Dynamically Reconfigurable Complex Liquid Crystal Emulsions

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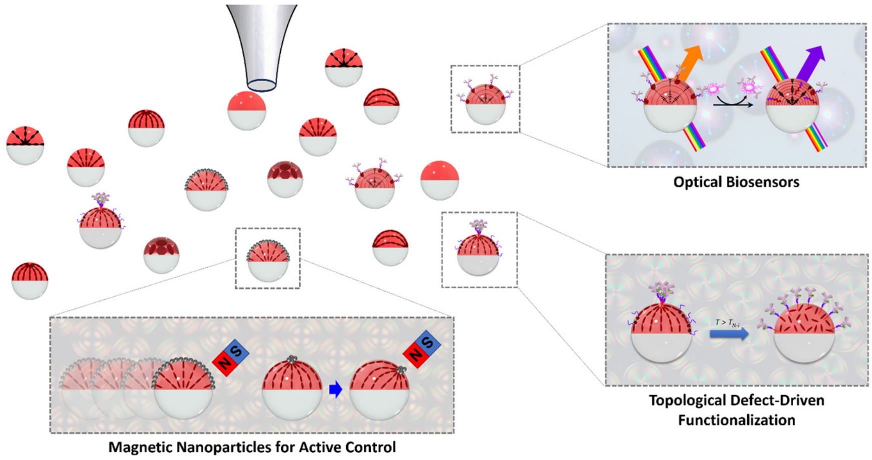
Complex emulsions, containing liquid crystals (LCs) and immiscible oils such as fluorocarbon or silicone oils, present innovative functionalities in soft materials. These emulsions exhibit dynamic reconfiguration in droplet morphology and internal LC organization, expanding applications in optics, sensing, and active matter. This review highlights the evolution and potential of LC-containing complex emulsions. Emphasis is placed on emulsions featuring dynamic and reversible morphological transformations and LC reorganization, underpinning their suitability for tunable micro-lenses, chemical sensing, and biosensing. Nematic LCs within complex emulsions allow for topological defect-driven functionalization, attaching antibodies to induce substantial changes in the LC director field upon interfacial recognition events. This feature may facilitate the development of ultrasensitive chemical and biological sensors. Moreover, cholesteric LCs, through their selective reflection, enable the rapid and sensitive detection of foodborne pathogens. The controlled assembly of magnetic nanoparticles at interfaces illustrates advancements toward magnetic field-responsive and active colloids. Future perspectives include exploiting these properties for intelligent colloidal systems capable of autonomous behavior, and furthering applications in dynamic photonic devices, high-security identification tags, and responsive lens systems.

Keywords: complex emulsions; liquid crystal emulsions; reconfigurable droplets

Table of Contents Image / Graphical Abstract



1. Introduction

An emulsion refers to a mixture of two or more liquids that are typically immiscible due to liquid-liquid phase separation. Emulsions are ubiquitous in everyday life, as evidenced by their presence in common products like milk, paint, and cosmetics. Furthermore, they play a crucial role in sectors such as medicine, food, and various performance materials.[1, 2, 3, 4] The simplest form of an emulsion is a single emulsion, composed of two immiscible liquids, where one acts as the dispersed droplet phase while the other serves as the continuous phase. Complex emulsions involve droplets with two or more phase-separated liquids, leading to diverse morphologies including core-shell droplets [e.g., water-in-oil-in-water (W/O/W), oil^1-in-oil^2-in-water ($O^1/O^2/W$)], or Janus droplets (biphasic oil droplets with equal hemispheres).[5, 6]

The control over the preparation of complex emulsions has gained increasing importance as their properties and functionalities are closely related to the droplet geometry and composition.[7] There has been significant advancement in fabricating these complex emulsions through various techniques, ranging from large-scale methods using high-shear mixers and membranes to small-volume, more precise microfluidic approaches.[8, 9, 10, 11] However, these methods typically do not allow alteration of droplet morphologies after the emulsification process.

Recent advancements have led to a novel class of complex emulsions capable of dynamic reconfiguration in response to surfactants and aqueous environments.[12] These systems, composed of two immiscible liquids—a fluorinated oil (F) and a hydrocarbon or organic oil (H)—are dispersed in an outer aqueous phase with surfactants (**Figure 1a**). The emulsification occurs as a single phase at temperatures above the upper critical solution temperature (UCST). Upon cooling, phase separation occurs, resulting in droplets with meticulously controlled compositions and structures (**Figure 1b**). These droplets demonstrate dynamic reconfigurability, transitioning among various forms, including hydrocarbon-in-fluorocarbon-in-water droplets (H/F/W), Janus droplets, or fluorocarbon-in-hydrocarbon-in-water droplets (F/H/W) through adjustments in the surfactant mass balance (**Figure 1c**). Such morphological reconfigurations can also be induced by various stimuli, including light, pH, enzymes, chemical analytes, or temperature.

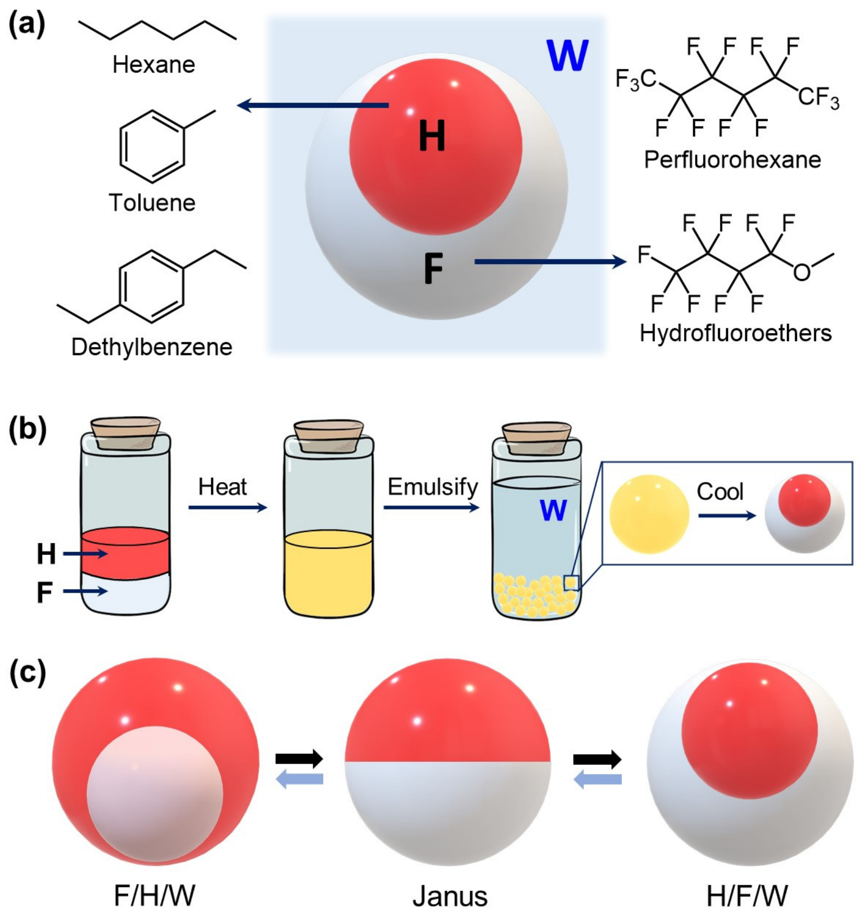


Figure 1. (a) Complex emulsions consisting of hydrocarbon (H) and fluorocarbon (F) oils dispersed in an aqueous phase (W) with surfactants. **(b)** Procedure for preparing complex emulsion droplets. **(c)** Reconfiguration of droplet morphology in response to aqueous surfactants.

The field of reconfigurable complex emulsions is rapidly evolving, presenting new possibilities in areas like tunable optics, sensors, and controlled release.[7] A notable application is the development of tunable micro-lenses for imaging devices and biomedical diagnostics, leveraging the ability of these complex droplets to modify the ordering and curvature of their fluid interfaces.[13, 14, 15] Moreover, they show promise in chemical sensing, capable of detecting enzyme activity, biomolecules, or pathogens through changes in optical properties, such as transparency, fluorescence intensity, or color, visible to the naked eye.[16, 17, 18, 19, 20, 21]

Nevertheless, current complex emulsions fall short in achieving the intricate and active compositions necessary for developing fully intelligent materials. Thus, liquid crystals (LCs) are garnering interest, as complex emulsions incorporating these nanostructured fluids offer a degree of responsiveness and anisotropy not found in colloidal systems composed solely of isotropic liquids.[22, 23] Consequently, several research groups are focusing on creating complex emulsions with immiscible LCs and various oils, such as fluorocarbon or silicone oils. These LC-containing complex emulsions represent a new frontier in designing responsive soft matter systems, with potential applications in smart inks, optical manipulation, photonics, and biosensors.

In this review, we aim to provide a comprehensive overview of complex emulsions containing LCs, discussing the various systems developed to date and categorizing them based on the immiscible oil blended with the LC oil (Section 2). In Section 3, we will place special emphasis on systems that exhibit dynamic and reversible reconfiguration in both their droplet morphology and internal LC organization, as well as some of their potential applications. The discussion will conclude in Section 4 with future perspectives on these recently developed systems.

