

## Electronic Supplementary Information

### **Brownian Motion Retarded Polymer-Encapsulated Liquid Crystal Droplets Anchored over Patterned Substrate via Click Chemistry**

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## Materials Used

Butanethiol, *N*-(bromomethyl)phthalimide, propargyl acrylate, poly(sodium 4-styrenesulfonate) (PSS, Molecular wt~70,000), poly(allylamine hydrochloride) (PAH, molecular wt~56,000), 3-aminopropyltriethoxysilane (APTES), 4'-pentyl-4-biphenylcarbonitrile (5CB), phospholipase A<sub>2</sub> (PLA<sub>2</sub> from porcine pancreas), 1,2-dimyristoyl-sn-glycero-3-phosphoethanolamine 7-nitrobenzofurazan-labeled (L-DLPC), sodium dodecyl sulfate (SDS), rhodamine B isocyanate-Dextran (RITC), [1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide methiodide (EDC), 4-pentynoic acid, dialysis tube, 3-chloropropan-1-ol, acryloyl chloride and 3-chloro-1-propanthiol were purchased from Sigma Aldrich and used without further purification.

Carbon disulfide, chloroform, dioxane, ethanol, hydrogen peroxide, copper sulfate pentahydrate, NaCl, hydroquinone, dichloromethane, dimethyl sulphoxide, caustic soda beads, TBS[tris(hydroxymethyl)aminomethane] were purchased from Merck. Triethylamine, sulfuric acid, calcium chloride, hydrochloric acid, sodium sulfide were purchased from Fisher Scientific and HF, sodium azide from Loba Chemie; ascorbic acid from Rankem- Ranbaxy; silica particles from Tessek (Berlin); PEI(Molecular wt~70,000) from Alfa Aesar; magnesium sulfate from BDH GPR E. Merck, acrylic acid from central drug house pvt. limited, azobisisobutyronitrile from Ajax Chemicals lab and nitrogen from BOC were used without further treatment and PBS buffer specification of DI water

## Azide and alkyne functionalization of glass substrate

A small piece of glass slides were cleaned by the Piranha solution (Sulphuric Acid and Hydrogen peroxide (30%) in 3:1) for 30 mins at 100°C (*Caution!! Piranha solution is highly corrosive*).Further, glass slides were placed in ethanolic solution of 3-chloro-1-propanthiol (25

mM for 60 h at room temperature. Further, chloro-functionalized glass slide were placed in 2.5 ml of sodium azide solution (25 mol %) for 48 h followed by washing with water.

For Alkyne functionalization of piranha washed glass slides, first slides were kept in APTES solution (5%v/v in ethanol) for 24 h and then kept in a solution of 4-pentynoic acid (50 mM) and EDC (100 mM) in PBS buffer solution for 7 h. Finally, alkyne-functionalized glass slides were washed with ethanol and water.

### **Preparation of butyl phthalimidomethyl trithiocarbonate (RAFT agent)**

Butanethiol (3.0 g, 0.033 mol), carbon disulfide (5.06 g, 0.066 mol) and chloroform (20 mL) were mixed in a dry round-bottomed flask and triethylamine (6.9 g, 0.068 mol) was added drop wise with continuous stirring. Color of solution changes to yellow as the addition proceeded due to formation of the intermediate triethylammonium butyl trithiocarbonate. Further, the solution was stirred at room temperature for a 3 h and followed by slow addition of *N*-(Bromomethyl) phthalimide (7.99 g, 0.033 mol) to form the bromide salt. The mixture was further stirred for 16 h and then diluted with an additional chloroform (20 mL). Washed the mixture twice with de-ionized water, 2 M H<sub>2</sub>SO<sub>4</sub>(aq), and saturated brine sequentially. The solution was dried and rotary evaporated the solvent to give a yellow solid.<sup>1</sup>

Yield=12 g (97%); <sup>1</sup>H NMR(CDCl<sub>3</sub>): 0.92 (tr,3H, CH<sub>3</sub>-), 1.41 (m,2H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 1.68 (m,2H, CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.37 (tr,2H, (-CH<sub>2</sub>- S), 5.65 (s, 2H, N-CH<sub>2</sub>-S), 7.74 (m, 2H, ArH), 7.87 (m, 2H, ArH).

### **Preparation of 3-chloropropyl acrylate**

3-chloropropan-1-ol (8.27 mL), triethylamine (17.57 mL) and hydroquinone (0.1 g) were added to dichloromethane (50 mL) and stirred for 10 min. Acryloyl chloride (9.53 mL) was added drop-wise under argon at 0 °C to above mixture and kept the solution on stirring for 60

min at 0 °C followed by overnight stirring at room temperature. The reaction was purified by washing with 100 mL water (twice), 0.5 M HCl, 100 mL water (twice) and then dried with magnesium sulfate (MgSO<sub>4</sub>). The crude product was purified by rotary evaporation. Approximately 3 mL (38% conversion) of clear liquid was produced.<sup>2</sup>

<sup>1</sup>H NMR (CDCl<sub>3</sub>): 2.11 (m, -CH<sub>2</sub>-), 3.60 (m, -CH<sub>2</sub>-Cl), 4.28 (m, -O-CH<sub>2</sub>-), 5.8 (d, =CH<sub>2</sub>), 6.09 (m, =CH-) 6.38 (d, =CH<sub>2</sub>).

