Experimental Section

Materials and experimental methods:

Bovine serum albumin (BSA), concanavalin A from Canavalia ensiformis (Jack bean) (Con A), cathepsin D from bovine spleen (CathD), lysozyme from chicken egg white (Lyz), human haemoglobin, fluorescein conjugated BSA (FITC-BSA), FITC labelled ConA (FITC-ConA), “poly-L-lysine (PLL) solution 0.1 % (w/v) in H₂O, 4-Cyano-4-pentylbiphenyl (5CB LC) and 5mM tris buffered saline (TBS) (pH 7.4) was obtained from Sigma-Aldrich (St. Louis, MO)” as mentioned in our earlier report [1]. “Deionization of a distilled water (DI water) source was performed using a Milli-Q-system (Millipore, Bedford, MA)” as reported earlier [1]. Glass microscopic slides (Fisher’s Finest Premium grade) were purchased from Fischer Scientific (Pittsburgh, PA).

Preparation of PLL modified 5CB (PLL-5CB) droplets

PLL-coated droplets were prepared according to our previous reported procedure. [1] As described in reference [1], “10 μL of 5CB in 1mL DI water was vortexed for 10 s and sonicated for 10 min. The resultant white emulsion was centrifuged at 5000 rpm for 5 min and the supernatant was replaced by 1 mg/mL PLL aqueous solution. The PLL-5CB droplets were kept for 15 min at room temperature for the adsorption of PLL on the 5CB droplets. The PLL-5CB droplets were then washed with DI water through centrifugation in order to remove the excess PLL and then the PLL-5CB droplets were re-suspended” in TBS for further experiments. As per our prior report [1], “size of the polydispersed PLL coated 5CB droplets ranges from 5 μm to 40 μm as observed by polarized optical microscopy.
(POM). To estimate the number of droplets in the emulsion, 1 μL of the PLL-5CB droplet solution was placed on a clean glass slide and multiple POM images were captured to illustrate the large sample area. From the POM images, the total number of droplets was counted to be ~ 2 x 10^3 droplets per μL.” Aqueous solutions of BSA, ConA, CathD and Lyz were prepared in TBS. In a typical experiment, a certain volume of emulsion was placed on the glass slide and 5 μl of the protein solution of required concentration was added on that. The droplets were imaged after certain time under polarized optical and bright field microscope. More information related to characterization of LC droplets can be found in Figure S1 and S2.

**Optical Characterization of PLL-modified 5CB droplets**

PLL-LC droplets were characterized as described earlier. [1] “The orientational ordering of the LC was determined using a Zeiss polarizing microscope Scope. A1 with cross polars (X200 and X1000). All the images were captured using a AxioCam Camera.”

**Epifluorescence Imaging of PLL-5CB droplets**

Epifluorescence imaging was carried out as per our previous described procedure. [1] “Fluorescence imaging was performed with a Zeiss (Scope. A1) fluorescence microscope. The samples were viewed using a fluorescence filter cube with a 460 nm excitation filter and a 534 nm emission filter. Images were obtained with an AxioCam camera.”

**Zeta potential measurements**

Zeta potential of LC droplets was measured by the following method as explained earlier. [1] Briefly, “Zeta potential measurements of the PLL coated 5CB droplets were carried out using Zetasizer Nano ZS90 (Malvern Instruments Inc.) at room temperature under a cell-driven voltage of 30 V, in which 40 μL of PLL-5CB droplets were diluted with TBS to make total 800 μL solution before adding into the zeta potential cuvets and the average of 5 scans was taken for each measurement.” For experiments with proteins, 10 μL of 1 mg/mL BSA or Con A or CathD was added to the 40 μL droplets solution and incubated for 15 minutes before diluting to 800 μL with TBS.