2. Complex Emulsions Containing Liquid Crystals

Morphology of Liquid Crystal Complex Emulsion Droplets

The morphology of complex emulsions, comprising two immiscible liquids such as a liquid crystal (LC) and an oil (O), dispersed in a third liquid like water (W), is primarily governed by the relative interfacial tensions: LC–W (γ_{LC}), O–W (γ_O), and LC–O ($\gamma_{LC/O}$). In these emulsions, each interface among the three phases forms a spherical section (**Figure 2**), resulting in an equilibrium droplet morphology influenced by the contact angles θ_{LC} and θ_O at the point where these phases converge, and the volume ratio $k = V_{LC}/V_O$. Force balances at the junction of these phases can be represented through Neumann's triangle, which correlates the contact angles with interfacial tensions as follows:[24, 25]

$$\gamma_{LC/O} \cos \theta_O + \gamma_O + \gamma_{LC} \cos(\theta_{LC} + \theta_O) = 0 \quad (eq. 1)$$

$$\gamma_{LC/O} \cos \theta_{LC} + \gamma_{LC} + \gamma_O \cos(\theta_{LC} + \theta_O) = 0 \quad (eq. 2)$$

The solutions to these equations dictate the droplet morphology, which can manifest in three distinct configurations:

1) *Complete engulfing:* Occurs when one droplet phase, such as LC, is completely encapsulated by the other phase O ($\gamma_{LC} > \gamma_O + \gamma_{LC/O}$), or *vice versa* ($\gamma_O > \gamma_{LC} + \gamma_{LC/O}$), resulting in LC-in-oil-in-water (LC/O/W) or oil-in-LC-in-water (O/LC/W) droplets.

2) *Non-engulfing:* The LC and O droplets remain separate, forming individual droplets in the water phase.

3) *Partial engulfing*: LC and O droplets share an interface and contact the external water phase, forming Janus droplets (O|LC/W). In this case, equations (eq.1) and (eq.2) can be solved in relation to θ_{LC}, yielding (eq. 3):

$$\cos(\theta_{LC}) = \frac{\gamma_O^2 - \gamma_{LC}^2 - \gamma_{LC/O}^2}{2 \cdot \gamma_{LC/O} \cdot \gamma_O} \quad (eq. 3)$$

When $\gamma_{LC/O}$ is significantly smaller than γ_{LC} and γ_O, droplets tend to adopt spherical shapes to minimize the total LC–W and O–W interfacial area. The previous physical equations also reveal that even slight alterations in the balance of the interfacial tensions at the water interface (i.e., γ_{LC} and γ_O) result in significant changes in the droplet's morphology. In fact, this is what was observed in complex emulsions containing isotropic liquids discussed in the *Introduction* (**Figure 1**), where there is a low internal interfacial tension ($\gamma_{H/F} \leq 0.5$ mN/m) compared to the external aqueous interfaces ($\gamma_{H/W}$ and $\gamma_{F/W} \geq 5$ mN/m).[12] Nevertheless, an increase in $\gamma_{LC/O}$ prompts droplets to minimize the LC–O interfacial area, leading to the formation of "snowman-shaped" or "dumbbell-shaped" structures.[25]

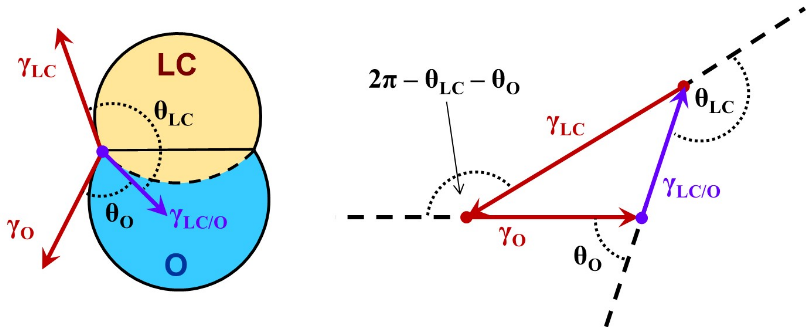


Figure 2. Schematic representation of a complex emulsion droplet and the effect of interfacial tensions that define a Neumann's triangle.

Internal Configurations of Liquid Crystal Complex Emulsion

Within micrometer-sized droplets, LCs can orient their director either parallel (planar) or perpendicular (homeotropic) to interfaces. This alignment results in various internal configurations, each with unique optical signatures under polarized-light optical microscopy (**Figure 3**).[26] These configurations depend on a balance of energetic forces from interfacial and elastic energies of the LC phase, as well as the presence of topological defects.[27]

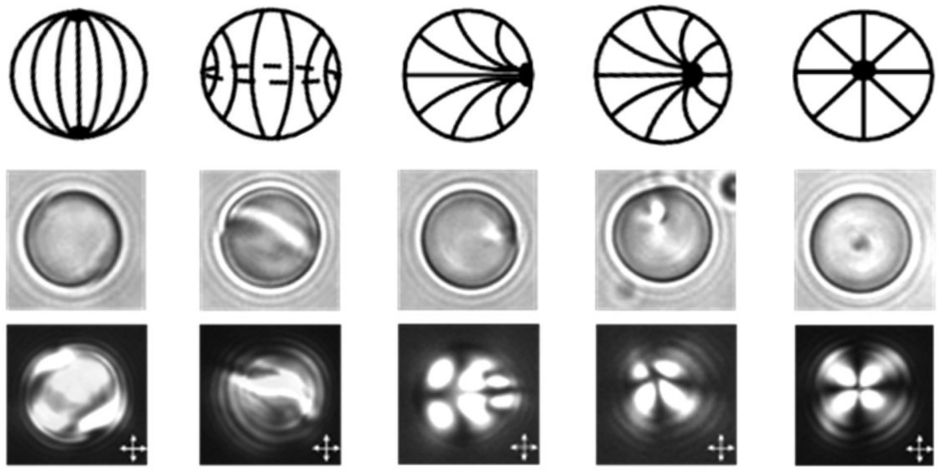


Figure 3. Schematic representation (top), bright field (middle), and polarized light (bottom) images of different LC configurations observed in nematic LC droplets. Adapted from Ref. [27] with permission. Copyright 2014 American Chemical Society.

Single-phase LC droplets exhibit a range of internal structures, including bipolar, radial, axial, pre-radial, and escaped radial configurations (**Figure 3**).[28] When LCs align tangentially (parallel to the droplet surface), a bipolar structure forms, characterized by the presence of two point defects, known as boojums, located at the droplet's opposite poles. If the LC director's anchoring at the surface shifts to a less tangential alignment, an axial configuration emerges, marked by the disappearance of the bipolar droplet's boojums and the emergence of a disclination ring around the droplet's equator. As the orientation of the LC director at the surface further transitions towards radial alignment, the ring defect migrates to one pole, transforming into a point defect and resulting in a pre-radial configuration. In the ultimate scenario, when LCs align perpendicularly at the droplet surface, a central point defect forms, indicative of a radial configuration.

However, in complex emulsions containing LCs, the introduction of an additional interface from a second oil in contact with the LC imposes new topological constraints. This leads to unique internal LC organizations not present in single LC emulsions (**Figure 4**). The morphology of these complex emulsion droplets, capable of reconfiguring between F/LC/W, Janus, or LC/F/W morphologies, also affects the LC anchoring, leading to various distinct internal LC organizations.[29, 30] For example, nematic Janus droplets have been reported to exhibit radial, monopolar, or bipolar LC configurations. In a radial configuration, the LC director aligns perpendicularly to the LC/W interface. Conversely, a bipolar configuration features tangential (locally parallel) alignment of the LC director to both LC/W and LC/F interfaces. In a monopolar configuration, LCs align parallel to the LC/W interface but perpendicular to the LC/O interface. Droplets with encapsulated morphologies, such as F/LC/W or LC/F/W, have been observed to adopt both radial and bipolar configurations. Specifically, in LC/F/W droplets, radial LC organizations display a central point defect within the LC compartment, while bipolar configurations exhibit two diametrically opposed surface point defects. Smectic phases also exhibit radial configurations, along with polygonal textures featuring several focal conic domains within the LC compartment. Complex emulsions containing cholesteric LC phases often display radial helical configurations.

