Electronic Supplementary Information

Blue Phase Liquid Crystal Microcapsules: Confined 3D Structure Inducing Fascinating Properties

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Experimental Section

Materials. The LC studied in this work was a mixture of nematic liquid crystal (NLC, BHR-59001, BaYi Space LCD Tech.) and chiral dopant S-811 (4-{[(1-methylheptyl)oxy]carbonyl}phenyl-4-(hexyloxy)benzo ate, Merck), where the dopant concentrations were set to be 28 wt%, 30 wt%, 32 wt% and 34 wt% for the 28-LC, 30-LC, 32-LC and 34-LC, respectively. Two LC samples with the S811 concentrations of 27wt% and 35wt% were used to figure out the critical chiral concentrations to induce BPLCs. The dispersed phases to incubate BPLCMs in the microfluidic chip were prepared by dissolving 2 wt% of 2, 4-tolylene diisocyanate (TDI, Sigma-Aldrich) into the 28-LC, 30-LC, 32-LC and 34-LC at 80 °C, and followed by incubating at 25 °C for 24 h to form stable BPLC solutions. The continuous phase and collecting phase were aqueous solution containing 5 wt% of

sodium dodecyl sulphate (SDS, Sigma-Aldrich) and 5 wt% of tetraethylenepentamine (TEPA, Sigma-Aldrich). All chemicals were directly used without further purifications.

Preparation of BPLCs with wide temperature range. The small-molecule BPLC mixtures were composed of a NLC ($\Delta n=0.195$, $\Delta \epsilon=31.0$) and a chiral dopant S-811 with a HTP of 10.3 μ m⁻¹, and made in two steps (Figure S1). Firstly, 0.72 g, 0.70 g, 0.68 g and 0.66 g of NLCs were added into four sample vials and slowly heated to a temperature 20 °C higher than the clearing point of NLCs, then 0.28 g, 0.30 g, 0.32 g and 0.34 g of S811 were slowly added into the above four vials. The resultant mixtures were kept at 80 °C in an incubator for 10 minutes to completely dissolve the solid S811 and resulted in four homogeneous isotropic fluids. Secondly, the above isotropic fluids were slowly (0.1 °C min⁻¹) cooled down to evolve from an isotropic state to a BPLC state.

Microfluidic device manufacture. The capillary microfluidic device was designed to have two tapered cylindrical capillaries assembled in a square capillary (Zhongcheng quartz glass, Beijing) (Figure 3a). The left cylindrical capillary was tapered by puller (P-1000, Sutter Instrument) and then carefully sanded to have a 120-µm-diameter orifice for the fabrication of 28-LCM and 30-LCM (80-µm-diameter orifice for the fabrication of 32-LCM and 34-LCM). A small amount of 2-[methoxy(polyethyleneoxy)propyl] trimethoxy silane (Sigma-Aldrich) was injected into the capillary to selectively render inner surface of the capillary hydrophilic, after incubation at 100 °C for 30 min, the residual hydrophilic agent was removed by washing with deionized water. The outer wall of the capillary was modified with trimethoxy(octadecyl)silane (Sigma-Aldrich) to render it hydrophobic, after immersion at 100 °C for 30 min, the residual hydrophobic agent was removed by washing with ethanol. The right cylindrical capillary was tapered and sanded to have a 240-µmsurface of the capillary diameter orifice. the whole was treated with 2-[methoxy(polyethyleneoxy)propyl] trimethoxy silane to render it hydrophilic. These two cylindrical capillaries were coaxially assembled in a square capillary (500 μ m×500 μ m).

Preparation of 3D confined BPLCMs using microfluidics and interfacial polymerization. The dispersed phase of LC solutions containing 2 wt% of TDI was injected into the left hydrophilic capillary, the continuous phase of aqueous solution containing 5 wt% of SDS and 2 wt% of TEPA was injected into the interstices between the left capillary and the square capillary. Oil-in-water (O/W) emulsion droplets having innermost oil of the LC/TDI mixture and outer layer of SDS were

generated as templates to incubate the LC microcapsules (LCMs) with single twist structure. The SDS layer could stabilize the O/W interface and create a 3D spherical exterior. A PU layer rapidly generated via polymerization between TDI and TEPA at the droplet interface can further confine the encapsulated LCs. Second, the LCMs were collected in an aqueous solution containing 5 wt% SDS and 2 wt% TEPA, followed by heating the LCMs to 80 °C to form isotropic microcapsules with random orientation. The unreacted TDI in the isotropic fluid with a low viscosity migrated toward the microcapsule surface to carry out the further polymerization and shell ripening. Finally, the mesogens in isotropic microcapsules gradually formed BPLCs via spontaneous self-assembly when decreasing the temperature.

