Electronic Supplementary Material (ESI) for Soft Matter.

[*Electronic Supplementary Information (ESI)*]

Compartmentalized Janus droplets of photoresponsive cholesteric liquid crystal and poly(dimethylsiloxane)-based oligomer

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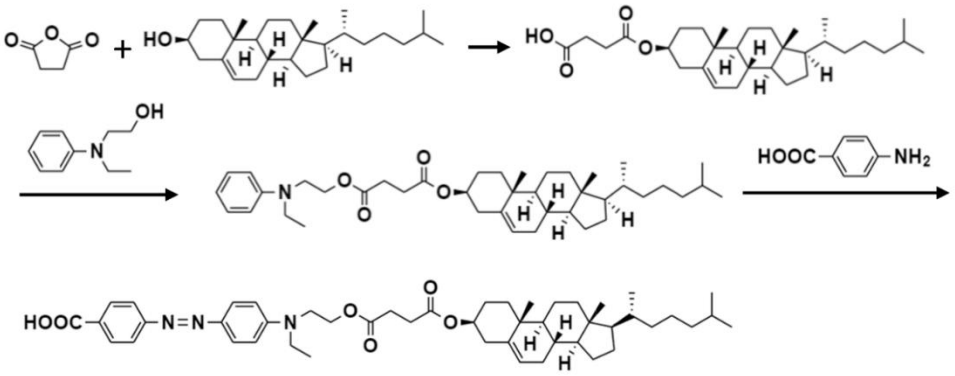
S1. Synthesis

Materials. 4′-Pentyl-4-biphenylcarbonitrile (5CB, 99.8%), *N*-ethyl-*N*-hydroxyethylaniline (99%), and 4-aminobenzoic acid (98%) were purchased from Alfa Aesar and used as received. *Bis*(3-aminopropyl)terminated PDMS (H_2N-PDMS-NH_2, M_n = 2500), 2,6-pyridinedicarbonyl dichloride (98%), succinic anhydride (99%) and cholesterol (98%) were purchased from Sigma-Aldrich. Concentrated sulfuric acid, glacial acetic acid, *N*, *N*-dimethylformamide, tetrahydrofuran, and chloroform were purchased commercially for the azo-coupling reaction and as the solvents. Poly(vinyl alcohol) (PVA, 87-89% hydrolyzed and average M_w 13 000-23 000) was purchased from Shanghai Aladdin biochemical technology. Other chemicals not mentioned above were commercially available products and used without further purification.

The azo-containing chiral compound CA-Chol was synthesized through the route shown in Scheme S1 according to our previous paper,[S1] which is described below in detail.



Scheme S1. Synthesis route of CA-Chol.

Synthesis of Succinic acid cholesteryl ester. Succinic acid cholesteryl ester was prepared according to the literature.[S2] Succinic anhydride (3.3 g, 33 mmol), cholesterol (12.7 g, 33 mmol), and pyridine (0.8 g, 10 mmol) were dissolved into 300 mL of heptane in a flask with stirring. After reaction under reflux for 24 h, the solution was cooled down to room temperature and filtered. The crude product was purified by recrystallization from acetone. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 2.55-2.70 (m, 4H, -OOCC*H*$_2$C*H*$_2$COO-); all the other resonance signals on ^{1}H NMR spectrum represent the protons of the cholesteryl group.

Synthesis of 2-(*N*-ethyl-*N*-phenylamino)ethyl 3′-((cholesteryl)oxycarbonyl)propionate. A solution of succinic acid cholesteryl ester (1.5 g, 3 mmol), *N*-ethyl-*N*-hydroxyethylaniline (0.5 g, 3 mmol), *N*, *N*-dicyclohexylcarbodiimide (DCC, 2.4 g, 11 mmol) and 4-dimethylamino pyridine (DMAP, 0.14 g, 1.1 mmol) in 50 mL of dichloromethane was stirred at room temperature for 24 h. Then, the formed *N*, *N*-dicyclohexyl urea was filtered out and the filtrate was washed with water (150 mL), 5% acetic acid solution (150 mL), water again (150 mL), and dried over Na_2SO_4. After evaporating the solvents, the residue was subjected to column chromatography on silica gel with DCM as the eluting solvent. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.23 (t, 2H, Ar*H*), 6.71 (m, 3H, Ar*H*), 4.25 (t, 2H, -C*H*$_2$-O-), 3.55 (t, 2H, -C*H*$_2$-N-), 3.41 (m, 2H, -N-C*H*$_2$-CH$_3$), 2.55-2.70 (m, 4H, -OOCC*H*$_2$C*H*$_2$COO-), 1.17 (t, 3H, -C*H*$_3$), all the other resonance signals on the ^{1}H NMR spectrum represent the protons of the cholesteryl group.

Synthesis of CA-Chol. 4-Aminobenzoic acid (0.69 g, 5 mmol) was dissolved in a mixture of acetic acid (10 mL) and sulfuric acid (1 mL) at 0 ℃. Then, $NaNO_2$ (0.69 g, 10 mmol) dissolved in 1.5 mL of water was slowly dripped into the above solution. The mixture was stirred in an ice bath for 30 min to obtain the solution of diazonium salt. 2-(*N*-Ethyl-*N*-phenylamino)ethyl 3′-((cholesteryl)oxycarbonyl)propionate (2.5 g, 4 mmol) was dissolved in 50 mL of DMF and the solution was cooled down to 0 ℃. The diazonium salt solution was added dropwise into the above DMF solution. After reaction for 5 h, the raw product was obtained by pouring the reaction solution into 100 mL of deionized water. The precipitate was collected by filtration and washed with excess water until the neutral state was achieved. Purification by column chromatography (silica gel, dichloromethane) yielded a dark red powder. ^{1}H NMR (600 Hz, $CDCl_3$) δ (ppm): 8.20 (d, 2H, Ar*H*), 7.87 (t, 4H, Ar*H*), 6.78 (d, 2H, Ar*H*), 4.31 (t, 2H, -OC*H*$_2$-), 3.67 (t, 2H, -NC*H*$_2$-), 3.51 (q, 2H, -NC*H*$_2$CH$_3$), 2.60 (m, 4H, -OOCC*H*$_2$C*H*$_2$COO-), 1.24 (t, 3H, -C*H*$_3$); all the other high-field resonance signals in the ^{1}H NMR spectrum represent the protons of the cholesteryl group.

Synthesis of H_2pdca-PDMS. The polydimethylsiloxane oligomer (H_2pdca-PDMS) was synthesized according to the literature.[S3] Triethylamine (Et_3N, 2 mL) was added into a solution of H_2N-PDMS-NH_2 (12.5 g, M_n = 2500) in anhydrous DCM (40 mL) cooling with an ice bath under argon atmosphere. After stirring for 2 h, a solution of 2, 6-pyridinedicarbonyl dichloride (1.02 g, 5 mmol) in DCM (10 mL) was added dropwise into the reaction flask. After continually stirring for 2 h with the ice bath cooling, the mixture was heated to 50 °C and stirred for 2 days. After the

reaction, the solution was concentrated to 1/3 of its original volume and then 60 mL MeOH was added into it. White viscous liquid precipitated and the mixture was set aside for 30 min. After decanting the upper clear solution, 20 mL DCM was added to dissolve the product. The dissolution-precipitation-decantation process was repeated for three times and the final product was obtained through vacuum evaporation. ^{1}H-NMR ($CDCl_3$, 600 MHz, δ, ppm): 8.34-8.35 (d, 2H, Ar*H*, *metho* to N), 7.99-8.02 (t, 1H, Ar*H*, *para* to N), 7.71 (br, 2H, -N*H*-), 3.47-3.50 (m, 4H, -CH_2-, *α* to -NH-), 1.67-1.68 (m, 4H, -CH_2-, *β* to -NH-), 0.61-0.63 (m, 4H, -CH_2-, γ to -NH-). GPC (THF): M_w = 29700 g mol^{-1}, M_n = 17100 g mol^{-1}, M_w/M_n = 1.7.