Several factors influence the alignment of mesogens within nematic droplets, including droplet size, temperature, and surfactant type.[31, 32, 33] However, the nature and concentration of the surfactant play a crucial role in directing the LC director's alignment at interfaces. Surfactants with long alkyl chains typically orient their hydrophobic tails perpendicular to the LC/W interface, inducing a homeotropic alignment of the LC. The homeotropic alignment is observed to intensify with longer chains due to their greater extension into the LC along the radial direction.[34] The internal alignment of LC emulsions also depends on surfactant concentration. At lower concentrations, short-chain surfactants may lead the LC director to adopt a planar alignment at the LC/W interface, whereas long-chain surfactants promote tangential alignment. Polymeric surfactants, widely used to stabilize LC emulsions, typically form a random coil conformation at the LC/W interface, promoting tangential alignment of the LC director to this interface.[35, 36]

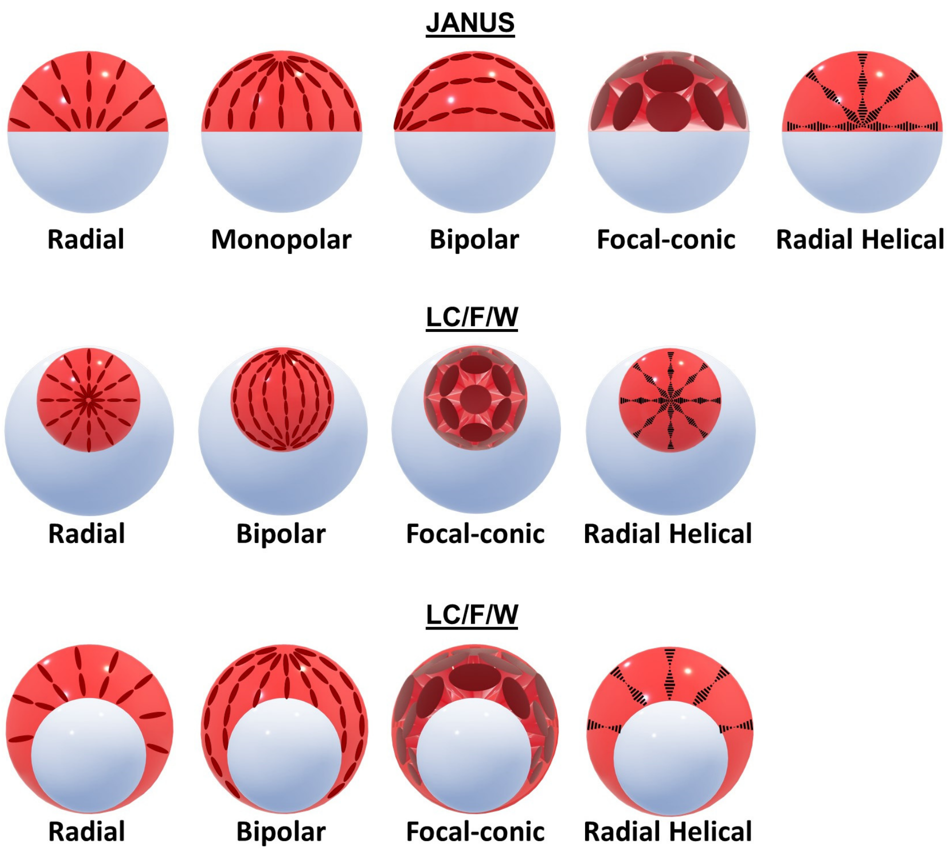


Figure 4. Representation of the different LC configurations observed in complex emulsions containing LCs.

Types of Liquid Crystal Complex Emulsion Droplets

This section delves into complex emulsions comprising two distinct phase-separated compartments: one constituted by a liquid crystal (LC) and the other by a different immiscible oil (O), dispersed within a third liquid. These emulsions are categorized based on the specific oil combined with the LC to form the dispersed droplet phase, such as silicon oils, perfluorinated oils, and hydrogels. Noteworthy studies on multicompartment LC droplets, such as LC shells surrounded by inner and outer aqueous phases (i.e., water-in-oil-in-water droplets), exist but are beyond this perspective's scope. Comprehensive reviews on these LC shells are available in the literature.[22, 37, 38]

Silicon Oils

Jeong and coworkers were the pioneers in reporting multicompartment emulsions containing LCs.[39] They created Janus droplets comprising a nematic LC oil (4-Cyano-4'-pentylbiphenyl, 5CB) and poly(dimethylsiloxane) (PDMS), utilizing microfluidics coupled with an evaporation-induced phase separation technique (**Figure 5a**). The oil phase, a blend of 5CB and PDMS dissolved in chloroform, was dispersed in an aqueous solution with various surfactants. Following the evaporation of chloroform, Janus droplets with distinct phase-separated compartments emerged. The substantial interfacial tension between the two oils led to the formation of non-spherical morphologies, such as snowman-shaped droplets. The study systematically explored the impact of surfactant type, concentration, and compartment volume ratio on the droplet morphology and internal LC organization. It was discovered that poly(vinyl alcohol) (PVA) induced planar alignment at the LC-water interface, resulting in a monopolar configuration with a defect near the droplet pole. Conversely, sodium dodecyl sulfate (SDS) fostered a radial configuration with the defect located within the LC compartment. Additionally, the surfactant type and concentration, as well as the phase-separated compartments' volume ratio, significantly influenced the droplet morphology, leading to a variety of non-spherical Janus droplet shapes (**Figure 5b**). The study also revealed the Janus morphology's instability upon adding certain surfactants, leading to droplet coalescence, while simultaneously offering a novel approach to create patchy LC droplets.

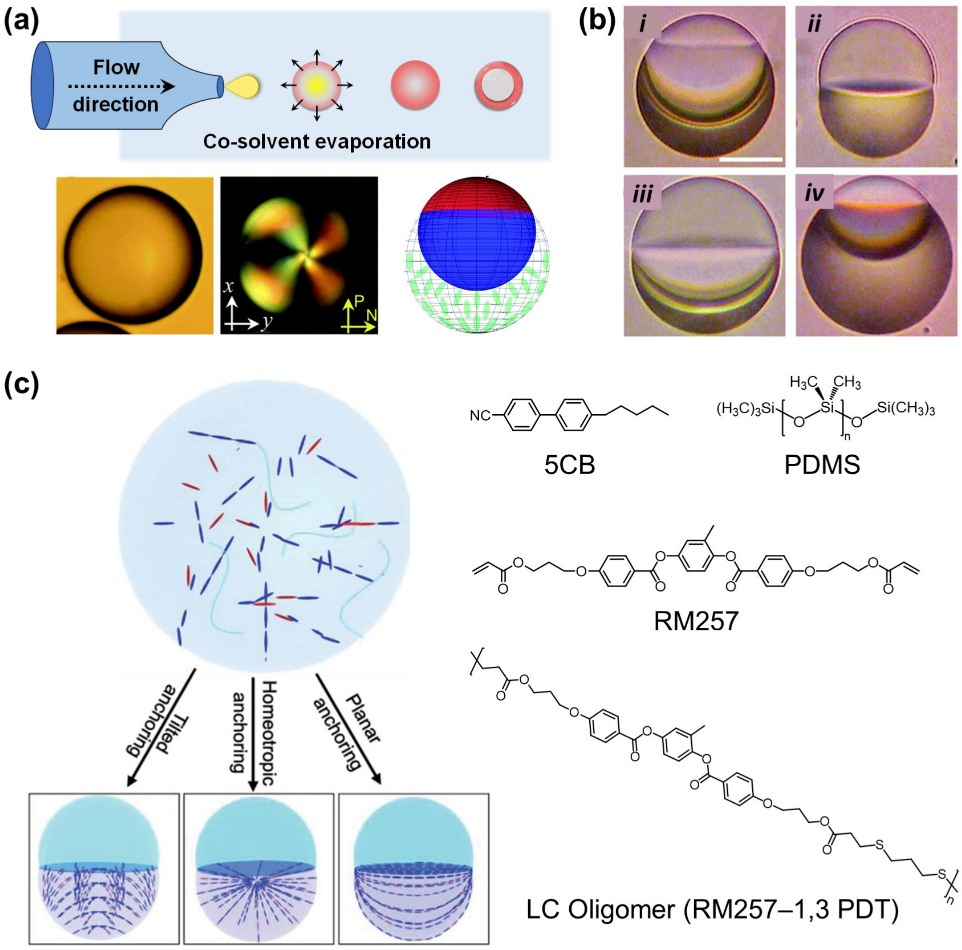


Figure 5. (a) Schematic of the preparation of complex emulsions using evaporation-induced phase separation (top), and Janus LC droplet schematics with corresponding polarized-light optical microscopy images (bottom). **(b)** Side-view optical microscopy images of Janus LC droplet morphologies. **(c)** Schematics of various LC complex emulsion droplet preparations with different LC organizations via evaporation-induced phase separation, and chemical structures of droplet components. Adapted from Ref. [39] with permission. Copyright 2015 The Royal Society of Chemistry. Adapted from Ref. [42] with permission. Copyright 2023 Wiley-VCH Verlag GmbH & Co. KGaA.

Subsequent studies reported complex emulsions containing immiscible smectic LC (4-Cyano-4'-octylbiphenyl, 8CB) and PDMS.[40] The lamellar arrangement within these droplets imposed additional constraints on LC molecule organization, resulting in diverse smectic textures, such as focal conic domains, dislocation rings, and undulations. Similarly, Janus droplets featuring cholesteric LC and PDMS compartments were prepared using an evaporation-induced phase separation method.[41] In these droplets, the LC compartment comprised 5CB doped with an azobenzene-containing chiral dopant, with the helix pitch of the cholesteric phase determined by the chiral dopant's concentration.