### **Preparation of alkyne-functionalized poly(acrylic acid) (PAA<sub>Alk</sub>)**

Acrylic acid (90.6×10<sup>-2</sup> g, 0.013 mol), propargyl acrylate (18.1×10<sup>-2</sup> g, 0.0016 mol), RAFT agent (butyl phthalimidomethyl trithiocarbonate) (7.6×10<sup>-4</sup> g, 0.00023 mol) were mixed in the molar ratio of 540:60:1 in 4 ml dioxane followed by addition of 10 wt% azobisisobutyronitrile (2.0×10<sup>-1</sup> mg, 0.0012 mmol) relative to the RAFT agent. After purging with nitrogen for 45 min solution were kept on constant stirring at 60 °C for 11 h to carry out the polymerization. After polymerization the product was dialyzed for 24 h to remove excess monomer and freeze dried to obtain the solid yellowish powder.<sup>3</sup> <sup>1</sup>H NMR (D<sub>2</sub>O): 0.90-1.42 CH<sub>2</sub> (polymer), 1.74-2.08 CH (polymer), 2.70-3.13 triple bond CH (polymer), the final polymer peak is combined with the solvent peak at 4.47-4.74 OCH<sub>2</sub> (polymer).

### **Preparation of azide-functionalized poly(acrylic acid) (PAA<sub>Az</sub>)**

Acrylic acid (89.9×10<sup>-2</sup> g, 0.012 mol), 3-chloropropyl acrylate (31.7×10<sup>-2</sup> g, 0.0021 mol), RAFT agent (butyl phthalimidomethyl trithiocarbonate) (15.3×10<sup>-3</sup> g, 0.00047 mol), and 5 mL dioxane are mixed in the molar ratio of 255:45:1 followed by addition of 10 wt% azobisisobutyronitrile (4.0×10<sup>-1</sup> mg, 0.0024 mmol). The mixture was purged by bubbling with nitrogen for 45 min and kept at 60°C for 14 hrs with constant stirring. The excess monomer was

removed by the dialysis for 12 h through the dialysis membrane. The dialysis product was then stirred for 24 h in 0.29g of sodium azide at 80°C. The final polymer was dialyzed again to remove the excess azide for 24 h and freeze dried to obtain the dry powder.<sup>3</sup> <sup>1</sup>H NMR (D<sub>2</sub>O): 1.79(s, -CH<sub>2</sub>- and -CH- polymer), 2.3(tri, pendant-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.66(tri, pendant CH<sub>2</sub>N<sub>3</sub>), 4.64 (tri, pendant OCH<sub>2</sub>).

### **LC droplets encapsulated polymer capsule**

10 mg of APTES-modified silica particles<sup>4</sup>, were washed with 0.5M NaCl. Further, 1ml of PSS polymer solution (1mg/ml of NaCl) was added to APTES-modified silica particles and incubated for 15 mins. Particles were precipitated through centrifugation at 1000 rcf for 2 min followed by thrice washing with DI water. Further, PAH solution (1mg/ml of NaCl) was added to PSS coated silica particles and repeated the same procedure upto eight layers of PSS/PAH polymer. Furthermore, additional 9<sup>th</sup> layer of either PAA<sub>Alk</sub> or PAA<sub>Az</sub> (1mg/ml NaCl concentration) were added to facilitate the click reaction with glass substrates. Silica core was then etched out using NH<sub>4</sub>F-HF buffer solution and washed 5 times with water. For LCs encapsulation, hollow capsules were washed with ethanol and incubated with 5CB LC for 24 h. followed by washing with water to remove excess LC and redispersed in water.<sup>5</sup>

### **Patterned functionalization of glass substrate using micro-contact printing process**

#### **a) Fabrication of Stamps**

The imprinting process was carried out using cross-linked PDMS (commercially available two parts cross linkable Polydimethylsiloxane (PDMS); Dow Corning, USA) stamps. The stamps were fabricated in two steps: (i) a master stamp pattern was fabricated using a Maskless

Lithography System (SF-100 from Intelligent Micro patterning LLC, St. Petersburg, FL); (ii) PDMS stamps were fabricated by replica molding of Sylgard 184 on this master stamp.

### **Fabrication of Master Stamp**

For making the master stamp a software mask was designed in MS Paint<sup>®</sup> which was used by the lithography system. Microscopic glass slide (Riviera<sup>™</sup>, India) of size 15 mm x 15 mm was used as substrate. The glass slide was sonicated in acetone and then water for 15 min each and then dried in a stream of nitrogen. On thoroughly cleaned glass slide Shipley 1818 (Rohm and Hass Electronic Materials, USA) positive photo resist of was spin coated at 1000 rpm for 30 s (Ducom, India). To remove the casting solvent the sample was then soft baked on the hot plate at 95 °C for 1 min prior to exposure. The photo-resist sample was then exposed to UV mercury lamp for 20 s (power density~15 mW/cm<sup>2</sup>) through a digital micro-mirror device (DMD) attached with the maskless lithography system. DMD micro-mirror arrays can pattern over ~ 1 cm<sup>2</sup> area. The samples were then developed in Shipley developer (Rohm and Hass Electronic Materials, USA) which was carried out in a glass beaker for 30 s with constant stirring. The surface patterns were characterized using an optical profiling system (NanoMap-D, Aep Technology, U.S.A.). The reproducibility of the structures was checked in 3 different samples.