S2. Characterization

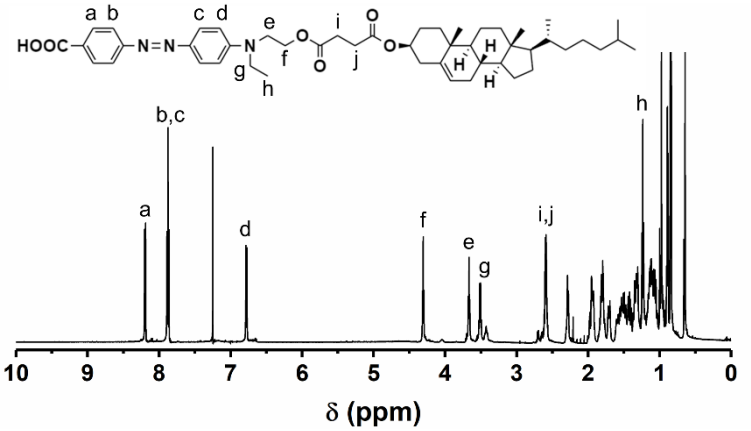


Fig. S1. ^{1}H-NMR spectrum of CA-Chol in $CDCl_3$.

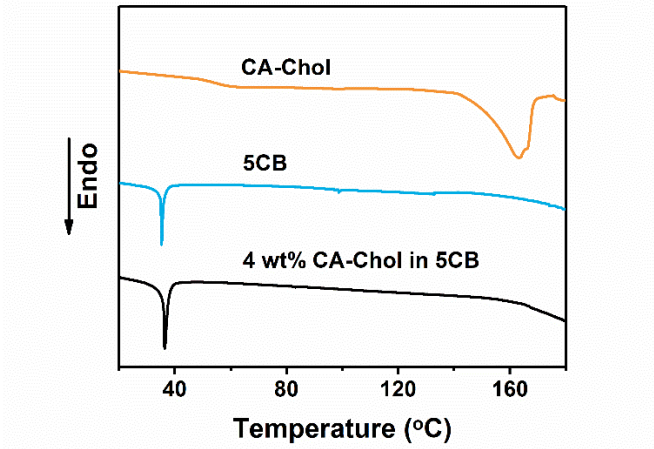


Fig. S2. Differential scanning calorimetry (DSC) curves of CA-Chol, 5CB, and CA-Chol dissolved in 5CB (4 wt%). DSC experiments were performed on TA Instrument (model Q2000) with a heating rate of 10 °C/min in nitrogen atmosphere.

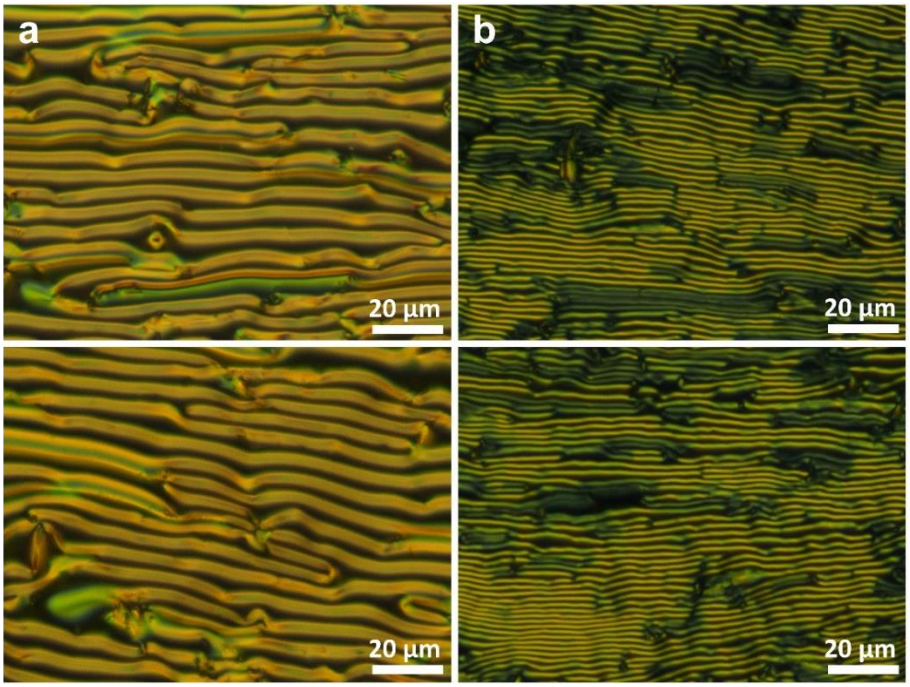


Fig. S3. Polarized optical microscopic (POM) images of cholesteric phase formed from 5CB/CA-Chol between two glass plates. The CA-Chol weight concentration is (a) 0.04 and (b) 0.10, respectively.

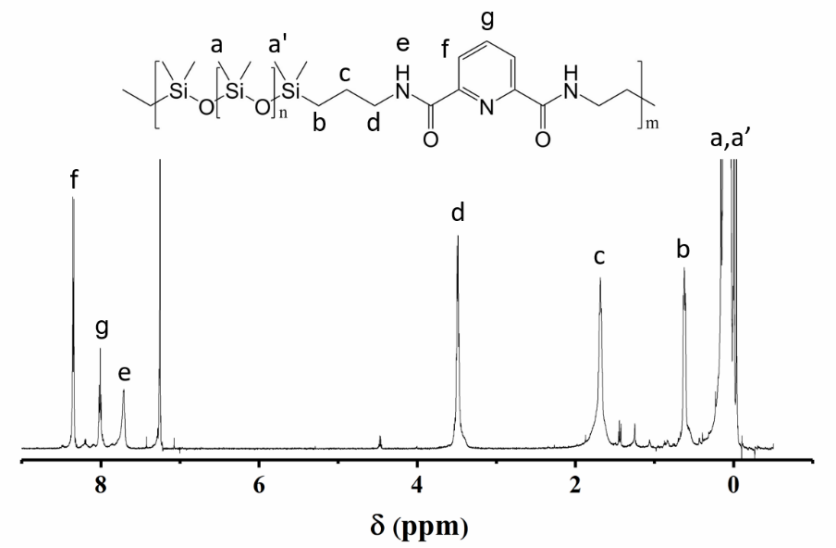


Fig. S4. ^{1}H-NMR spectrum of H_2pdca-PDMS in $CDCl_3$.