Yang and coworkers also created complex emulsions containing PDMS and an LC phase.[42] They employed an LC elastomeric material to form the LC compartment, using a reactive mixture of non-polymerizable mesogen 5CB and acrylate-functionalized LC monomers and oligomers (**Figure 5c**). The synthesis of LC elastomeric Janus microparticles involved a two-step process. Initially, Janus microparticles were formed using microfluidics with chloroform as a co-solvent, followed by UV light irradiation to polymerize the reactive LC mixture. By varying the surfactant composition, they achieved different director field orientations within the LC compartment, including bipolar, radial, and hybrid configurations (**Figure 4c**). Post-chloroform evaporation, phase separation resulted in Janus LC droplets consisting of LC and PDMS compartments. The second step involved extracting unreacted PDMS and 5CB, leading to the formation of elastomeric microparticles. These particles exhibited distinct anisotropic shapes, influenced by factors such as surfactant concentration and composition, the weight ratio of LC to silicone oil components, and the extraction solvent choice. Additionally, these microparticles showed unique temperature-dependent shape responsiveness. In subsequent research, they introduced a reactive chiral dopant into the LC mixture to produce cholesteric LC complex emulsions with tunable reflective structural colors, ranging from red to violet by adjusting the chiral dopant concentration in the LC phase.[43]

Flurocarbon Oils

Abbott and coworkers introduced Janus emulsion droplets consisting of coexisting nematic and isotropic oil compartments, made from a mixture of nematic E7 and perfluorobenzene (FB) oils in a 1:9 volume ratio.[44] The coexistence of nematic and isotropic phases within the E7-FB mixture over a broad temperature range (approximately 10°C) enabled the formation of two compartments. This unique coexistence allowed for convenient and reversible control of each compartment's volume in the Janus droplets (**Figure 6a**). By maintaining a similar composition in both compartments—comprising E7 and FB oils—the droplets retained their spherical shape despite internal morphology changes induced by temperature variations or surfactant additions. Additionally, they demonstrated droplet morphology adjustment using hydrocarbon or fluorocarbon surfactants, revealing a preference for surfactant adsorption at the nematic interface over the isotropic compartment's interface.

In a related study, Abbott and coworkers detailed the creation of multiphase emulsions using a nematic LC (5CB) and immiscible perfluoroalkane oils dispersed in water.[45] Employing perfluorocarbon and hydrocarbon surfactants, these complex emulsion droplets exhibited various morphologies, including core-shell and Janus structures (**Figure 6b**). The high interfacial tension between 5CB and perfluorononane (γ = 13.7 mN/m) led to snowman-shaped Janus morphologies in all cases. These droplets also displayed diverse internal LC organizations, highly dependent on the surfactant type and concentration used. Specifically, they focused on SDS and PFOA surfactants and noted that, while both surfactants led to similar internal configurations in single-phase LC droplets, SDS and PFOA resulted in different internal organizations within the LC compartments of multiphase droplets. They also demonstrated the formation of core-shell emulsion droplets, consisting of a 5CB shell and a perfluoroalkane core. These droplet systems could undergo thermal actuation by heating the droplet above the fluorocarbon oil's boiling point. The vaporization of the fluorocarbon core caused rapid expansion of the 5CB shell, a solvent-induced reconfiguration that is entirely reversible (**Figure 6c**). Cooling the system below the fluorocarbon oil's clearing point led to the recovery of the initial 5CB shell state.

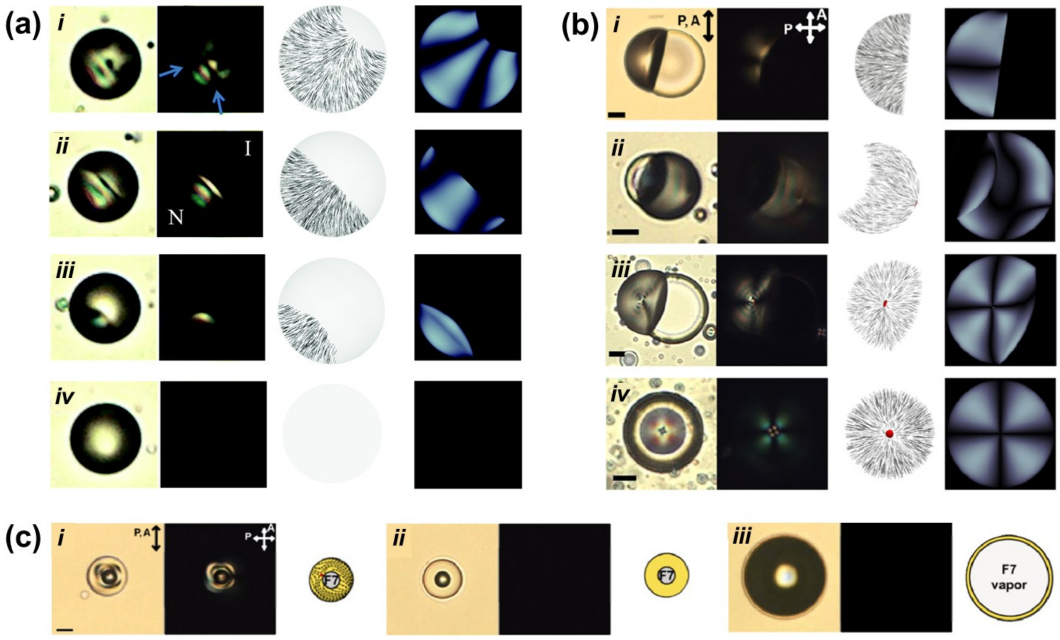


Figure 6. (a) Thermal reconfiguration of an FB-E7 mixture complex droplet via nematic-to-isotropic phase transition: i) 45.0 ºC, ii) 46.0 ºC, iii) 47.0 ºC, v) 47.5 ºC. **(b)** Influence of surfactant type on the morphologies and LC organization of F9-5CB emulsion droplets: i) 2mM SDS, ii) 1mM PFOA, iii) 2mM PFOA, iv) 2mM PFOA. [Columns 1 and 2: polarized-light micrographs (parallel and crossed polarizers, respectively); column 3: director field configuration obtained from simulations; column 4: associated (simulated) polarized-light micrographs]. **(c)** Thermal reconfiguration of a FB-E7 mixture shell: i) 50.0 °C (liquid core, nematic shell), ii) 130.0 °C (liquid core, isotropic shell), iii) 170.0 °C (vapor core, isotropic shell). (Left: parallel-polar micrographs; middle: crossed-polar micrographs; right: schematic illustrations). Adapted from Ref. [44] with permission. Copyright 2019 The Royal Society of Chemistry. Adapted from Ref. [45] with permission. Copyright 2019 American Chemical Society.

Simultaneously, Swager and coworkers described the preparation of dynamically reconfigurable complex emulsions containing immiscible LCs and fluorocarbon oils.[29] To mitigate the high interfacial tension between the 5CB and fluorocarbon oils that initially resulted in snowman-shaped Janus morphologies, they developed a new family of suitable LC/F internal surfactants. These complex LC emulsions exhibited various internal LC configurations, with morphologies capable of transitioning between LC-in-fluorocarbon-in-water double emulsions (LC/F/W), spherical Janus emulsions, and inverted double emulsions (fluorocarbon-in-LC-in-water, F/LC/W). Moreover, more intricate internal arrangements were achieved using both smectic and cholesteric phases.[29, 30] These complex LC emulsion droplets exhibit dual dynamic reconfigurability, as both their droplet morphology and internal LC alignment can be dynamically altered. This feature introduces new functionalities of interest in fields such as optics, active matter, and biosensing. Consequently, these systems will be discussed in detail in Section 3.

Hydrogels

Hydrogel-based compartments have been integrated with LC compartments to create complex LC emulsions. For instance, Zentel and coworkers reported actuating LC Janus particles composed of an LC elastomer compartment demonstrating significant shape changes during the nematic-to-isotropic transition.[46] The other compartment contained a non-actuating polyacrylamide-based hydrogel. Their approach involved dispersing two immiscible monomer mixtures in a dual capillary microfluidic device, using photoinitiated radical polymerization (**Figure 7a**). In a subsequent study, they replaced the polyacrylamide-based hydrogel with a poly(N-isopropylacrylamide) (PNIPAM) hydrogel.[47] This modification resulted in dual-responsive Janus particles with two actuating compartments: the LC elastomeric compartment exhibited substantial temperature-induced shape changes upon isotropization, while the PNIPAM hydrogel compartment showed volumetric expansion due to water swelling at temperatures below the lower critical solution temperature (**Figure 7b**).