Characterization. The rheological characteristic of LCs at different temperatures was analysed by rotary rheometer (Malvern, Kinexus Pro). The infrared absorptions of TDI, TEPA, LCs and LCMs were determined using a fourier transform infrared (FTIR) spectrometer (PerkinElmer, Spectrum one). The observation of polarized optical textures and reflected optical images of LCMs at different temperatures was conducted by using polarized optical microscope (POM) (Olympus, BX51). The Braag selective reflection experiment of LCs and LCMs was carried out with UV-Vis-NIR spectrophotometer (PerkinElmer, lambda 950). The scanning electron microscopy (SEM) of LCMs was performed using a JEOL JSM-6700F field emission scanning electron microscope. The surface affinity of SDS/PU hybrid film was analysed by contact angle instrument (dataphysics, OCA25). The optical images of LCMs in vials were obtained by a digital camera (Canon, 6D). The temperatures in the whole study were controlled by a Linkam heating and cooling stage at a rate of 0.1 °C min⁻¹. The electric field in electro-optical response measurements of BPLCMs was provided by a LCD tester (North LCD Engineering Center).

Phase behaviour of BPLCs. The fabrication procedure for BPLCs is very simple and controllable, the NLC host is commercially available rod-like biphenyl mixture with a clearing point of 80 °C, the chiral dopant is widely used S811 with a HTP of 10.3 μ m⁻¹. To investigate the effects of the chiral dopant concentration on the generation and thermal stability of induced BPLCs, four kinds of LCs with different S811 concentrations (28 wt%, 30 wt%, 32 wt% and 34 wt%) are prepared (Figure S1), and called the 28-LC, 30-LC, 32-LC and 34-LC, respectively. The function of chiral dopants in the BPLC formation was two folds, one is to induce short pitch in the double twist cylinders by endowing the NLC host with enough twisted power, the other is to enhance the thermal

stability of ordered three-dimensional lattices of BPLCs by minimizing the free energy density. Since the chiral dopant in this work possesses a moderate HTP, therefore, it is important to control the S811 concentration at a relatively high level in order to induce stable BPLCs. The LCs containing 27 wt% and 35 wt% S811 are also prepared by the same procedure as that of above BPLCs to identify the possible concentration range of S811 to induce BPLCs. These LCs are injected into 5 µm thick ITO cells and the textures are observed using a POM with crossed polarisers. When the concentration of S811 is 27 wt%, the clearing point at which sample changes from isotropic phase (IP) to chiral nematic phase (CNP) is determined to be 57.6 °C, and the textures gradually grow from sphere droplets to focal cones (typical texture of CNP^[1]) (Figure S2a1-a4), and BP textures are not observed with the decrease of temperature due to the insufficient chirality. When increasing the concentration of S811 to 28 wt%, a clearing point at 54.4 °C at which sample changes from IP to BP is observed, on cooling, the isotropic liquid firstly exhibits some small platelets (typical texture of BP^[1]) without focal cones, and finding all areas are finally occupied by the platelets textures, on further cooling, the LC mixture experiences the transition from BP to CNP, and the texture changes to focal cones, however, these tiny platelets seem to be dim and can not reflect bright colour (Figure S2b1-b4). When the concentrations of S811 are further increased to 30 wt%, 32 wt% and 34 wt%, LC mixtures exhibited the phase transition from IP to BP to CNP. Due to the solubility limit of solid S811 in the chiral nematic liquid crystals, when the concentration of S811 reaches 35 wt%, on one hand, a BPLC with green platelets can be formed at higher temperature (42.0 °C). On the other hand, the BPLC mixture occurs phase separation at lower temperature (32.2 °C) (Figure S2f).