S3. Calculation of the binary interaction parameters

For convenience of expression, we adopt the suffixes 1, 2, 3, and 4 to indicate the nematic liquid crystal (5CB), the chiral azo dopant (CA-Chol), the PDMS-based oligomer (H_2pdca-PDMS), and the solvent (chloroform). χ_{ij} (i = 1, 2, 3, 4; j = 1, 2, 3, 4) are the monomeric binary interaction parameters. The relative degree of polymerization of H_2pdca-PDMS was obtained using the number-average molecular weight measured by GPC and volume per unit calculated by summing up the volumes of groups in the unit. For the nematic LC (5CB) and the chiral azo molecular glass (CA-Chol), the relative sizes were directly calculated by summing up the volumes of groups contained in the molecule. The volumes of the groups and the solvents were taken from literature.[S4] By normalizing the solvent molecular volume, the relative degree of polymerization (N_1 = 2.8, N_2 = 8.0, N_3 = 280.2) were obtained. χ-values were estimated using the relation,[S5]

$$\chi_{12} = \alpha \frac{v_1}{RT}\left(\left(\delta_{1,d} - \delta_{2,d}\right)^2 + 0.25\left(\delta_{1,p} - \delta_{2,p}\right)^2 + 0.25\left(\delta_{1,hb} - \delta_{2,hb}\right)^2\right) \qquad \text{(S2)}$$

where $\delta_{i,d}$, $\delta_{i,p}$, and $\delta_{i,hb}$ are the dispersive, polar and hydrogen-bonding Hansen parameters of the substance i, v_1 is the solvent molar volume and R is the gas constant. Previous study has suggested that by using α = 0.6 in equation S2 for minimum average absolute deviations, the procedure is proved to perform well for solutions containing polar and hydrogen-bonding compounds.[S6] The Hansen parameters of chloroform were obtained from the literature.[S4] By the method of Hoftyzer and van Krevelen,[S7] the Hansen parameters of IAC-4 and H_2pdca-PDMS were estimated by

$$\delta_d = \frac{\sum F_{di}}{V}$$

$$\delta_p = \frac{\sqrt{\sum {F_{pi}}^2}}{V} \qquad \text{(S3)}$$

$$\delta_h = \frac{\sqrt{\sum E_{hi}}}{V}$$

where F_{di}, F_{pi}, and E_{hi} are the dispersive force, polar force, and hydrogen bonding energy of group i, which were obtained from literature.[S7] Thus, all χ-values were estimated and summarized in Table S1.

Table S1. Binary interaction parameters and the relative sizes of the four substances.

	5CB	**CA-Chol**	**H₂pdca-PDMS**	**chloroform**	***N***
5CB	/	$\chi_{12} = 0.120$	$\chi_{13} = 0.381$	$\chi_{14} = 0.116$	2.8
CA-Chol	$\chi_{21} = 0.120$	/	$\chi_{23} = 0.092$	$\chi_{24} = 0.035$	8.0
H₂pdca-PDMS	$\chi_{31} = 0.381$	$\chi_{32} = 0.092$	/	$\chi_{34} = 0.089$	280.2
chloroform	$\chi_{41} = 0.116$	$\chi_{42} = 0.035$	$\chi_{43} = 0.089$	/	1

Table S2. Critical values of the binary interaction parameters.

	5CB	**CA-Chol**	**H₂pdca-PDMS**	**chloroform**
5CB	/	$\chi_{12,c} = 0.451$	$\chi_{13,c} = 0.215$	$\chi_{14,c} = 1.274$
CA-Chol	$\chi_{21,c} = 0.451$	/	$\chi_{23,c} = 0.085$	$\chi_{24,c} = 0.916$
H₂pdca-PDMS	$\chi_{31,c} = 0.215$	$\chi_{32,c} = 0.085$	/	$\chi_{34,c} = 0.562$
chloroform	$\chi_{41,c} = 1.274$	$\chi_{42,c} = 0.916$	$\chi_{43,c} = 0.562$	/

In order to identify the driving force for the demxing of this ternary blend, the critical values of all binary interaction parameters were calculated as $\chi_{ij,c} = \frac{1}{2}\left(\frac{1}{\sqrt{N_i}} + \frac{1}{\sqrt{N_j}}\right)^2$, which were listed in Table S2. Comparing the interaction parameters in Table S1 with the corresponding values in Table S2 reveals that the incompatibility between the CLC phase (5CB/CA-Chol) and the PDMS oligomer (H₂pdca-PDMS) is the driving force for liquid-liquid phase separation, since $\chi_{13} \gg \chi_{13,c}$ and $\chi_{23} \gg \chi_{23,c}$. In contrast, the fact that $\chi_{12} < \chi_{12,c}$ demonstrates that 5CB and CA-Chol is compatible with each other to form the cholesteric LC phase.

S4. More images of droplet formation and cholesteric structures

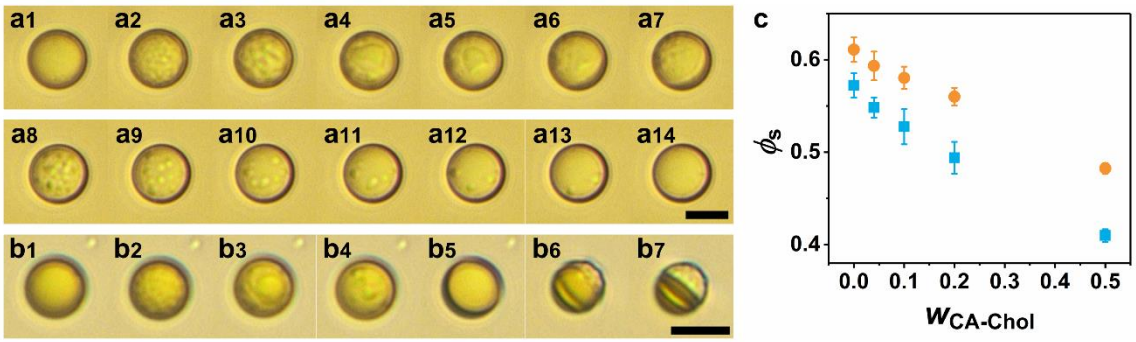


Fig.S5. (a-d) Real-time optical microscopic (OM) images. (a1-a14) 5CB/H_2pdca-PDMS Janus droplet formation ($w_{CA\text{-}Chol}$ = 0) in the dispersed chloroform droplets observed at different times, (a1) 0 s, (a2) 0.5 s, (a3) 1.0 s, (a4) 1.5 s, (a5) 2.0 s, (a6) 2.3 s, (a7) 2.8 s, (a8) 7.0 s, (a9) 9.0 s, (a10) 10.5 s, (a11) 11.0 s, (a12) 12.0 s, (a13) 13.0 s, (a14) 14.5 s. (b1-b7) (5CB/CA-Chol)/H_2pdca-PDMS Janus droplet formation ($w_{CA\text{-}Chol}$ = 0.10) observed at different times, (b1) 0 s, (b2) 1 s, (b3) 2 s, (b4) 4 s, (b5) 14 s, (b6) 148 s, (b7) 5 min. The scale bars represent 10 μm. (c) Variation of the total solvate volume fractions within the dispersed phase at the onset of demixing (in blue) and at the completion of phase separation (in orange) versus the CA-Chol weight concentration $w_{CA\text{-}Chol}$.