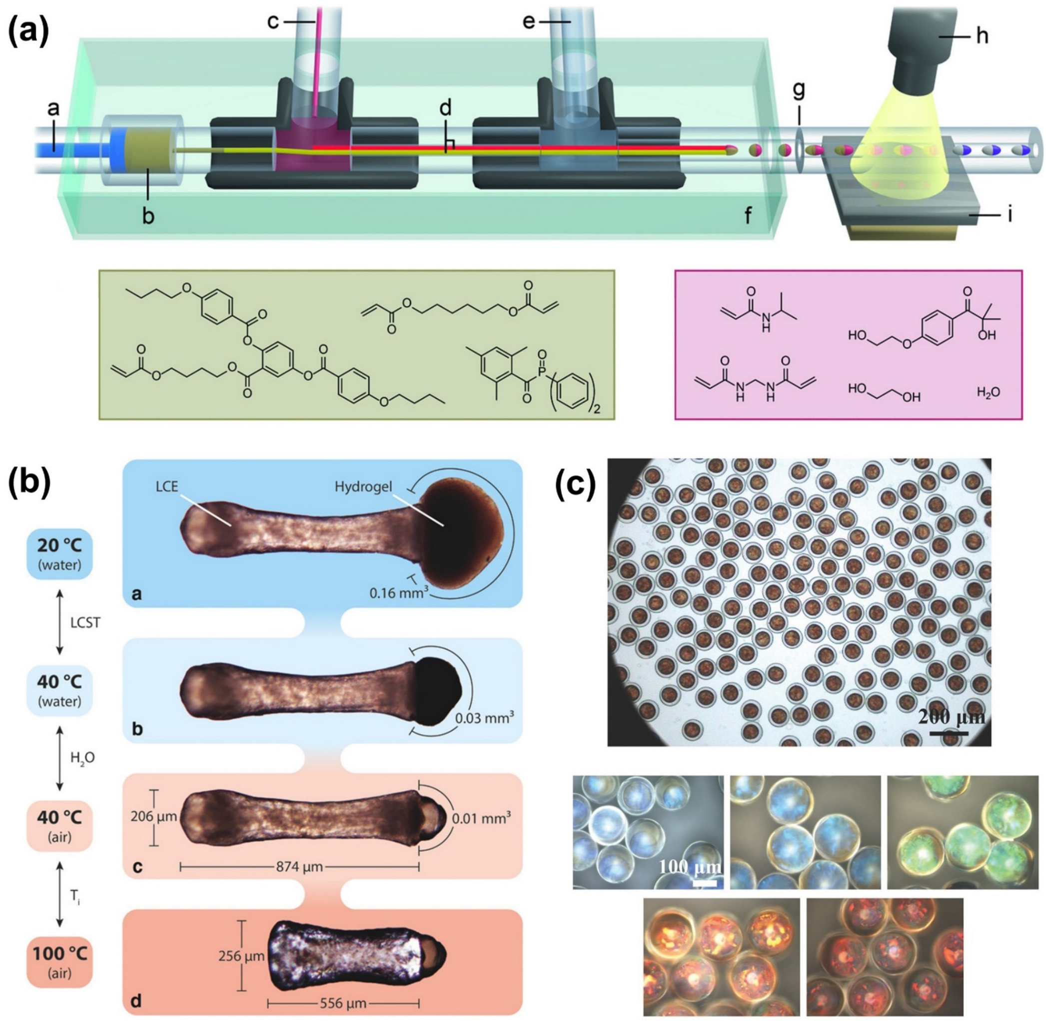


Figure 7. (a) Continuous flow microfluidic setup for producing dual-temperature responsive Janus particles: a) Hydraulic silicone oil, b) LC monomer mixture reservoir, c) PNIPAM hydrogel monomer mixture, d) two parallelly aligned glass capillaries of different lengths, e) continuous phase silicone oil, f) heated water bath at 90 °C, g) tapering of the polymerization tube, h) UV-lamp, and i) heating plate at 40 °C. **(b)** Dual-responsive Janus particles consisting of LC elastomer and hydrogel compartments, exhibiting strong shape changes at two different temperatures. **(c)** Micrographs of cholesteric droplets encapsulated in hydrogel shells (top), showing different reflection colors depending on their composition (bottom). Adapted from Refs. [47, 48] with permission. Copyright 2018 and 2015 Wiley-VCH Verlag GmbH & Co. KGaA.

Kim and coworkers developed complex emulsions where the LC compartment, composed of a cholesteric LC, was encapsulated by a poly(ethylene glycol) diacrylate (PEGDA)-based hydrogel (**Figure 7c**).[48] These emulsions were formed using capillary microfluidics and then exposed to UV irradiation to form the hydrogel around the cholesteric LC, creating stable photonic 'ink' capsules. These microcapsules exhibited remarkable reflective properties that could be adjusted in situ, demonstrating significant potential for a wide range of photonic applications (**Figure 6c**).

3. Dynamically Reconfigurable Complex Liquid Crystals Emulsions

This section highlights dynamically reconfigurable complex emulsions composed of immiscible LCs and fluorocarbon oils, a significant development by Swager and coworkers. These emulsions demonstrate dynamic and reversible reconfiguration in both their droplet morphology and internal LC organization. The classification of these systems is based on the LC phase confined within the emulsion droplets.

Nematic Liquid Crystals

Preparation and Stabilization of Complex LC Emulsions

Dynamically reconfigurable complex LC emulsions containing a nematic LC phase (5CB) and several hydrofluoroethers (HFEs) were fabricated using an evaporation-induced phase separation method (**Figure 8a**).[29] Initially, a homogeneous mixture was created using a 1:1:2 volume ratio of 5CB, HFE, and dichloromethane (DCM) for the dispersed phase. This mixture was then dispersed in an aqueous solution with 0.1 wt.% Tween-20, a non-ionic surfactant. Following the evaporation of DCM, Janus complex droplets emerged, exhibiting two-phase-separated compartments. The evaporation-driven phase separation method is also applicable for generating monodisperse droplets on a large scale via microfluidics. These droplets exhibited a minimization of the LC-F interfacial area, driven by the high interfacial tension between LC and HFE oils ($\gamma_{LC/F}$), resulting in "snowman-shaped" morphologies. A comparative study of droplet morphology in relation to different HFEs revealed that as $\gamma_{LC/F}$ decreased, Janus droplets displayed an increased LC-F surface area, forming more spherical droplets.

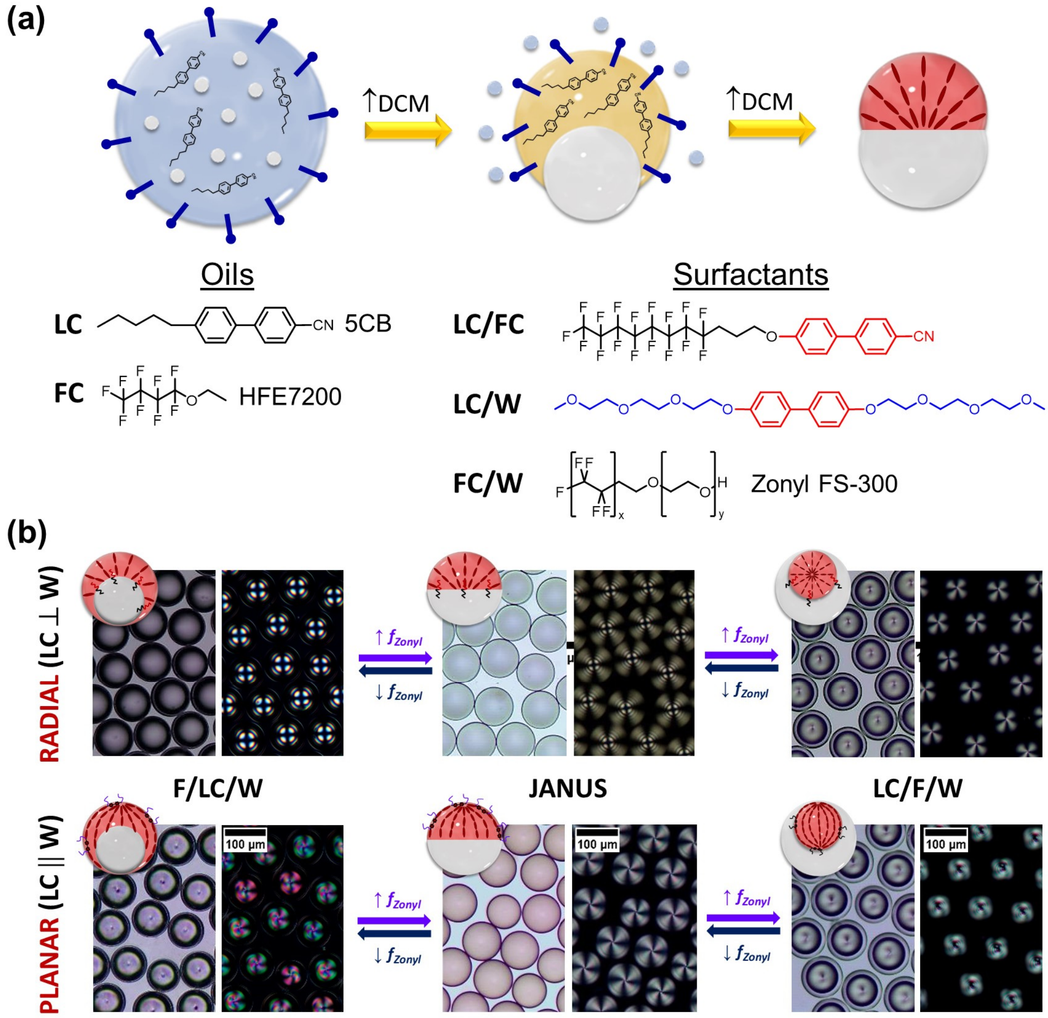


Figure 8. (a) Preparation of dynamically reconfigurable complex LC emulsions through an evaporation-induced phase separation method and composition of both the dispersed and continuous phases. **(b)** Complex LC emulsions with radial (top) and planar (bottom) alignment, dynamically reconfiguring in response to surfactant variations between F/LC/W, Janus, and LC/F/W droplets. Adapted from Ref. [29] with permission. Copyright 2019 American Chemical Society.