### **Fabrication of PDMS Stamps for Imprinting**

Sylgard 184 consisting of oligomer (part A) and cross-linking agent (part B) was used to prepare the stamps for imprinting. Part A and part B were thoroughly mixed in the ratio 10:1 by volume followed by degasification to remove the entrapped air. It was then poured on the master stamp. The thickness of the PDMS stamp was maintained by forming a wall around the patterned area made of glass slides (1 mm thick) cut into small narrow pieces. After molding, it was cured

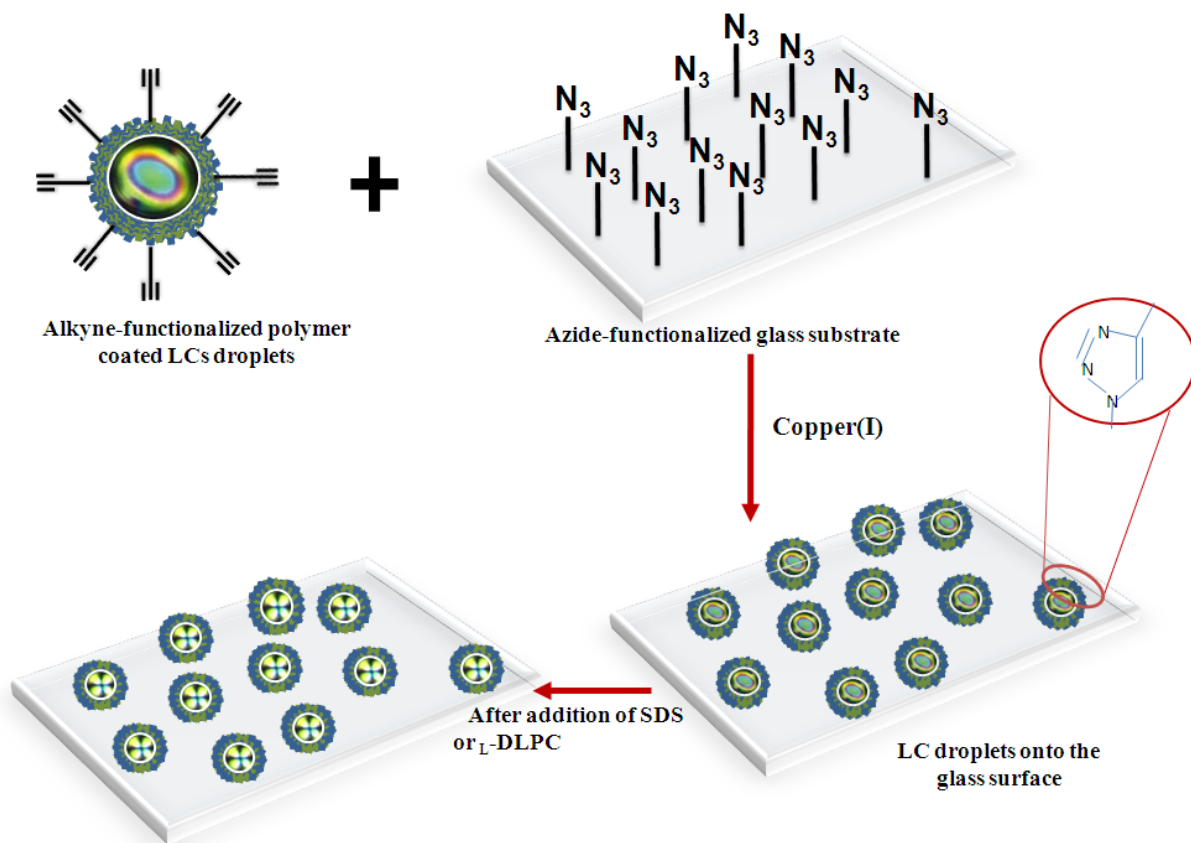
at 120 °C for 12 h to complete the cross-linking which made the patterns permanent. The cured PDMS elastomeric stamps were cooled to room temperature and then peeled from the master.<sup>6</sup>

### **b) Imprinting Process to form the Chemical Patterns**

The imprinting process was carried out on thoroughly cleaned glass slides/silicon wafer. For micro-contact printing the PDMS stamp was soaked in the 3-bromopropyltrichlorosilane solution in n-hexadecane and chloroform (7:3) for 5 min. Next, the PDMS stamp was dried in a stream of nitrogen to remove the solvents and then placed in conformal contact with the substrate for 1 min. Further, the patterned bromine functionalized glass substrate was placed in sodium azide solution for 48 h to replace the bromine group with azide group.<sup>7</sup>