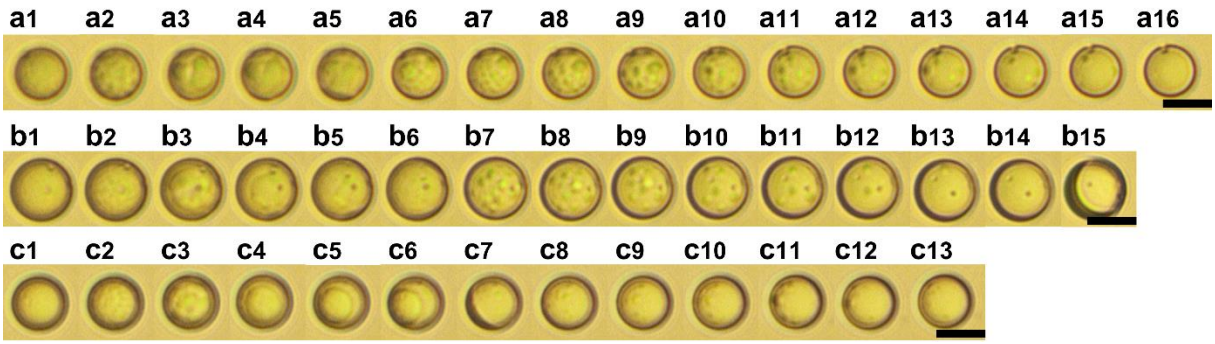


Fig. S6. Real-time OM images showing phase separation to form 5CB/H_2pdca-PDMS Janus droplets. (a1-a16) Phase separation observed at the time, (a1) 0 s, (a2) 1.0 s, (a3) 1.3 s, (a4) 1.5 s, (a5) 1.8 s, (a6) 2.5 s, (a7) 2.8 s, (a8) 3.3 s, (a9) 3.8 s, (a10) 4.3 s, (a11) 4.5 s, (a12) 5.0 s, (a13) 5.5 s, (a14) 6.0 s, (a15) 7.0 s, (a16) 8.5 s. (b1-b15) Phase separation observed at the time, (b1) 0 s, (b2) 0.5 s, (b3) 1.0 s, (b4) 2.0 s, (b5) 2.5 s, (b6) 2.8 s, (b7) 8.0 s, (b8) 9.0 s, (b9) 10.0 s, (b10) 11.0 s, (b11) 12.0 s, (b12) 12.5 s, (b13) 14.0 s, (b14) 14.5 s, (b15) 30.0 s. (c1-c13) Phase separation

observed at the time, (c1) 0 s, (c2) 0.5 s, (c3) 0.8 s, (c4) 1.0 s, (c5) 2.0 s, (c6) 2.5 s, (c7) 3.0 s, (c8) 3.5 s, (c9) 4.0 s, (c10) 5.0 s, (c11) 6.0 s, (c12) 7.0 s, (c13) 8.0 s. The scale bars represent 10 μm.

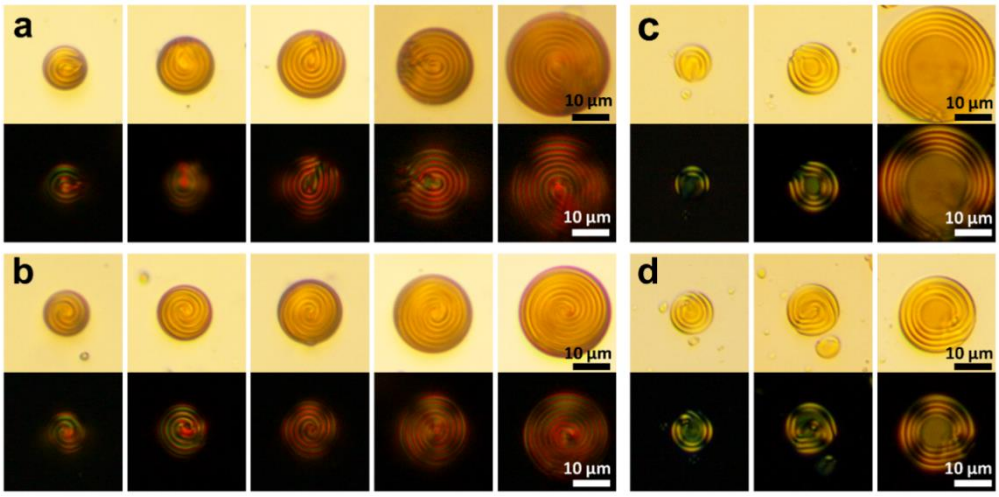


Fig. S7. Full-transmission (FT) and polarized optical microscopic (POM) images of CLC (5CB/CA-Chol) droplets with the CA-Chol weight concentration of 0.10, (a, b) suspended in PVA (3 wt%) aqueous medium and (c, d) spreading on the glass slides. The disclination line of the cholesteric droplet is (a, c) perpendicular to the viewing direction and (b, d) parallel to the viewing direction, respectively showing onion-like texture with a radial defect and a spiral at the center of the droplet. The N values are (a) 9.6, 12.7, 14.8, 17.1, and 23.4 from left to right, (b) 9.9, 12.1, 14.2, 17.7, and 20.6 from left to right. The scale bars represent 10 μm.

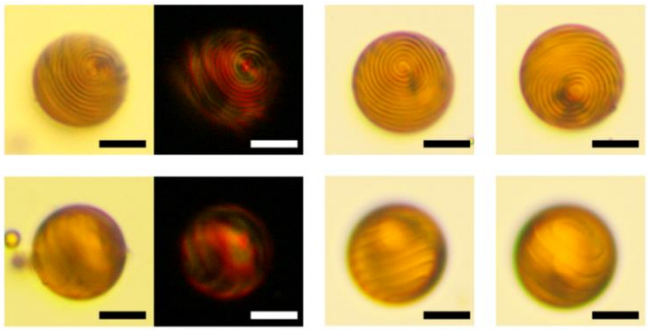


Fig. S8. Typical FT microscopic images of CLC (5CB/CA-Chol) droplets with the CA-Chol concentration of 0.10 suspended in PVA(3 wt%)/SDS(0.5 wt%) aqueous medium. The two rows of pictures correspond to different planes that allow to visualize the equatorial plane (top row) and the surface (bottom row). The N values are 17.6, 18.5, and 19.1 from left to right. The scale bars represent 10 μm.

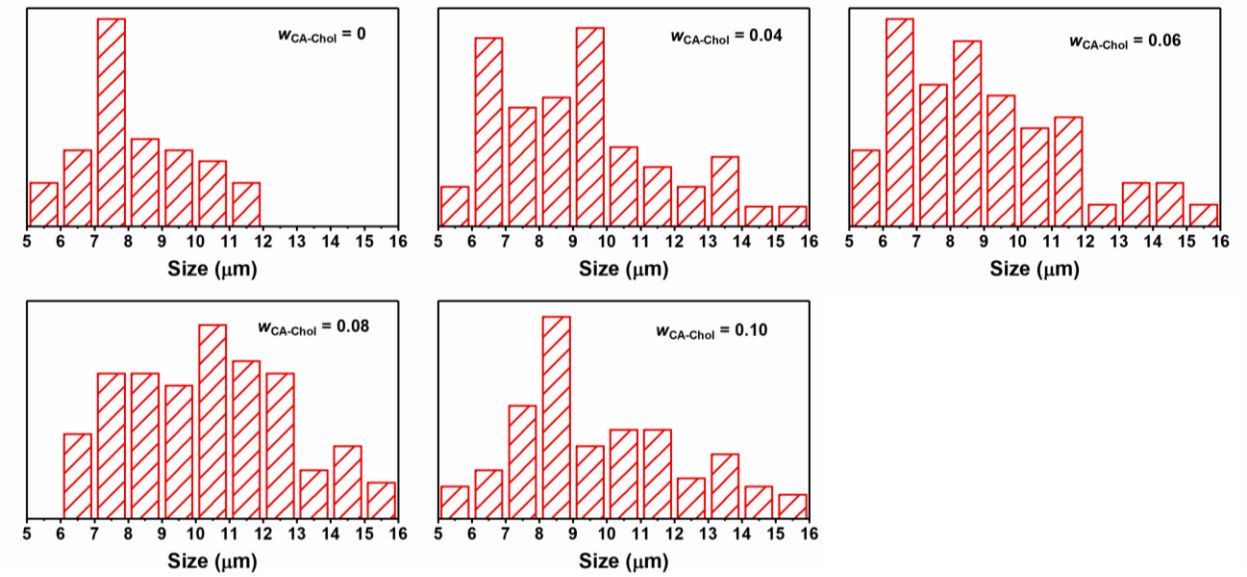


Fig. S9. Size distributions of the (5CB/CA-Chol)/H_2pdca-PDMS Janus droplets with the CA-Chol weight concentration of 0, 0.04, 0.06, 0.08, and 0.10 suspended in the PVA(3 wt%)/SDS(0.5 wt%) aqueous medium, where the size of a Janus droplet is defined as the length along the minor axis.