Polarized-light optical microscopy was utilized to characterize these complex emulsion droplets. While the isotropic HFE oil appeared black under crossed polarizers, the LC compartment exhibited birefringence. Specifically, the LC compartment displayed a characteristic Maltese cross texture, indicating that the LC director was anchored perpendicular to the LC/W interface, resulting in a radial LC internal configuration.

To create spherical Janus droplets and enable dynamic switching between Janus and encapsulated morphologies (e.g., LC/F/W or F/LC/W), a new family of LC/F internal surfactants was developed. These surfactants, designed to reduce the interfacial tension between LC and F ($\gamma_{LC/F}$), consist of two distinct building blocks: one featuring LC motifs and the other containing fluorinated units. For emulsion preparation, these LC/F internal surfactants were dissolved in the dispersed phase, which included 5CB, HFE-7200, and DCM in a 1:1:2 volume ratio. The emulsification process in an aqueous solution resulted in single emulsions. Post-DCM evaporation, complex emulsion droplets formed with two-phase-separated compartments, incorporating the LC/F internal surfactants. By analyzing the contact angles between LC, F, and W phases, the precise amount of internal surfactant required to achieve spherical droplets and avoid snowman-like morphologies was determined.

Successful reduction of $\gamma_{LC/F}$ facilitated dynamic reconfiguration of these complex LC emulsions by altering the mass balance of aqueous surfactants (**Figure 8b**). Typically prepared in Tween-20 aqueous solutions stabilizing the LC/W interface, these complex emulsion droplets initially resulted in F/LC/W droplets with the LC compartment encapsulating the fluorocarbon oil. Introducing a non-ionic fluorocarbon surfactant, Zonyl FS-300, dynamically altered the droplet morphology. F/LC/W droplets transitioned gradually to a spherical Janus morphology before transforming into spherical LC/F/W droplets. Optical microscopy with crossed polarizers illustrated these morphological changes, revealing radial configurations with LC phase director perpendicular to the interfaces.

Controlling the Internal LC Ordering

Controlling the LC organization within complex emulsions is crucial for creating systems with customized functionality, achievable by adjusting the LC's surface anchoring using surfactants. A bola-amphiphilic surfactant with a mesogenic core and two hydrophilic triethylene glycol chains was designed (**Figure 8a**).[29] This surfactant stabilizes the LC/W interface and induces planar anchoring of the LC director. Introducing this surfactant to complex emulsion droplets resulted in the LC phase aligning parallel to the LC-W interface (**Figure 8b**). Consequently, Janus and F/LC/W droplets exhibited a monopolar configuration with a single point defect at the LC compartment's north pole. For LC/F/W droplets, a similar LC/F surfactant with fluorous alkyl chains was used, inducing planar alignment of LC director at the LC/F interface, resulting in a bipolar configuration with two defect points at the poles of the LC compartment.

Templated Assembly via Topological Defect-Driven Functionalization

Topological defects in LCs, exhibiting a lower level of local orientational order compared to surrounding LC material, can serve as assembly sites for various entities such as small amphiphiles and nano- or micro-particles. These defects, typically around 10 nm in size in thermotropic LCs, attract nanoscopic inclusions due to the higher free energy density in the disordered molecular arrangement within the defect core. Swager and coworkers have explored this property, particularly in monopolar-configured complex LC droplets, for bioconjugation.[29] They introduced amphiphilic polymers with boronic acid groups, which selectively localize at topological defects located at droplet poles, thereby adding chemical functionality. These boronic acid surfactants preferentially partition towards the defect core, decreasing the free energy cost associated with elastic deformations of LCs near defects and diminished orientational ordering of molecules in the core. Subsequently, the boronic acids react reversibly with N-glycans in the fragment crystallizable (Fc) region of IgG antibodies, immobilizing these antibodies within the topological defect (**Figure 9**)—the Fc region of an antibody is the tail of an antibody that binds to Fc receptors on cell surfaces and certain complement proteins. FITC-labelled IgG antibodies and confocal microscopy with crossed polarizers confirmed the successful functionalization of topological defects, revealing that the fluorescent signal (green spots) from surface-bound IgG antibodies correlated with the localization of the topological defect in the monopolar Janus droplets. This LC topological defect-templated functionalization establishes an innovative approach for introducing recognition specificity into LC-based biosensors, potentially amplifying molecular-level recognition events and contributing to the development of highly sensitive LC biosensors.

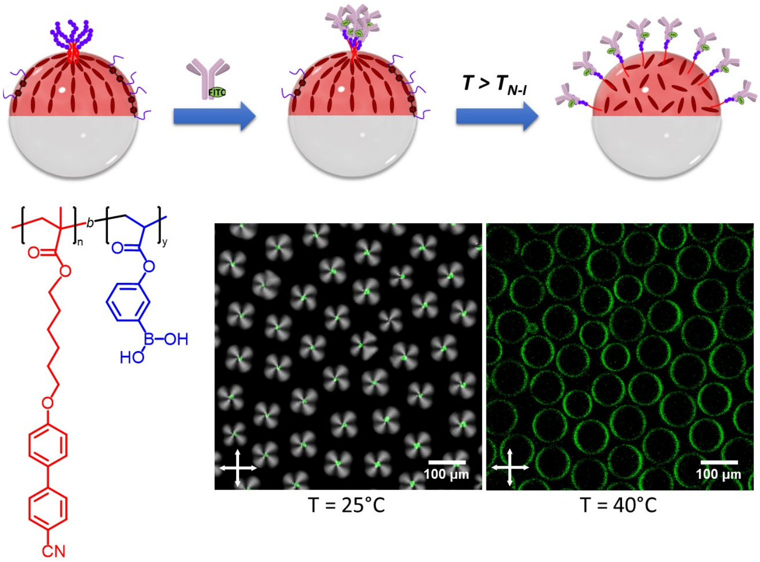


Figure 9. Antibody immobilization at topological defects: schematic representation (top), chemical structure of the boronic acid block copolymer surfactant employed for topological defect functionalization (bottom left), and confocal microscopy images of LC Janus droplets functionalized with a dye (FITC)-labeled IgG antibody at different

temperatures. Adapted from Ref. [29] with permission. Copyright 2019 American Chemical Society.

Functionalization with Magnetic Nanoparticles for Active Control

Advancing the controlled movement and orientation of complex LC emulsions involves the precise positioning of magnetic nanoparticles (MNPs) at emulsion interfaces, explored through interfacial imine chemistry.[49] This approach selectively binds amine-functionalized MNPs to one of the interfaces of complex LC emulsions using aldehyde-functionalized surfactants. Complex emulsions with various internal LC director configurations were investigated for increased precision in MNP assembly.

Initially, MNPs were attached to Janus droplets exhibiting a radial configuration (**Figure 10a**). The homogeneous distribution of aldehyde-functionalized surfactant along the LC/W interface in the radial LC Janus droplets facilitated the formation of an MNP shell around the interface. Confocal microscopy, using rhodamine-functionalized MNPs, demonstrated interfacial attachment. Without an external magnetic field, MNP-functionalized Janus droplets were randomly dispersed in water. However, when exposed to a magnetic field, the droplets magnetized, exhibiting translational motion towards the magnet and forming short-range linear chains without altering the LC ordering of the Janus radial droplets. Once the magnetic field was removed, the droplets ceased movement, the chains disintegrated, and the droplets dispersed back into the water.

