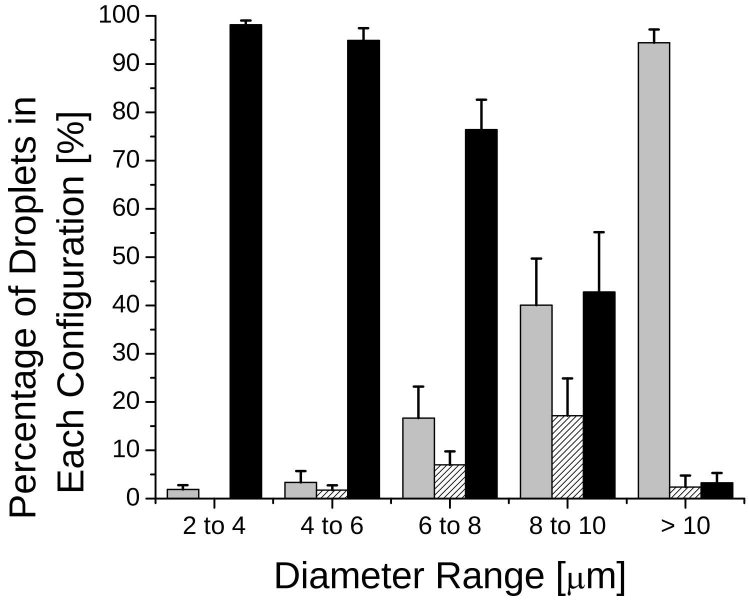

Fig. S3 Histogram of the size dependent response of 5CB droplets to the presence of 100 pg/mL endotoxin in PBS buffer, pH = 7.2. The percentages of 5CB droplets that exhibited a bipolar (grey bar), transition (preradial or escaped-radial, striped bar), and radial (black bar) configuration in the presence of 100 pg/mL endotoxin are plotted for each droplet diameter range. The data corresponds to the solid black bars in Fig. 3 of the main text.

Size-dependent ordering of LC droplets as a function of the pH of the bulk aqueous phase

The percentage of 5CB droplets exhibiting a radial configuration when dispersed in PBS buffers, certified to contain < 2 pg/mL of endotoxin, was characterized at pH values ranging from 5.0 to 12.8 for droplets with diameters ranging from just below 1 μm to 10 μm (Fig. S4A). Below pH = 12.8, a majority of the droplets were not observed to exhibit a radial configuration. However, at pH = 12.8, 51 ± 10 % of the droplets were observed to exhibit a radial configuration. Additionally, at a pH of 12.8, the percentage of droplets exhibiting a radial configuration was quantified as a function of droplet diameter by creating a histogram with a bin width of 2 µm for droplets with diameters ranging from below 1 µm to 10 µm (Fig. S4B). Above a droplet diameter of 5 ± 1 µm, no droplets were observed to exhibit a radial configuration. In contrast, as the diameter of droplets was lowered from 5 ± 1 µm to 1 ± 1 µm, the percentage of droplets exhibiting a radial configuration was observed to increase from 29 ± 11 % to 97 ± 3 %.

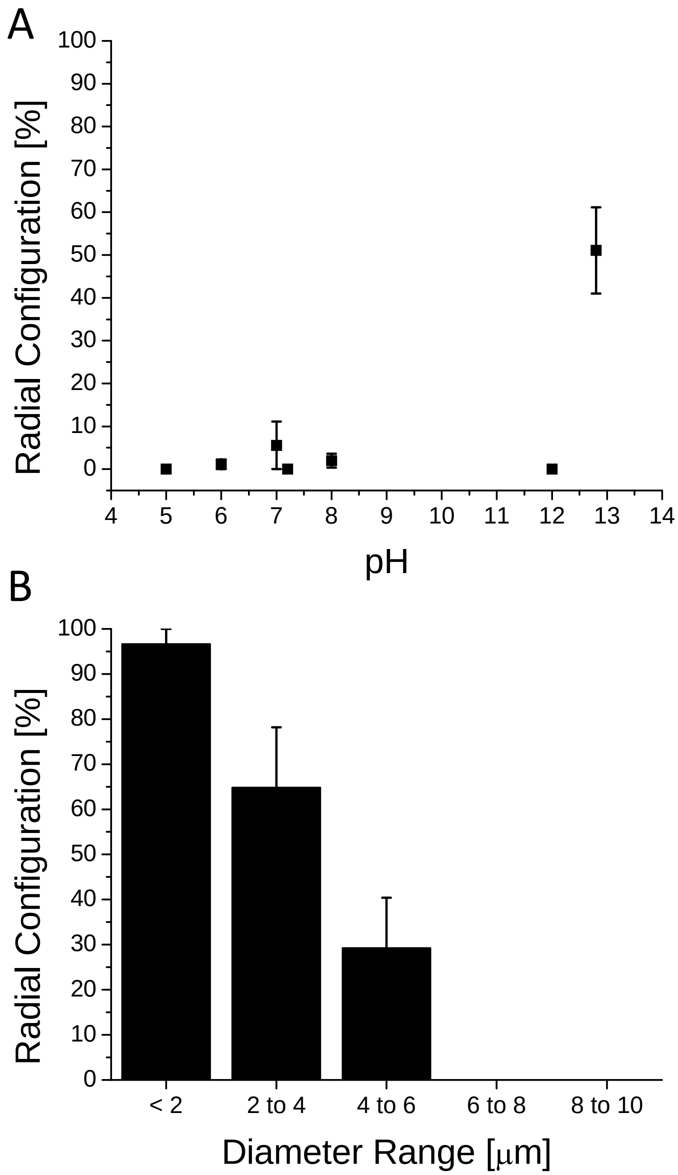

Fig. S4 (A) Percentage of 5CB droplets in 40 μL of PBS buffer that exhibited a radial configuration in the absence of any added endotoxin, plotted as a function of the pH of the PBS buffer solution. (B) Histogram of the size dependent ordering of 5CB droplets in PBS buffer with a pH = 12.8.

Ionic strengths of the components of PBS buffer after dilution

Table S1 displays the total ionic strength of each dilution, as well as the ionic strength of each component in the PBS buffer for the data presented in Fig. 4 of the main text.

Table S1 Ionic strengths of the components of PBS buffer after dilution

Percentage of Initial Ionic Strength [%]	Ionic Strength of Na_2HPO_4 [mM]	Ionic Strength of NaCl [mM]	Total Ionic Strength [mM]
100	10	80	90
50	5	40	45
20	2	16	18
10	1	8	9

Electronic Supplementary Information References

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