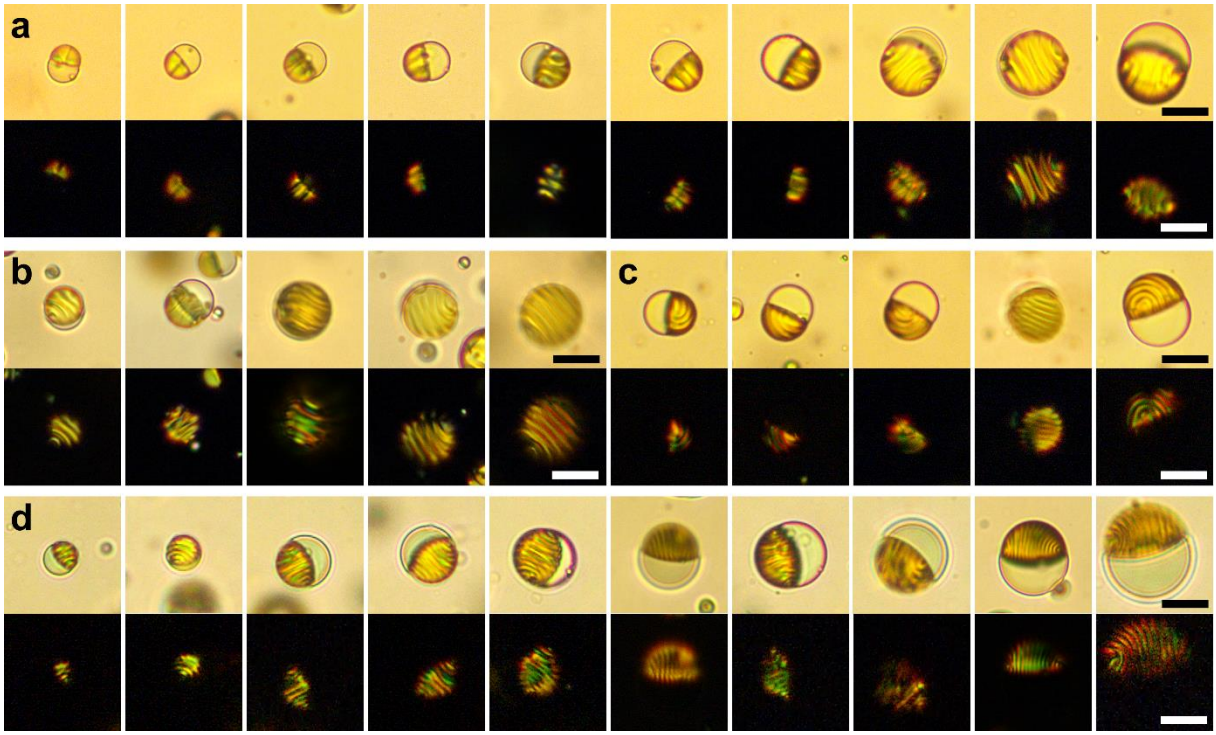


Fig. S10. FT and POM images of (5CB/CA-Chol)/H_2pdca-PDMS Janus droplets with the CA-Chol weight concentration of (a) 0.04, (b) 0.06, (c) 0.08, (d) 0.10 suspended in PVA(3

wt%)/SDS(0.5 wt%) aqueous medium. The disclination line in each droplet is located at the interface between the (5CB/CA-Chol) and H_2pdca-PDMS phases. The pitch length is (a) 6.0 μm, (b) 4.0 μm, (c) 3.1 μm, and (d) 2.3 μm. The N values are (a) 2.3, 2.3, 2.5, 2.7, 3.0, 3.2, 3.4, 4.0, 4.7, and 5.0 from left to right, (b) 4.2, 4.2, 6.0, 6.0, and 6.8 from left to right, (c) 6.1, 6.2, 6.6, 7.5, and 8.7 from left to right, (d) 5.7, 6.3, 8.9, 9.9, 10.7, 10.9, 11.8, 12.2, 12.7, and 15.5 from left to right, respectively. The scale bars represent 10 μm.

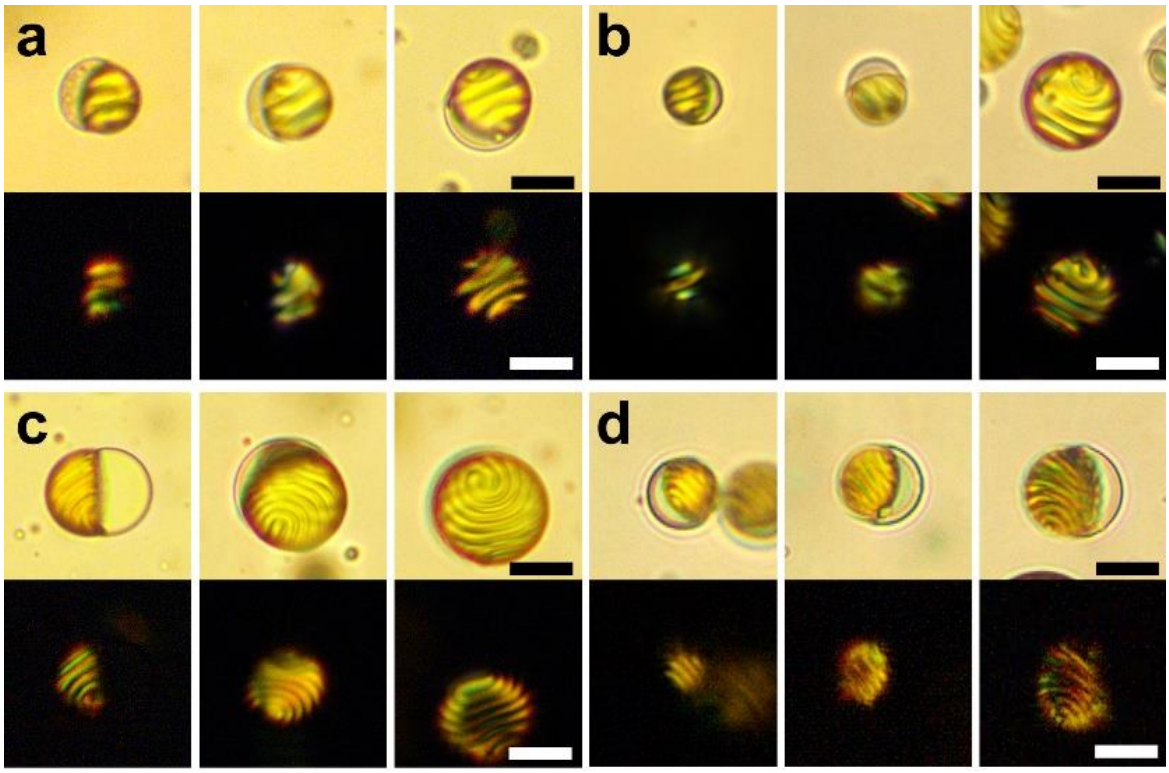


Fig. S11. FT and POM images of (5CB/CA-Chol)/H_2pdca-PDMS Janus droplets with the CA-Chol weight concentration, (a) 0.04, (b) 0.06, (c) 0.08, (d) 0.10 suspended in PVA(3 wt%)/SDS(0.5 wt%) aqueous medium. The ends of disclination lines of the droplets are located on the surface of the CLC phase and some are away from the boundary between the (5CB/CA-Chol) and H_2pdca-PDMS phases. The scale bars represent 10 μm.