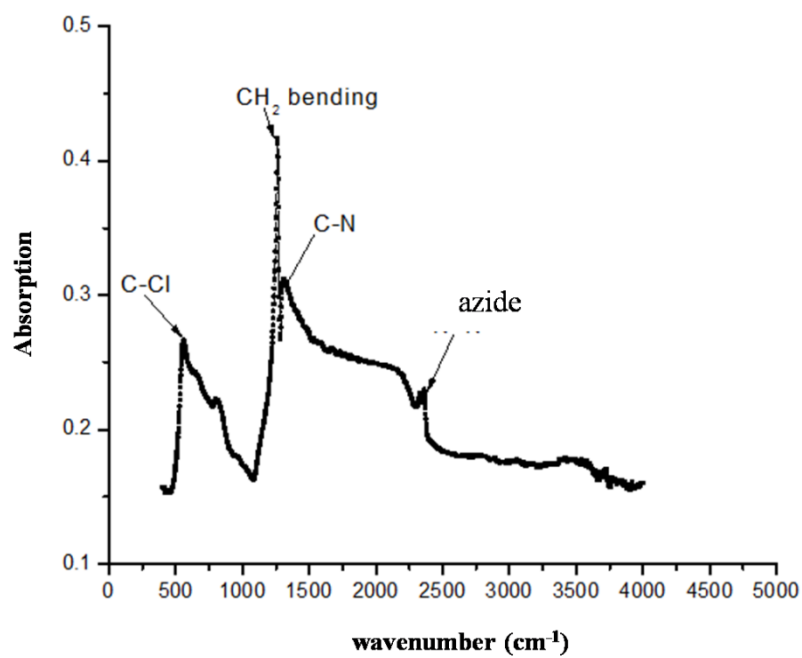
### **Reference**

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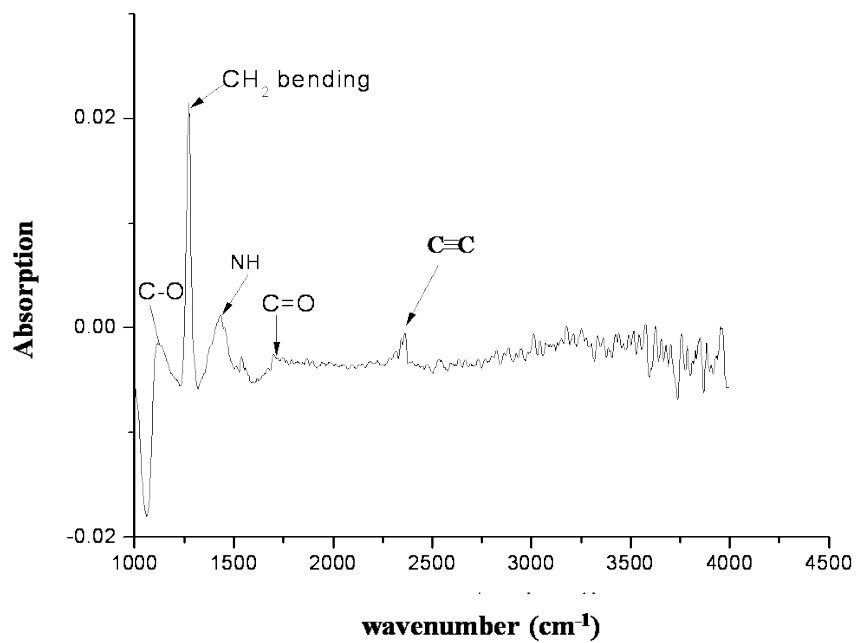


**Scheme S1.** The schematic representation of anchoring of alkyne-functionalized LC droplets encapsulated polymer-capsule on azide-functionalized glass substrate via click chemistry.