**Characterization of LC droplets and addition of protein:**
It should be noted that images in manuscript were captured after several attempts to show the transition in same droplets by using the following method. The protein solution was added very carefully from the side at an angle avoiding the contact of pipette tip with emulsion so as to not disturb the focused frame hastily. Also the subsequent protein/water addition on focused PLL-LC droplets causes more disturbances on the upper droplets as compared to the bottom droplets. The small droplets (1-5 μm) (even if at the bottom) were found more dislocated, however the larger droplets were found very stable and more or less at the same location after addition of proteins. If the protein solution is added abruptly (Figure S1), the majority of LC droplets abruptly moves out of the frame and settles at different place. Therefore, adsorption of LC droplets on glass surface can be ruled out.

**Figure S1.** Polarized optical microscopic (POM) images of PLL-LC droplets before (A) and just after (B) abrupt addition of 2 mg/mL BSA. Few droplets are on the same position (indicated by circles), however majority of the droplets are moved to different location and also out of the focused frame. The droplets cannot be considered adsorbed on surfaces.

Next, we demonstrate that protein adsorbed PLL-LC droplets show bipolar configuration regardless of their location (diffusing or on surface) on the glass slide. PLL-LC droplets (50 μL) were incubated with 2 mg/mL BSA (50 μL) for 15 min in a small tube. Upon transferring on glass slide, again the droplets were found in different planes (Figure S2). However, the configuration was bipolar in the diffusing droplets as well as in droplets on the bottom plane also confirming that the radial to bipolar transition is due to the adsorption of protein on PLL-LC droplets and not due to glass surface.
Figure S2. POM images of PLL-LC droplets after incubating with 2 mg/mL BSA: A) mobile droplets in upper plane and B) less mobile droplets in bottom plane showing bipolar configuration. Insets show the magnified yellow marked area.

Figure S3. Polarized optical (a) and corresponding bright-field (b) micrographs of BSA modified PLL coated LC droplets after 3 days of addition of 1 mg/mL BSA. Scale bar = 50 µm.
**Figure S4.** (a-h) Polarized optical (top) and corresponding bright-field (bottom) micrographs of PLL coated LC droplets before (a,c,e,g) and after 15 min in contact with (b) 20 (d) 10 (f) 1 (h) 5 ng/mL BSA on 1 µL PLL-coated LC droplets at pH 7.4. The insets within (a-p) illustrate the higher magnified version of the arrow marked LC droplet. Scale bar = 100 µm.

**Figure S5.** Epi-fluorescence (a) and corresponding bright field (b) images of PLL-coated 5CB droplet suspended in 5mM Tris buffer at pH 7.4 after incubation with 1 mg/mL FITC-labelled ConA. Green fluorescence at droplet surface confirms the adsorption of ConA on PLL modified 5CB droplet.
Figure S6. Polarized optical (a,b) and corresponding bright-field (c,d) micrographs of PLL coated LC droplets before (a,c) and 15 min after addition of (b,d) 0.05 mg/mL Con A on 5 µL of PLL-coated LC droplets at pH 7.4. The LC droplets were in radial states before and remained radial. The insets within (a-d) illustrate the higher magnification version of the arrow marked LC droplet. Scale bar = 100 µm.
Figure S7. (a-h) Polarized optical (top) and corresponding bright-field (bottom) micrographs of PLL coated LC droplets before (a,c,e,g) and after 15 min of subsequent addition of b) 0.5 mg/mL d) 0.1 mg/mL f) 0.05 mg/mL h) 0.5 µg/mL Con A on 1 µL PLL-coated LC droplets at pH 7.4. The LC droplets were in radial states before but transitioned to bipolar state after addition of ConA. The insets within (a-h) illustrate the higher magnification version of the arrow marked LC droplets. Scale bar = 100 µm
Figure S8. Polarized optical microscopy images of PLL droplets at 0 min (a,c) and 10 min (b,d) after addition of 250 μg/mL (b) and 100 μg/mL (d) of aqueous solution of Hemoglobin. Scale bar = 100 μm.

Reference:

[1] Verma I, Sumyra S, Pal SK. Poly(l-lysine)-coated liquid crystal droplets for sensitive detection of DNA and their applications in controlled release of drug molecules. ACS Omega 2017;2:7936–7945.