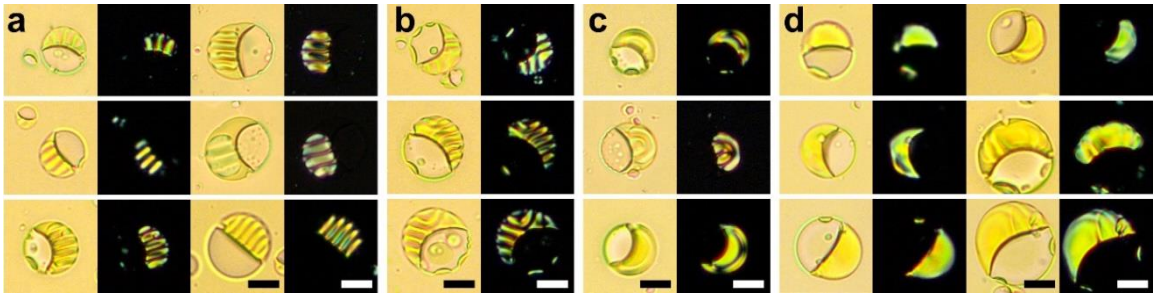


Fig. S12. FT and POM images of (5CB/CA-Chol)/H_2pdca-PDMS Janus droplets spreading on the glass slides with the CA-Chol weight concentration of 0.04. The cholesteric structures belong to (a) type I, (b) type II, (c) type III, and (d) type IV, respectively. The scale bars represent 10 μm.

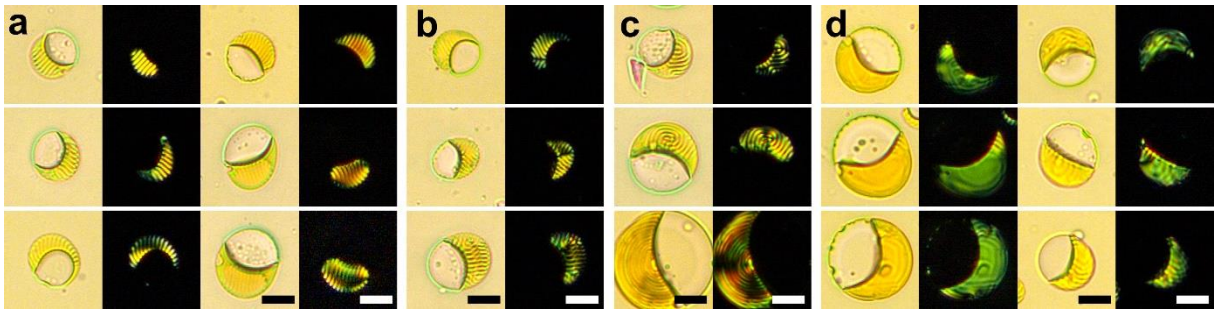


Fig. S13. FT and POM images of (5CB/CA-Chol)/H_2pdca-PDMS Janus droplets spreading on the glass slides with the CA-Chol weight concentration of 0.10. The cholesteric structures belong to (a) type I, (b) type II, (c) type III, and (d) type IV, respectively. The scale bars represent 10 μm.

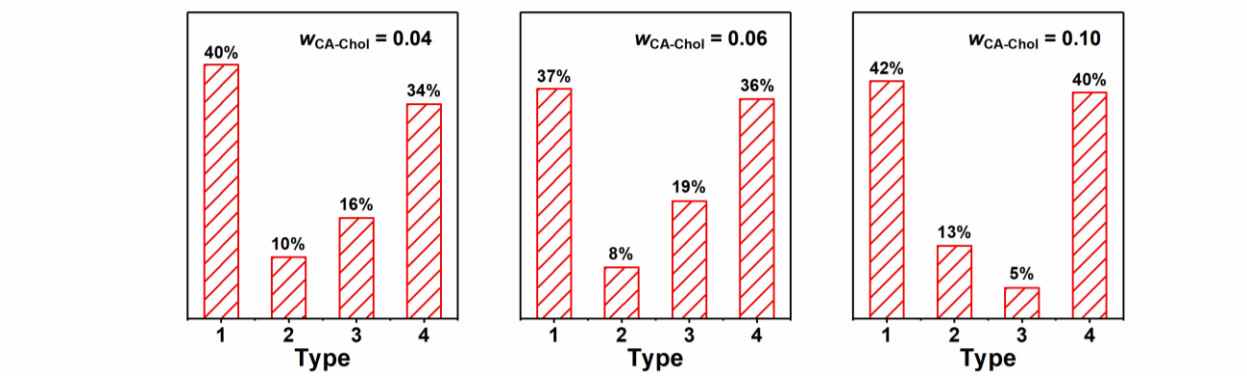


Fig. S14. The percentages of the four types of cholesteric structure of (5CB/CA-Chol)/H_2pdca-PDMS Janus droplets with the $w_{CA-Chol}$ value of 0.04, 0.06, and 0.10, respectively.