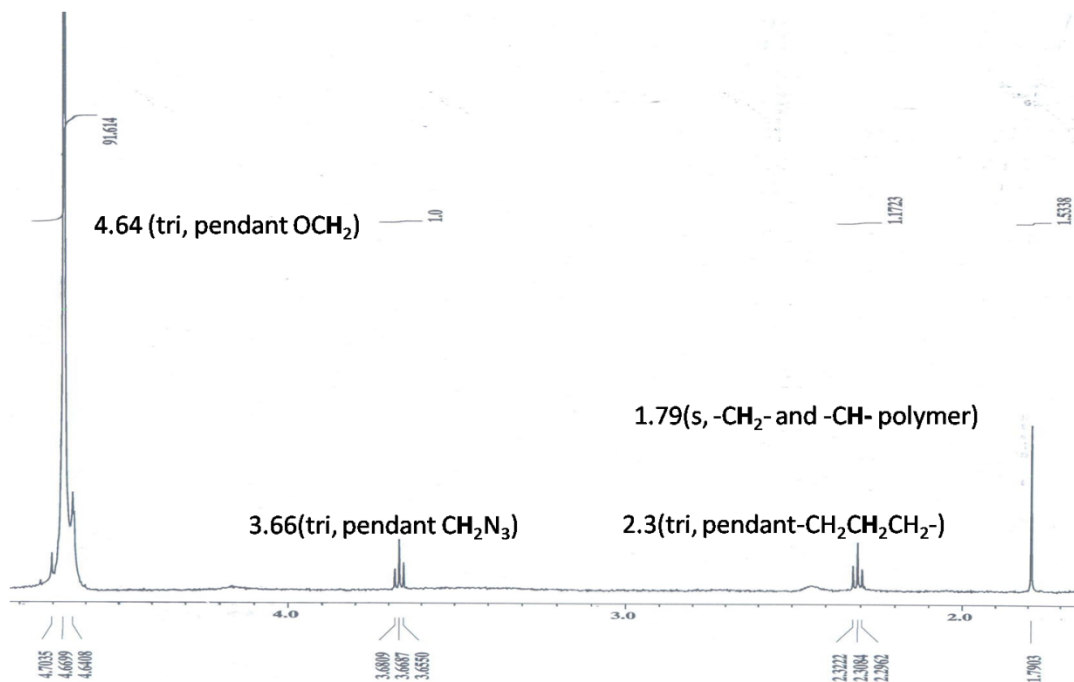




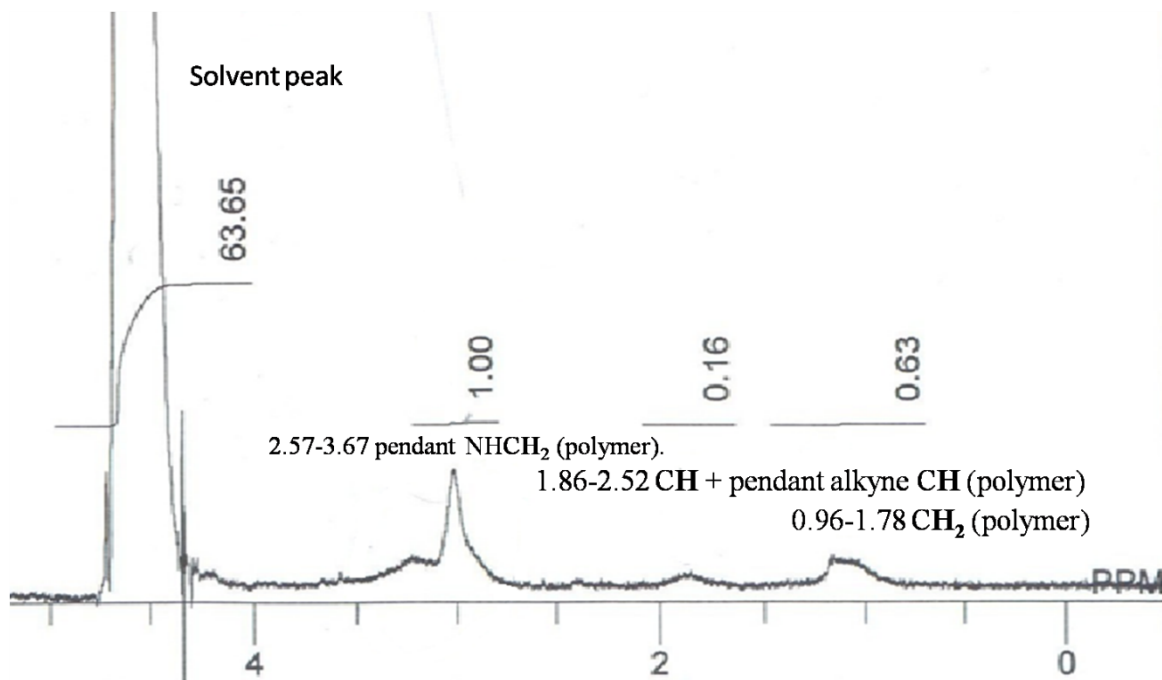
**Fig. S1.** FTIR spectra of azide-functionalized glass substrate. Spectra were taken in absorption mode.



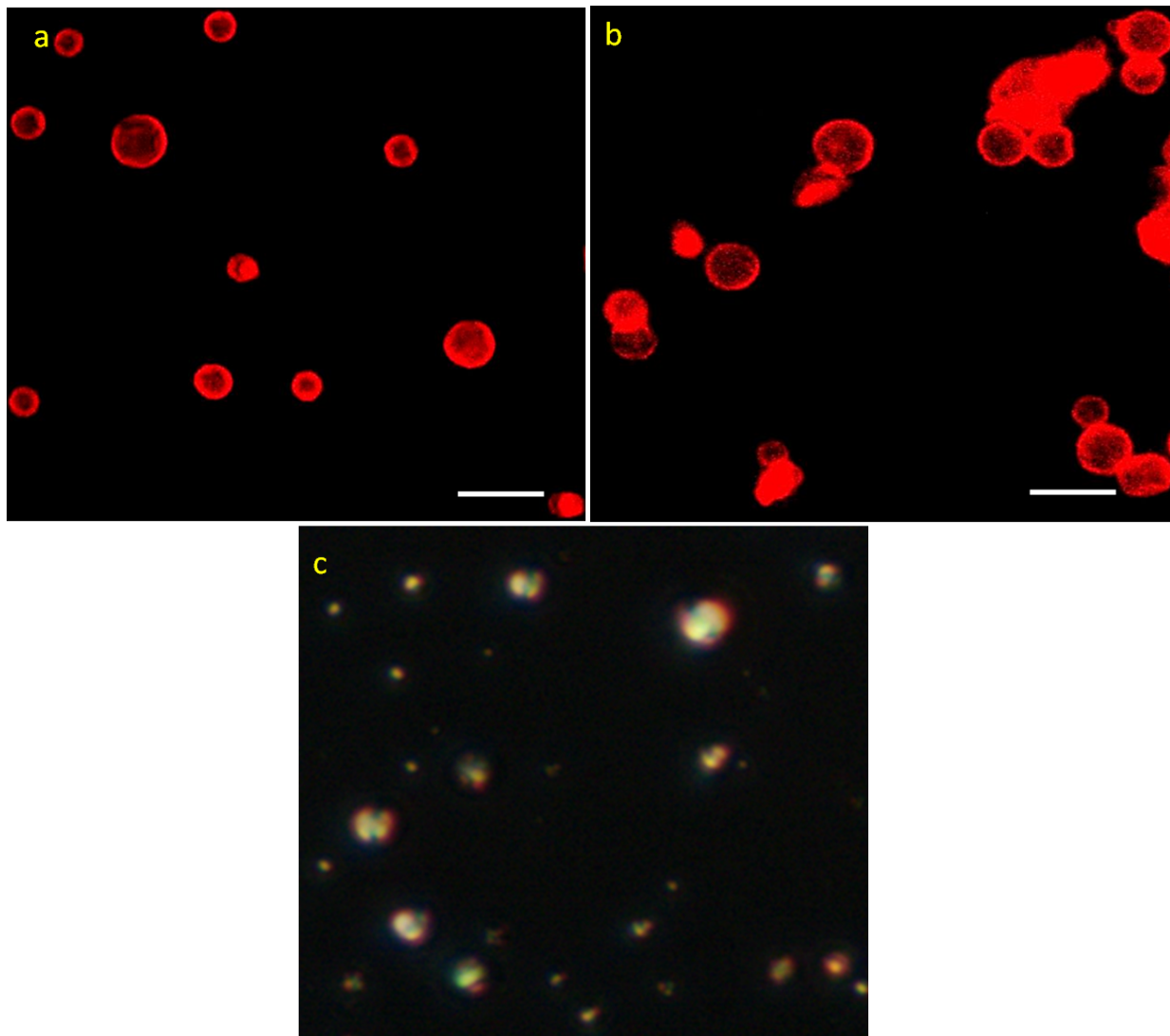
**Fig. S2.** FTIR spectra of alkyne-functionalized glass substrate. Spectra were taken in absorption mode.