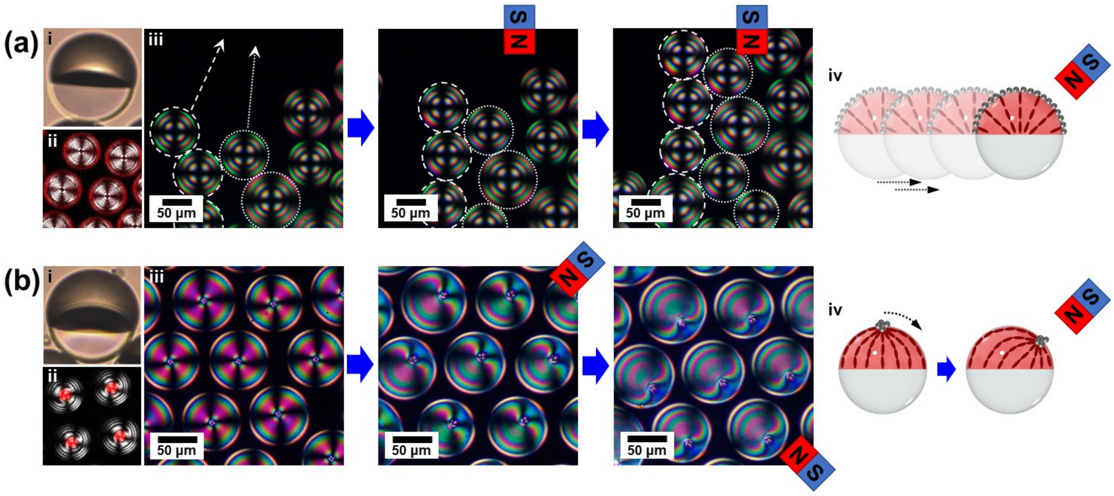


Figure 10. Magnetic response of MNP-functionalized complex LC emulsions with **(a)** radial and **(b)** monopolar organizations: (i) side-view microscopy images, (ii) confocal microscopy images, (iii) polarized-light optical microscopy images, (iv) schematic representations. Adapted from Ref. [49] with permission. Copyright 2019 American Chemical Society.

The study extended to Janus droplets with a monopolar configuration featuring a topological defect at the LC/W interface, positioned at the droplet's pole (**Figure 10b**). These droplets exhibit a topological defect at the LC/W interface, naturally positioned at the pole of the droplet. Incorporating an aldehyde-functionalized surfactant into these droplets resulted in preferential partitioning towards the defect core to decrease free energy. The subsequent imine formation between the aldehyde surfactant, concentrated in the topological defect of the LC Janus droplets, and the amine-functionalized MNPs led to the assembly of MNPs concentrated around the topological singularity at the droplet's pole without altering their monopolar internal organization. Confocal microscopy with rhodamine-labelled MNPs showed a discernible fluorescence signal (red spots) consistent with the localization of MNPs at the topological defects of the monopolar Janus droplets. In the presence of a magnetic field, the MNPs-functionalized topological defect migrated towards the magnet, maintaining the orientation of the Janus droplets without physically moving them. Removal of the magnetic field allowed the topological defects to revert to their initial state and location.

This LC templating approach for precisely controlling the interfacial organization and positioning of MNPs represents a novel method for programmable NP assemblies with different compositions, shapes, and dimensions. Achieving precise organization of MNPs in three-dimensional interfacial space broadens the manipulation spectrum of complex emulsions, advancing the creation of active emulsion systems.

Smectic Liquid Crystals

Smectic LCs were incorporated into complex emulsion droplets to enhance the complexity within the LC compartment. This system shows promise in supporting and manipulating a variety of novel LC textures in suspended droplets. CB8, known for its smectic A phase at room temperature, was selected for this purpose. Using the evaporation-induced phase separation method and internal surfactants designed to decrease $\gamma_{LC/F}$, spherical complex droplets containing smectic LCs were successfully created.[29] In an aqueous solution of Tween-20, 8CB's smectic A phase displayed perpendicular alignment to the LC/W interface, resulting in Maltese cross textures indicative of radial configurations. These textures featured concentric layers emanating from the droplet's center. When using a bola-amphiphilic surfactant to promote planar alignment of LC, multiple focal-conic defects emerged within the LC compartment, forming a polygonal structure. Moreover, these smectic Janus droplets displayed dynamic reconfiguration, transitioning between encapsulated configurations (LC/F/W and F/LC/W) and the Janus configuration by adjusting the aqueous surfactant mass balance.

The confinement of smectic LCs within complex emulsions with controllable geometry and boundary conditions has been proposed as a new class of soft building blocks. Precisely controlling LC defect/texture formation and evolution expands our toolkit for fabricating functional soft materials. Exploring how these smectic textures configure and reconfigure in response to external fields or tunable anchoring conditions is an intriguing prospect. The existing system could also serve as a template for embedding nanoparticles for photonic applications.

Cholesteric Liquid Crystals

Preparation, Stabilization, and Controlling the Internal Helical Arrangement

Complex emulsions containing immiscible cholesteric LC (N*) and hydrofluoroether oil (HFE-7200) were developed (**Figure 11**).[30] These emulsions were prepared by emulsifying a single oil phase, consisting of immiscible oils dissolved in dichloromethane (DCM), within an aqueous phase containing surfactants. The slow evaporation of DCM led to emulsion droplets with highly controlled morphology and composition. This evaporation-induced phase separation method is compatible with microfluidics, enabling the creation of monodisperse droplets.

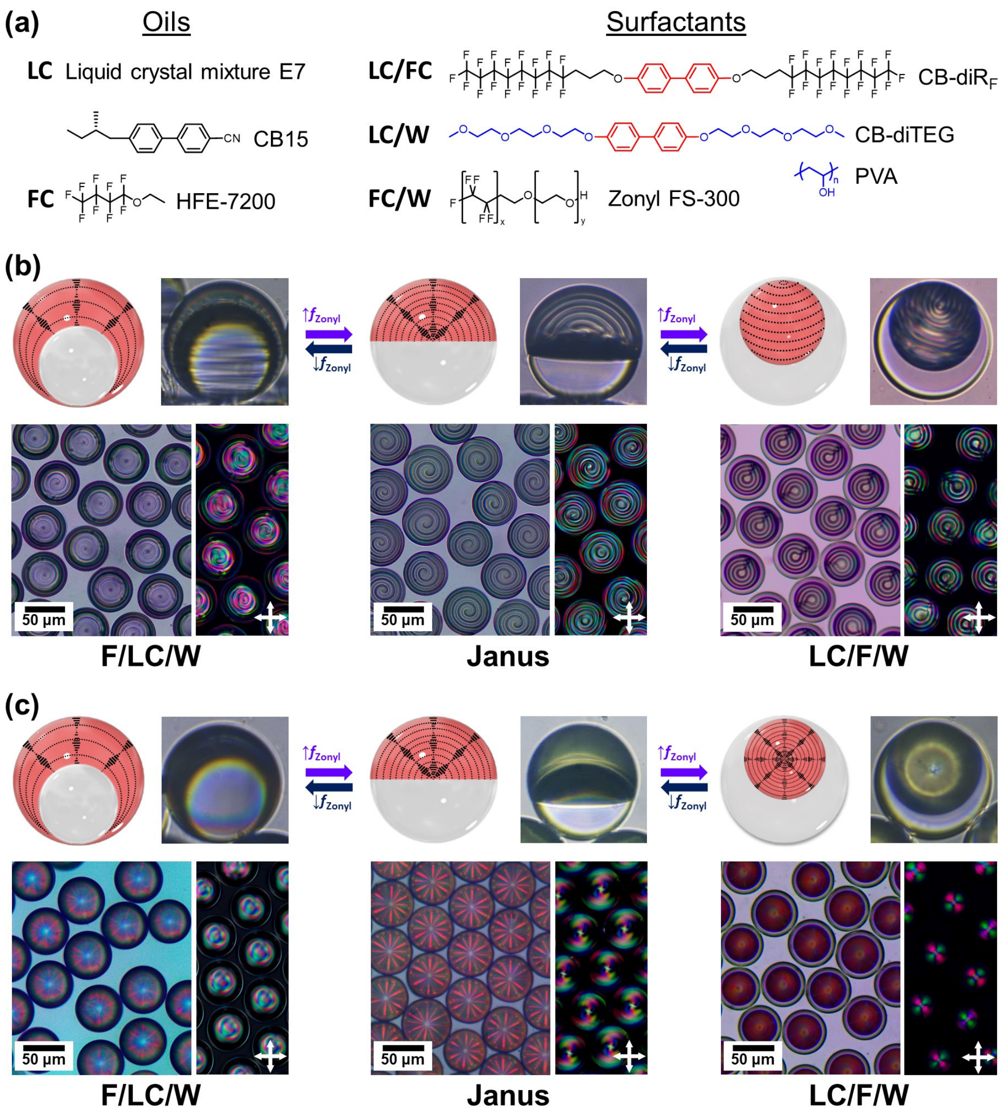


Figure 11. Dynamically reconfigurable complex emulsions composed of immiscible cholesteric LCs and fluorocarbon oils dispersed in water: (a) Composition of both the dispersed and continuous phases. (b) Schematic representation, side-view images, and top-view polarized-light optical microscope images of complex emulsions containing 1 wt.% of CB15. (c) Schematic representation, side-view images, and top-view polarized-light optical microscope images of complex emulsions containing 32 wt.% of CB15.5. Adapted from Ref. [30] with permission. Copyright 2021 American Chemical Society.