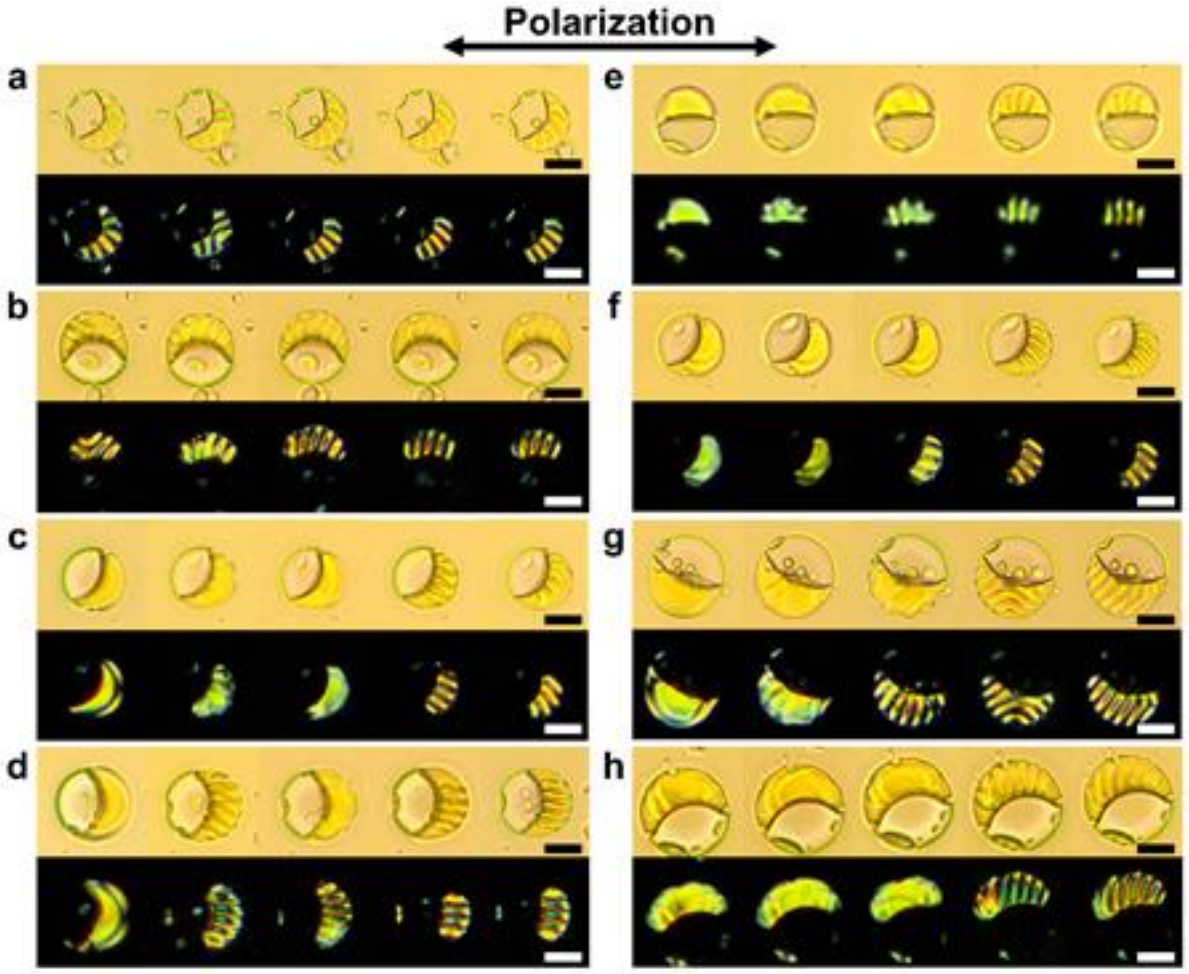


Fig. S15. FT and POM images of single (5CB/CA-Chol)/H_2pdca-PDMS Janus droplets spreading on the glass slide with the $w_{CA\text{-}Chol}$ value of 0.04 after linearly polarized light irradiation (50 mW/cm^2,488 nm) for 0, 2, 4, 6, and 8 min from left to right. The scale bars represent 10 μm.

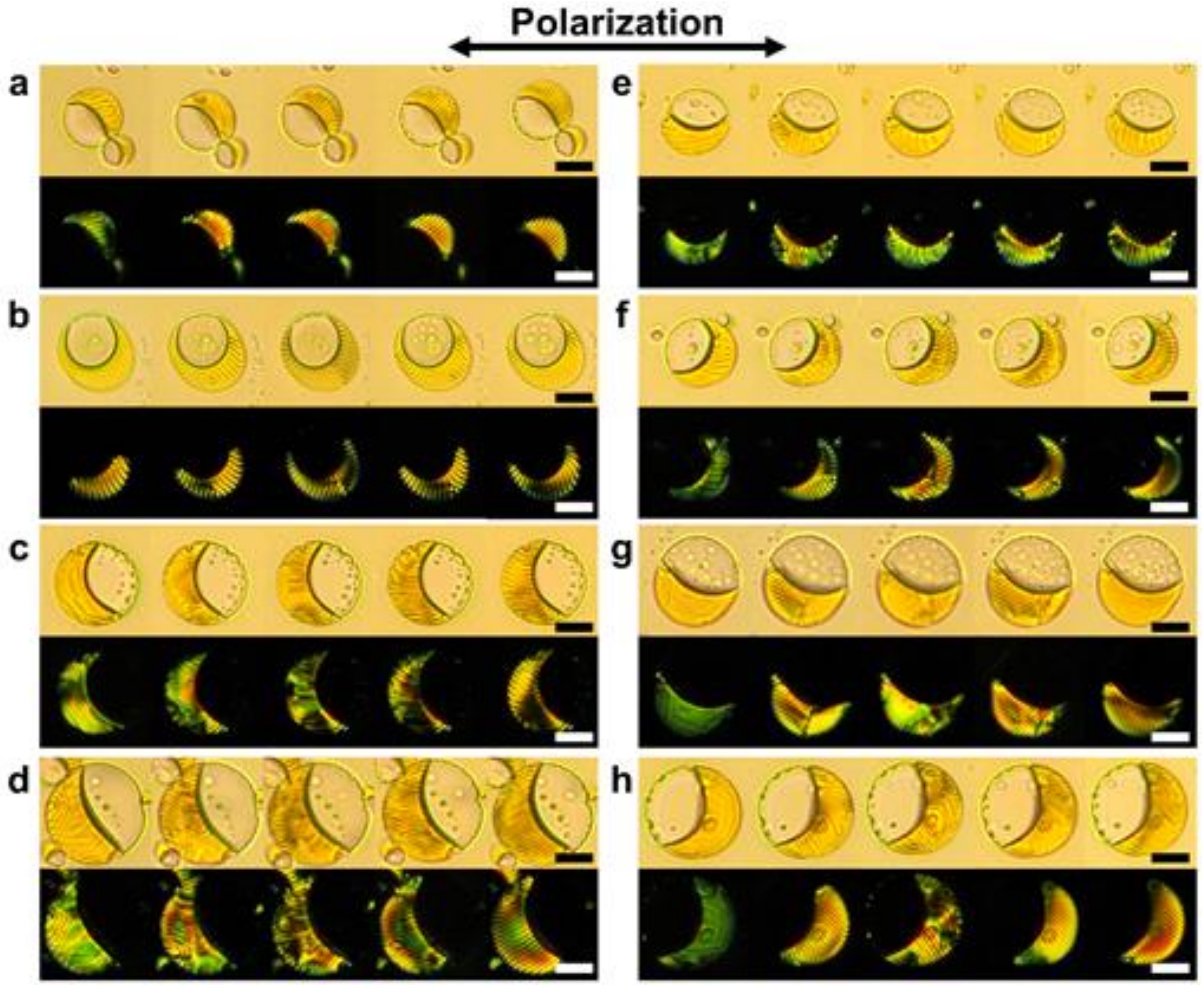


Fig. S16. FT and POM images of single (5CB/CA-Chol)/H_2pdca-PDMS Janus droplets spreading on the glass slide with the $w_{CA\text{-}Chol}$ value of 0.10 after linearly polarized light irradiation (50 mW/cm^2,488 nm) for 0, 2, 4, 6, and 8 min from left to right. The scale bars represent 10 μm.