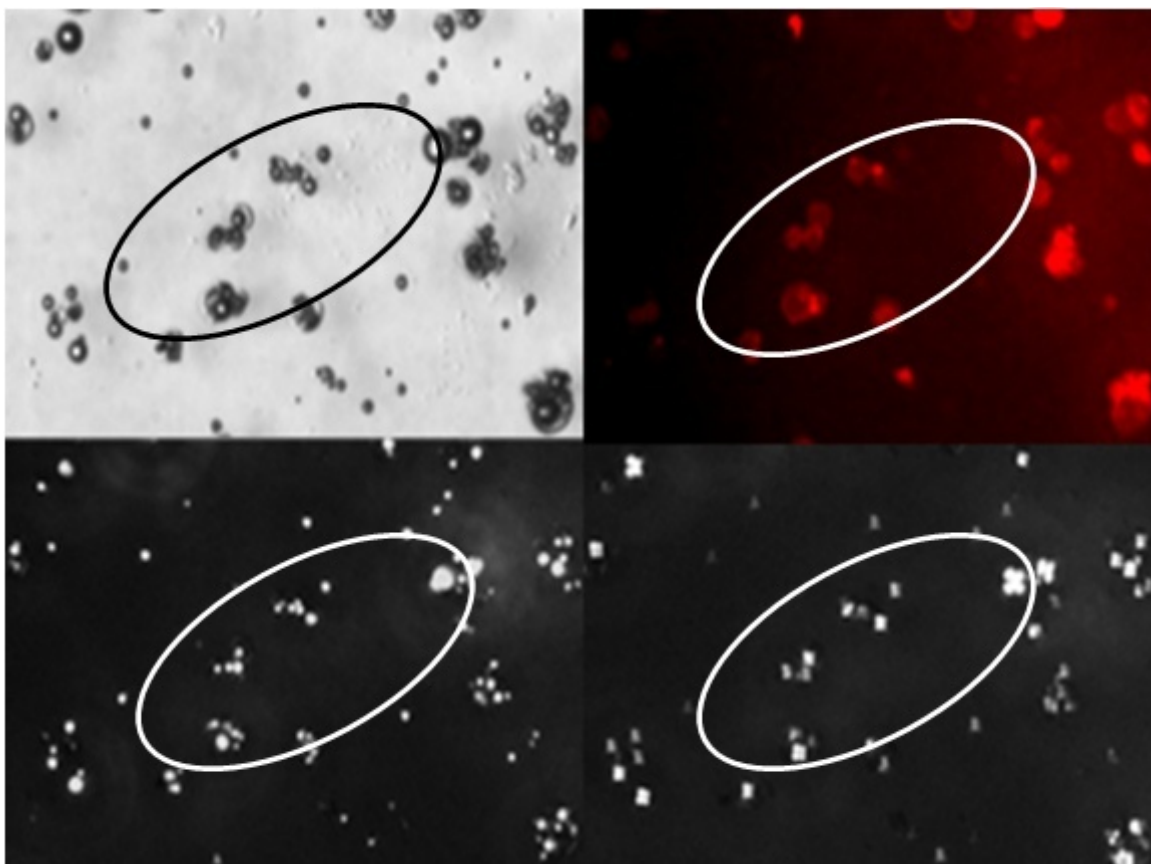
**Fig. S3.** <sup>1</sup>H NMR spectra of azide-functionalized poly (acrylic acid) polymer.