The LC phase consisted of a doped N*, obtained from mixing (*S*)-4-cyano-4´-(2-methylbutyl)biphenyl (CB15) as chiral dopant and E7 as the nematic LC matrix (**Figure 11a**). The selection of such a N* was due to the possibility to tune the helical pitch (*P*) by varying the chiral dopant concentration. As firstly described by Lagerwall and coworkers, N* emulsion droplets exhibit omnidirectional light reflection, achieved through radial organization of the N* within the droplets.[50] In complex emulsions containing N*, a radial disposition of the N* helical organization was attained using new generations of LC/W and LC/FC surfactants (**Figure 11a**) that stabilize interfaces and control LC interfacial anchoring.[30]

A N* mixture containing 1 wt.% of CB15 displayed helical pitch values in the micrometer range (P = 14 μm), enabling visualization via optical microscopy. Owing to the radial arrangement of the N* helices, all three droplet morphologies (Janus, FC/LC/W, and LC/FC/W) exhibited a periodic pattern of dark and bright concentric rings with a P/2 inter-ring periodicity (**Figure 11b**). However, increasing the CB15 concentration to 32 wt.% reduced the helical pitch to an unobservable level under optical microscopy (P = 0.44 μm). Nevertheless, the N* compartment displayed light reflection properties, indicating a periodic internal structure derived from the N* (**Figure 11c**). The reflection patterns included a bright central point and radial lines emanating from it, with the central point resulting from normal reflection of the N* arrangement and the radial lines from photonic inter-droplet communication. This communication among neighboring droplets diminished with increasing distance. Photonic patterns were also observed in FC/LC/W double emulsion droplets, while LC/FC/W droplets did not exhibit such patterns due to complete internal reflection at the LC/FC interface.

Application as Optical Biosensors

Complex emulsions containing N* are promising candidates for biosensing applications, capable of modifying their reflection wavelength (and thereby changing the emulsions' color) in response to variations in the pitch of the N* organization induced by specific analytes.[51, 52] Prior approaches to N* biosensing relied on the solubility of analytes in the N* phase, where their absorption altered the N* pitch.[53, 54] However, these methods lacked specificity and were limited by the solubility of certain analytes, like biomolecules and microorganisms.

To address these limitations, amphiphilic block copolymers containing LC and water-soluble blocks were utilized (**Figure 12a**). The LC-soluble block, composed of binaphthyl motifs known for high helical twisting power (HTP) values, was randomly copolymerized with a cyanobiphenyl methacrylate to enhance solubility in the nematic LC matrix. The water-soluble block featured boronic acid functionalities, positioned at the LC/W interface for reversible binding with anti-Salmonella Typhimurium IgG antibodies. It was observed that bioconjugation with IgG antibodies increased the interfacial activity of the polymeric surfactant, as the large IgG molecules (≈150 kDa) added hydrophilic character. Bioconjugated surfactants mainly located at the LC/W interface due to their higher interfacial activity, thereby minimally affecting the N* LC's helical structure. In contrast, non-bioconjugated block copolymer surfactants exhibited potent chiral dopant activity due to their lower tendency to assemble at the LC/W interface. Notably, even minor changes in the interfacial activity of the boronic acid surfactants were sufficient to alter the pitch of the cholesteric organization, detectable by monitoring the normal reflection of the N* complex emulsions. This sensing scheme relied on changes in the interfacial activity of boronic acid surfactants associated with competitive binding/unbinding of IgG antibodies at the LC/W interface, producing optically readable and triggered reflectance changes, effectively serving as an optical read-out for Salmonella detection. Specifically, initial N* complex droplets displaying a red reflection band underwent gradual blue shifting upon adding increasing concentrations of Salmonella cells (**Figure 12b**). This shift enabled the creation of a calibration curve, facilitating quantitative detection with competitive limits of detection around 10^3 cells/mL. Remarkably, this detection capability was achieved without complex specialized equipment, using only a simple spectrophotometer.

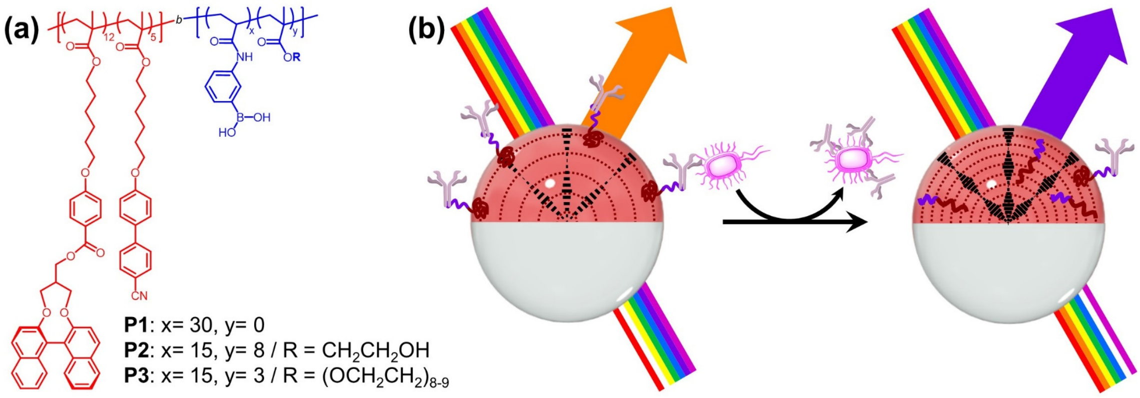


Figure 12. (a) Chemical structures of boronic acid surfactants for bioconjugation with IgG antibodies. **(b)** Schematic representation of the mechanism for *Salmonella* detection using cholesteric complex emulsions: changes in reflection induced by alterations in the interfacial activity of boronic acid polymeric surfactants that competitively bind/unbind to IgG antibodies at the LC/W interface. Adapted from Ref. [30] with permission. Copyright 2021 American Chemical Society.

4. Conclusions and Outlook

The integration of LCs into complex emulsions represents a significant advancement in the design of functional soft materials. The fabrication of emulsions with phase-separated LC compartments introduces novel functionalities and enables dynamic alterations in both the internal LC organization and droplet morphology. This review has offered a comprehensive overview of complex emulsions containing LCs, categorizing them based on the immiscible oil mixed with the LC oil, and highlighting systems that demonstrate dynamic and reversible reconfiguration in droplet morphology and internal LC organization.

Advances in producing dynamic complex LC droplets now facilitate large-scale generation of uniform and controllable morphologies. This progress encompasses the ability to manipulate internal LC configurations, droplet actuation, and, in some instances, modify droplet geometries. Real-time monitoring of these processes further enriches our understanding and control over these systems. Future developments could lead to the creation of highly intelligent micro-colloids, capable of exhibiting multiple responsive units, inter-colloidal communication, and even self-regulatory and autonomous behaviors.

The dynamic and responsive nature of LC emulsions, particularly sensitive to molecular-level interactions at their interfaces, positions them as potent tools for chemical and biological sensing. Progress in the functionalization, stabilization, and organization of complex LC emulsions is anticipated to play a pivotal role in advancing droplet-based sensor technologies. The feasibility of preparing these stimuli-responsive droplets in diverse environments, combined with straightforward, non-laboratory-based read-out techniques, offers substantial advantages for in situ monitoring and rapid detection applications. A particularly intriguing advancement in this area has been the controlled creation of topological singularities in complex emulsions containing nematic LCs. This breakthrough has paved the way for the precise attachment of recognition elements capable of inducing significant changes in the LC director field in response to interfacial recognition events with targeted analytes. These features are especially pertinent for developing ultrasensitive chemical and biological sensors that may surpass current detection limits.

Complex emulsions incorporating cholesteric LCs have been employed for their selective reflection properties, offering a rapid and sensitive method for detecting foodborne pathogens. The simplicity and adaptability of this system suggest its potential application to a broad spectrum of analytes in complex media, highlighting the versatility of LC-based complex emulsions in creating efficient and responsive sensing platforms. Additionally, cholesteric emulsion systems hold considerable potential in photonics due to their omnidirectional reflection of constant wavelength, exhibiting minimal dependence on viewing angle. This attribute, coupled with their tunability, unlocks vast possibilities in dynamic photonic applications, such as retroreflectors, adaptive camouflage systems, autonomous sensors, and high-security identification tags.

Moreover, LCs have facilitated the controlled assembly of functional structures via interfacial reactions, showcasing novel magnetic field-responsive systems. Such functionalization of LC interfaces has been instrumental in structuring and confining magnetic particles at interfaces, potentially giving rise to ferromagnetic droplets. This innovation permits manipulation and controlled deformation of liquid crystal director fields, marking a significant step forward in the field of responsive and active colloids.

In optics, the dynamic manipulation of fluid interfaces in LC emulsions creates exciting prospects for developing fluidic lens systems with unique optical properties. The gravitational alignment of droplet phases and the ability to alter the LC organization within droplets may enable complex LC droplets to modulate transmitted light paths, exhibiting unique angular anisotropic refraction, reflectivity, and switchable color. Integrating stimuli-responsive units within droplets can facilitate the creation of dynamically controlled lensing materials, holding great promise for enhancing and diversifying existing optical technologies.

As research progresses, the collaboration between chemists, biologists, physicists, and engineers will be crucial in harnessing the full potential of these complex LC emulsions. The objective is not only to comprehend their fundamental properties but also to translate this knowledge into practical applications in optics, photonics, (bio)sensing, and active and autonomous materials. Although integrating these systems into real-world applications remains a significant challenge, the recent advancements in LC emulsion research inspire confidence that their practical realization is only a matter of time.

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Conflicts of interest

There are no conflicts to declare.

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