The addition of S811 leads to a dramatic decrease of clearing point from 80 °C to 44.9 °C (Figure S2g), although S811 exhibits a monotropic smectic A (S_mA) phase.^[2] The reason for this reduced temperature points corresponding to the transition from IP to LC phase (CNP or BP) (T_{IP-LC}) is caused by the relatively low T_{IP-LC} of S811 (isotropic state-41°C-S_mA-22°C-crystal)^[3] and the disturbance to interactions of pristine NLCs by the heterogeneous doping of S811. When the concentrations of S811 increase from 28 wt% to 35 wt% in BPLC mixtures, the phase transition temperatures from BP to CNP (T_{BP-CNP}) also show an obvious decrease from 45.2 °C to 32.2 °C (Figure S2g). It is worth noting that temperature range of BPLCs ($\Delta T=T_{IP-BP}-T_{BP-CNP}$) is increased from 9.2 °C to 12.0 °C when the concentrations of S811 are increased from 28 wt% to 34 wt%



Figure S1. Schematic of two-step preparation of BPLCs with three-dimensional architecture.



Figure S2. Temperature dependence of reflected POM textures of LC mixtures in 5-µm thick cells, images in a-f correspond to the representative textures of different mixtures where the concentrations of S811 are 27 wt%, 28 wt%, 30 wt%, 32 wt%, 34 wt% and 35 wt%. g) Phase diagram determined by POM observation for the LC mixtures. h) BP temperature ranges of 28-LC, 30-LC, 32-LC, 34-LC and 35-LC against the S811 concentrations.

(Figure S2h), this phenomenon may be explained by the following mechanism, increasing the S811 concentration in the LC mixture corresponds to the reduction of NLCs that have a large dielectric anisotropy ($\Delta \varepsilon$ =31.0), hence the decreased $\Delta \varepsilon$ of BPLC mixture, and BPLCs will be more thermostabilized when the $\Delta \varepsilon$ is smaller based on the defect theory and Landau theory for BPLCs.^[4]

In order to confirm the thermal stability of BPLCs, these samples are kept for 24 h within their BP temperature range, the POM images are maintained without any texture change (Figure S3). Thus, it is confirmed that the formation of BPLC is not due to super-cooling but the obtained BP is a thermally stable phase.



Figure S3. a1-e1) The typical BP textures for 28-LC, 30-LC, 32-LC, 34-LC and 36-LC at 51.0 °C, 45.0 °C, 41.0 °C, 40.0 °C and 36.0 °C, a2-e2) BP Textures after preserved for 24 h.



Figure S4. The polymerization equation of TDI and TEPA to form the PU layer.



Figure S5. a) The POM images of the TDI solution (tetrahydrofuran as solvent), b) the collecting phase at 25 °C, both of them are isotropic solution, therefore presenting dark vision between crossed polarizers. c) After mixing together, they form PU network within 2s and present bright vision between crossed polarizers.



Figure S6. The FTIR absorption spectra of TDI, TEPA, pure 32-LC and the 32-LCM.

FTIR results (Figure S6) showed that the LCs possessed characteristic absorption peaks at 1743 cm⁻¹ and 2237 cm⁻¹ corresponding to the C=O and C=N stretching vibrations, respectively. The unreacted TDI possessed strong characteristic absorption peaks at 2265 cm⁻¹, which was attributed to the N=C=O stretching vibration. The unreacted TEPA possessed moderate characteristic absorption peaks at 1474 cm⁻¹ and 1315 cm⁻¹ corresponding to the CH₃/CH₂ asymmetric bending vibration and C-N stretching vibration, respectively. After interfacial polymerization, the resultant BPLCMs did not exhibit absorption at 2265 cm⁻¹, indicating that the TDI mixed in the LCs was completely changed into a part of the PU network. Moreover, the absence of absorption at 1474 cm⁻¹ and 1315 cm⁻¹ in BPLCMs proved that LCs were successfully confined in the PU shell.



Figure S7. a-d) Size distribution of 28-LCM, 30-LCM, 32-LCM and 34-LCM at different flow rate profiles, Q_d is fixed at 2 μ Lmin⁻¹, whereas Q_c varies from 40 μ Lmin⁻¹ to 300 μ Lmin⁻¹. e-f) The flow rate dependence of the average size of strictly mono-dispersed LCMs.



Figure S8. a-d) The C_{VS} of 28-LCM, 30-LCM, 32-LCM and 34-LCM prepared at different flow rates.



Figure S9. Sets of photographs of 28-LCM with a size of 304 μ m (a1, a2) and a size of 262 μ m (a3, a4), 30-LCM with a size of 370 μ m (b1, b2) and a size of 334 μ m (b3, b4), 32-LCM with a size of 332 μ m (c1, c2) and a size of 312 μ m (c3, c4) and 34-LCM with a size of 267 μ m (d1, d2) and a size of 239 μ m (d3, d4) precipitated and suspended in deionized water produced by microfluidic capillary chip.