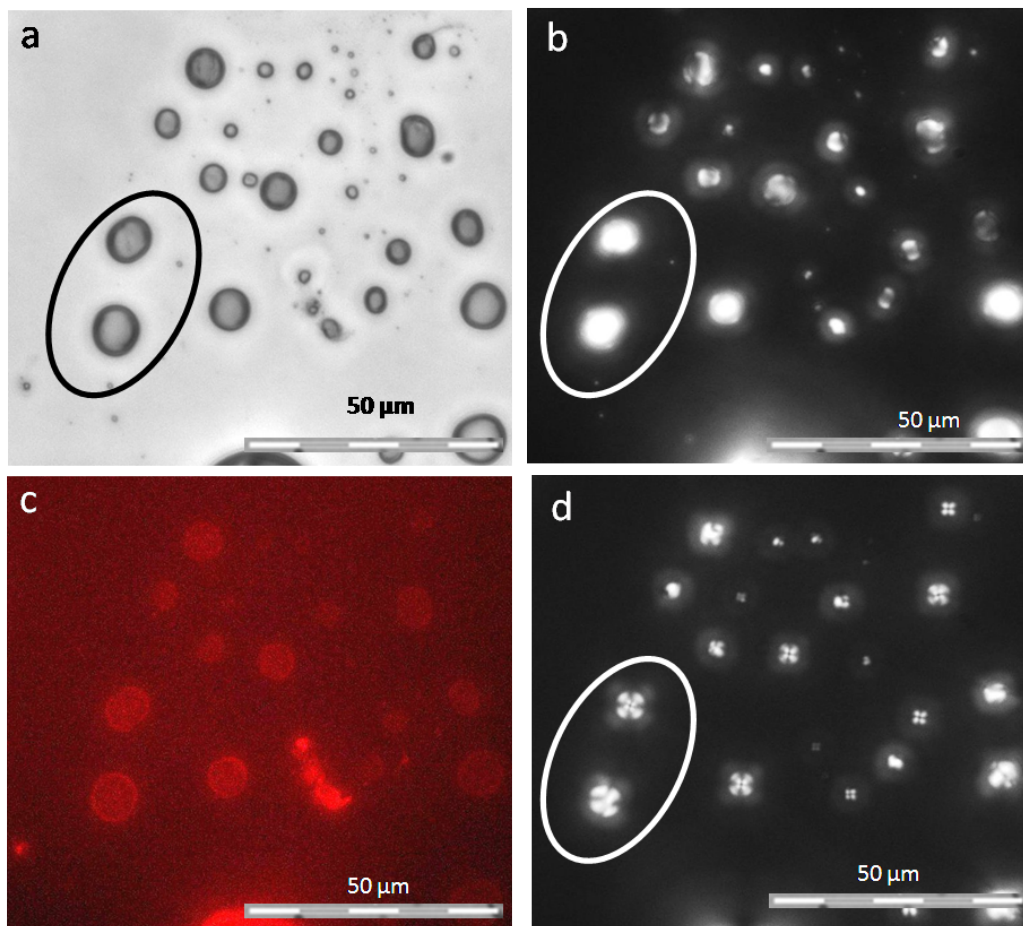
**Fig. S4.**  $^1\text{H}$  NMR spectra of azide-functionalized poly (acrylic acid) polymer.