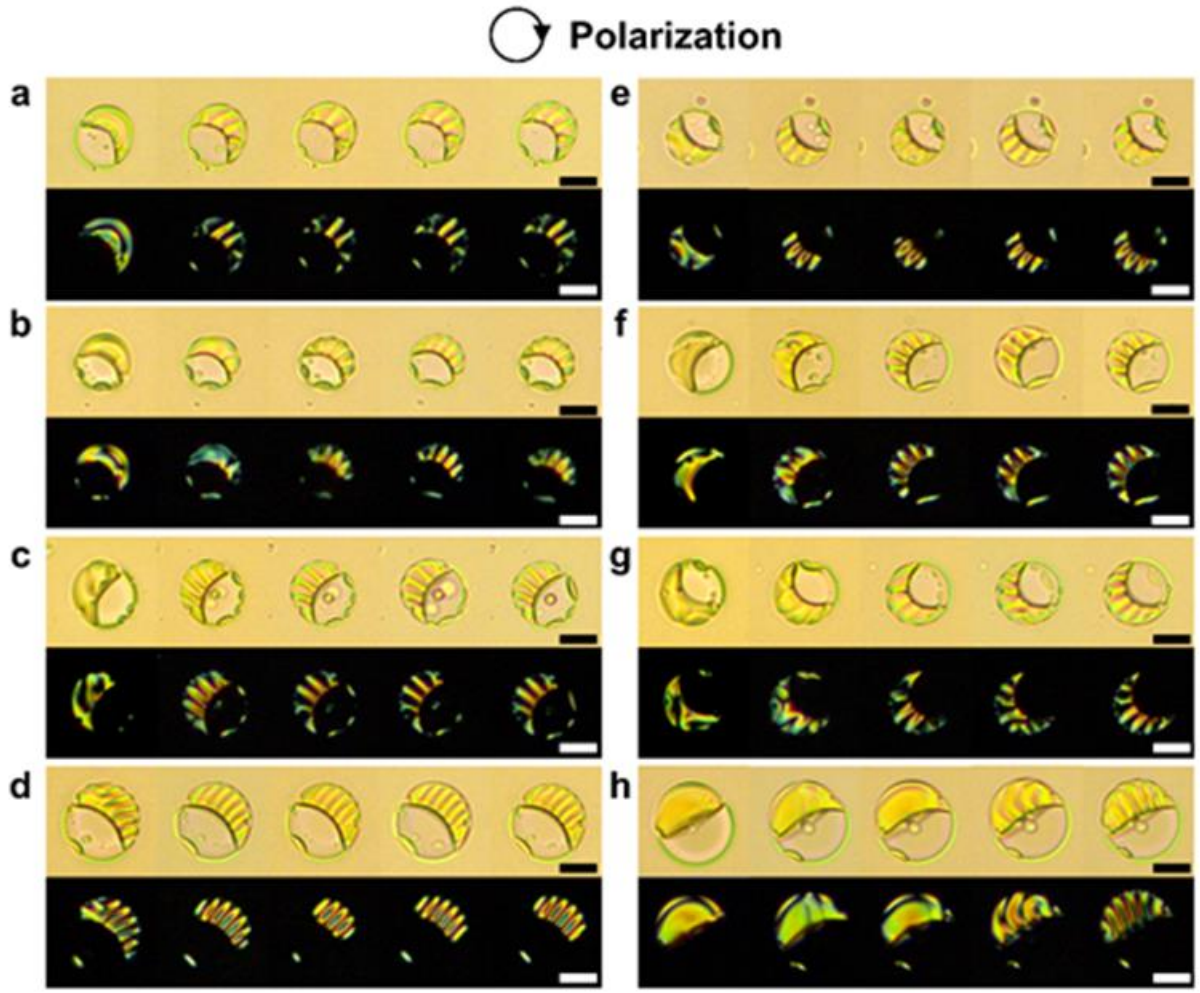


Fig. S17. FT and POM images of single (5CB/CA-Chol)/H_2pdca-PDMS Janus droplets spreading on the glass slide with the $w_{CA\text{-}Chol}$ value of 0.04 after circularly polarized light irradiation (50 mW/cm^2,488 nm) for 0, 2, 4, 6, and 8 min from left to right. The scale bars represent 10 μm.

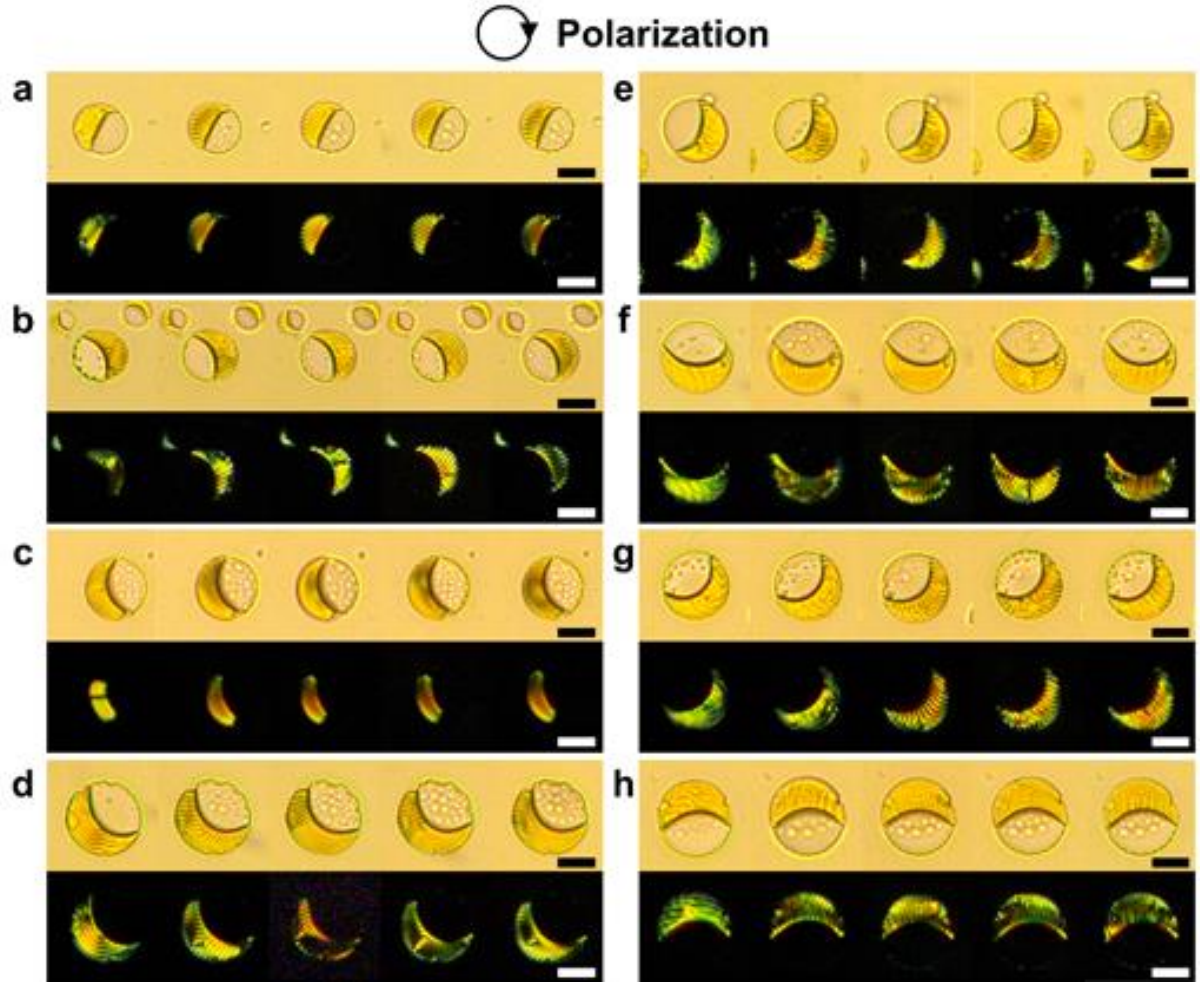


Fig. S18. FT and POM images of single CLC (5CB/CA-Chol)/H_2pdca-PDMS Janus droplets spreading on the glass slide with the $w_{CA\text{-}Chol}$ value of 0.10 after circularly polarized light irradiation (50 mW/cm^2,488 nm) for 0, 2, 4, 6, and 8 min from left to right. The scale bars represent 10 μm.

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