Figure S10. a) Sets of the water contact angles on flat SDS/PU film at 25 °C, 40 °C and 55 °C, b-c) the 30-LC and 34-LC contact angles on flat SDS/PU film at 25 °C, 40 °C and 55 °C.

The outside confinement of the microcapsule consisted of PU and SDS. To identify the surface affinity of microcapsule shell, a SDS/PU hybrid film was obtained by successively adding the TDI solution (tetrahydrofuran as solvent) and the collecting phase onto a glass substrate, because the chemical composition of the hybrid film was the same with that of the microcapsule shell. Therefore, the surface affinity of the microcapsule shell was estimated by analyzing the surface affinity of the hybrid film. Results in Figure S10 show that the contact water angle on the hybrid SDS/PU film was 19.9°±0.6° at 25 °C, which indicated excellent hydrophilicity of the SDS/PU microcapsule shell. The contact angles presented a decreased trend with the increase of temperature. The contact angles of nonpolar 30-LC and 34-LC on the SDS/PU hybrid film were also measured to be 32.8°±0.5° and 42.8°±0.4° at 25°. This affinity between LCs and the SDS/PU film was possibly ascribed to the π - π stacking between aromatic rings on the PU network and BPLC mesogens, and the contact angles also decreased with the increase of temperature as a result of the increased fluidity of mesogens at high temperatures. Meanwhile, the contact angles of 34-LC on the SDS/PU hybrid film were significantly larger than those of 30-LC at 25 °C, 40 °C, and 55 °C. This phenomenon was due to the large viscosity resulting from high concentrations of chiral dopant, which restricted the spread of mesogens on the SDS/PU hybrid film.



Figure S11. a1-d1) The typical POM textures for 28-LCM, 30-LCM, 32-LCM and 34-LCM at 46.0 °C, 42.0 °C, 44.0 °C and 34.0 °C respectively, a2-d2) Textures after preserved for 24 h.



Figure S12. The temperature-dependency of reflectance spectra of 32-LCM.

Table S1. RGB values, tristimulus values, and chromaticity coordinates of 28-LCMs in the process

 of decreasing the temperatures.

Temperature	R	G	В	Х	Y	Ζ	Х	у
50 °C	142	221	150	949.83	1165.55	851.63	0.320	0.393
45 °C	138	235	198	1017.53	1228.71	1120.95	0.302	0.365
40 °C	45	232	211	769.46	1122.72	1193.51	0.249	0.364
38.2 °C	48	231	209	773.76	1121.01	1182.26	0.251	0.364

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Temperature	R	G	В	Х	Y	Ζ	Х	у
48 °C	119	70	76	538.01	444.91	429.12	0.381	0.315
42 °C	162	91	65	681.42	583.66	368.77	0.417	0.357
37 °C	134	63	41	527.72	425.67	232.92	0.445	0.359
32.8 °C	26	56	126	312.49	290.65	708.04	0.238	0.222

Table S2. RGB values, tristimulus values, and chromaticity coordinates of 30-LCMs in the process of decreasing the temperatures.

 Table S3. RGB values, tristimulus values, and chromaticity coordinates of 32-LCMs in the process

Temperature	R	G	В	Х	Y	Ζ	Х	у
40 °C	161	151	70	789.41	858.40	400.13	0.385	0.419
34 °C	62	174	90	578.18	866.19	513.31	0.295	0.442
31 °C	39	129	137	488.79	639.43	773.71	0.257	0.336
28.4 °C	31	77	136	374.42	392.66	765.17	0.244	0.256

Table S4. RGB values, tristimulus values, and chromaticity coordinates of 34-LCMs in the process of decreasing the temperatures.

Temperature	R	G	В	Х	Y	Ζ	Х	у
40 °C	78	213	85	685.15	1060.93	487.55	0.307	0.475
33 °C	186	187	70	921.69	1048.66	402.16	0.388	0.442
27 °C	53	156	99	531.90	775.09	562.64	0.284	0.415
25.4 °C	49	89	89	392.16	462.92	502.92	0.289	0.341

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of decreasing the temperatures.

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Author Contributions

L. -P. C. conceived and designed the study. C.-Y., C. -Z. D., W. -W., and X. -J. L. supervised the research. L. -P. C., Y. -Q., and W. –Z. performed the experiments. All authors discussed the results and contributed to the data interpretation. L. -P. C. wrote the manuscript and all authors commented on the manuscript.