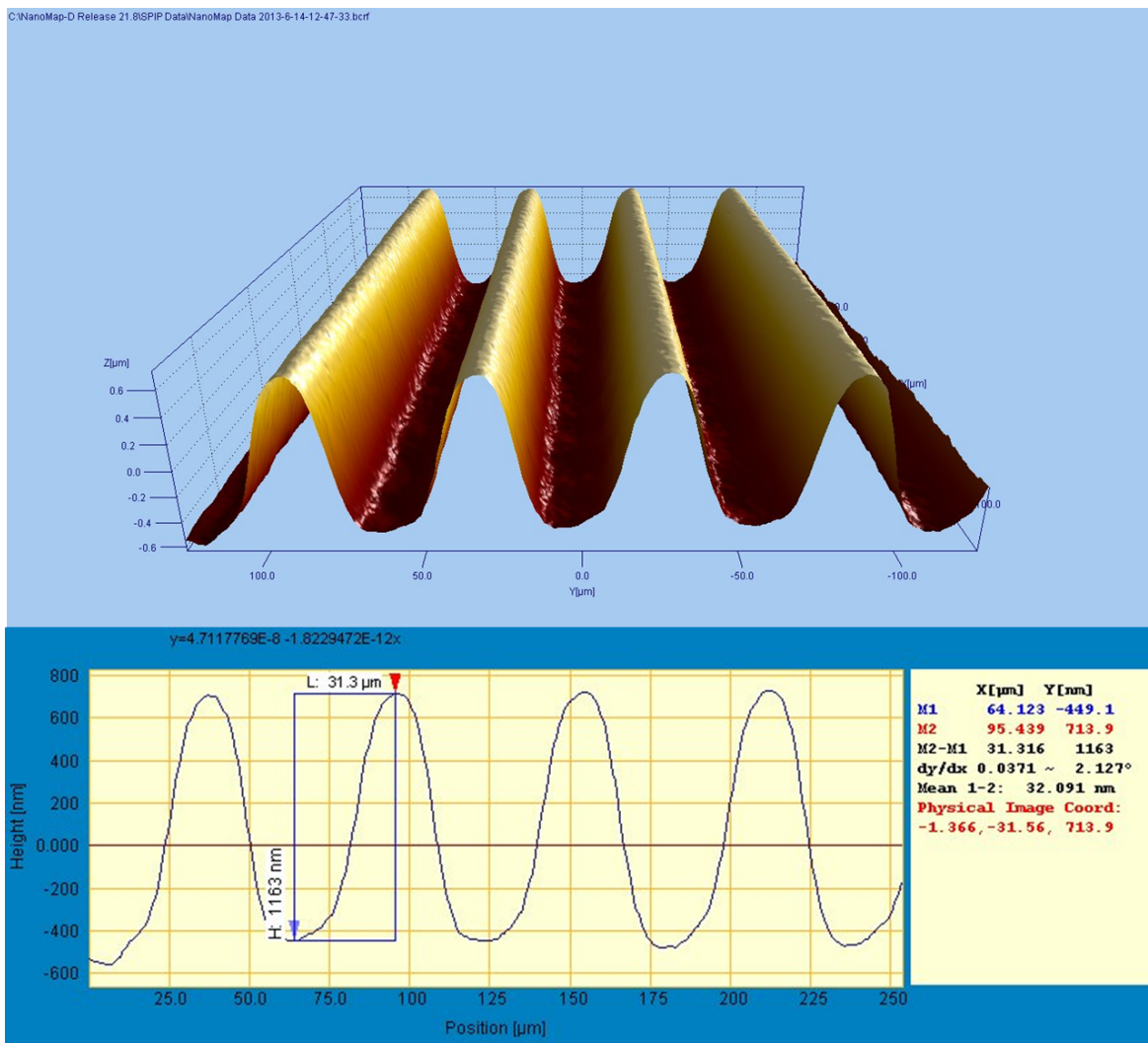
**Fig. S5.** Confocal fluorescence image of (a) hollow polymer capsules, (b) polymer capsules after encapsulation of LC (5CB) and (c) polarized light micrograph of LC encapsulated in polymer capsules before immobilization on glass substrate via click reaction (scale 10 $\mu$ m).



**Fig. S6.** (a) Bright field, (b) polarized light and (c) fluorescence microscopy images of immobilized alkyne-functionalized LC encapsulated PEM capsules on azide-functionalized glass substrate via click chemistry and (d) polarized after the addition of SDS after ~ 6 months in water. Scale 50 $\mu$ m.

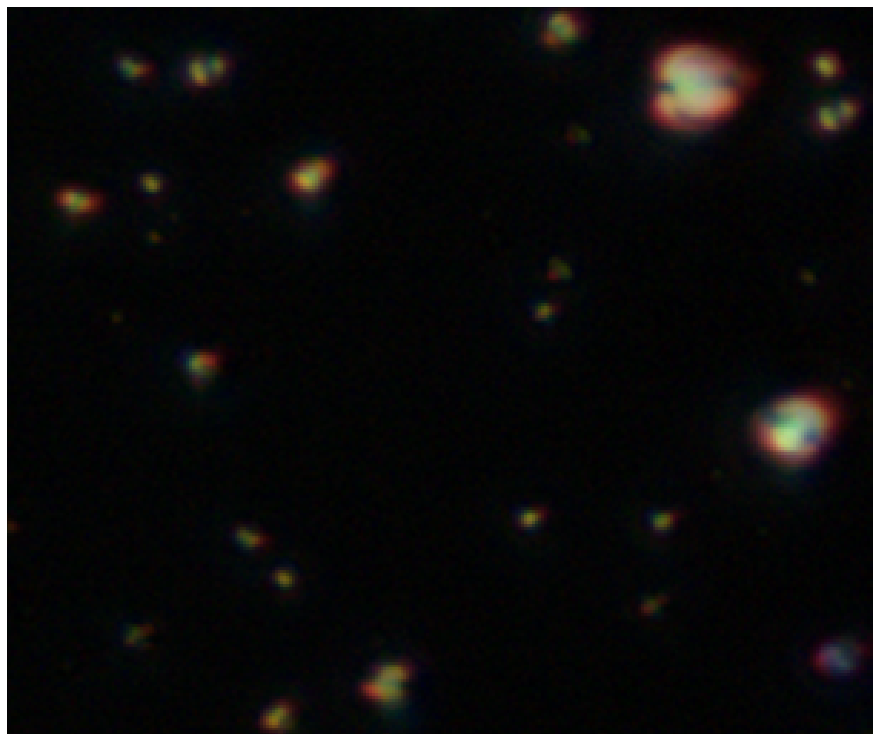


**Fig. S7.** (a) Bright field, (b) polarized light and (c) fluorescence microscopy images of anchored alkyne-functionalized LC droplets encapsulated polymer-capsule on azide-functionalized glass substrate via click chemistry and (d) polarized after the addition of  $L$ -DLPC. Scale 50 $\mu$ m.



**Fig. S8.** Profilometer image of fabricated PDMS stamp.





**Fig. S9.** (a) Bright field images of patterned immobilized alkyne-functionalized LC encapsulated PEM capsules on azide-functionalized glass substrate via click chemistry. Scale 10 $\mu$ m.