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Construction and application of multicomponent fluorescent droplets

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ABSTRACT

The rapid development of microfluidic technology has led to the evolution of microdroplets from simple emulsion structures to complex multilayered and multicompartmental configurations. These advancements have endowed microdroplets with the capability to contain multiple compartments that remain isolated from one another, enabling them to carry different molecules of interest. Consequently, researchers can now investigate intricate spatially confined chemical reactions and signal transduction pathways within subcellular organelles. Moreover, modern microdroplets often possess excellent optical transparency, allowing fluorescently labelled, multi-layered, and compartmental droplets to provide detailed insights through real-time, *in situ*, and dynamic fluorescence imaging. Hence, this review systematically summarizes current methodologies for preparing multicomponent microdroplets and their applications, particularly focusing on fluorescent microdroplets. Additionally, it discusses existing critical challenges and outlines future research directions. By offering a comprehensive overview of the preparation methods and applications of fluorescent microdroplets, this review aims to stimulate the interest of researchers and foster their utilization in more complex and biomimetic environments.

1. Introduction

Over the past few decades, microfluidic technology has undergone significant progress and found widespread applications across diverse fields, including biomedicine, chemical analysis, and materials science [1–6]. Microfluidic droplets, often ranging in size from picoliters to nanoliters, represent tiny liquid compartments or discrete volumes manipulated within microfluidic systems. These droplets serve various purposes, including conducting chemical reactions, analyzing biological samples, transporting materials, and facilitating chemical and biological separations. Microfluidic droplets offer numerous advantages, such as high controllability, efficiency, precise sample handling, and automation capabilities, making them highly appealing to researchers and practitioners alike [7–12]. The preparation methods for microfluidic droplets are diverse, with their properties and applications heavily influenced by the chosen method [13]. The methods can be broadly categorized based on droplet structure into simple emulsion droplets, multilayered droplets, and multicompartmental droplets [14–16].

It is commonly known that simple emulsion droplets represent one of the most basic types of droplets, formed by mixing one fluid with another immiscible fluid (Fig. 1a). Currently, single emulsion droplets, typically composed of water in oil or oil in water, are extensively studied and relatively easy to prepare. Various conventional methods, such as mechanical stirring, high-pressure homogenization, and high-speed jetting, can be employed for the production of monodisperse emulsion droplets [17,18]. However, these methods often yield droplets with unpredictable particle size distributions, characterized by a high coefficient of variation, and achieving uniform encapsulation of contents remains challenging. Microfluidic technology offers a promising approach for creating simple droplets by precisely controlling the fluids and microchannels, thereby allowing for the manipulation of droplet size and content. There has been a growing interest in multilayered droplets, which contain more than one liquid layer, compared to simple emulsion droplets [19,20]. The structure of multilayered droplet enables the mixing of multiple reagents within a single droplet or the analysis of multiple chemical components. Although microdroplets can encapsulate a larger quantity of substances than

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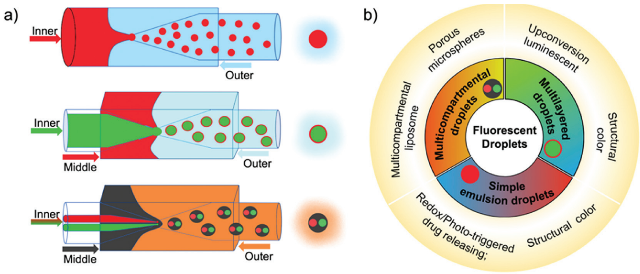

Fig. 1. (a) Schematic diagram illustrating microfluidic chips for producing simple emulsion droplets, simple emulsion droplets, multilayered droplets, and multicompartmental droplets, respectively. (b) Representative applications of multicomponent droplets in some key areas are discussed in this review.

monolayer droplets, traditional mechanical mixing methods become impractical due to the increasing number of internal layers within the droplets, leading to non-negligible interactions between these layers. Hence, employing a more sophisticated microfluidic system is typically necessary for the preparation of multilayered droplets to ensure stability among multiple layers, including maintaining tension balance across various interfaces. Additionally, alongside the production of multilayered droplets, microfluidic technology can also be utilized to create multicompartmental droplets, which consist of two or more immiscible cores loaded with different compositions [21–23]. This approach enables the simultaneous testing of multiple conditions in a single experiment, facilitating high-throughput screening. Since each core resides within its own distinct liquid phase, cross-contamination and interference between different cores are minimized. In general, achieving consistent distribution of each core throughout the droplet requires a high degree of precision in the preparation of multicore droplets. While Janus droplets represent another common form of droplets [24], our review primarily focuses on the multiple layers and multicore features of droplets. Therefore, Janus droplets are not included in this overview. The progress in the field of Janus droplets has already been summarized in numerous comprehensive reviews, and readers are encouraged to refer to these important reviews for further details [25–29].

Fluorescence technology refers to a phenomenon where a substance emits light when it absorbs light of a particular wavelength as a result of electrons in the substance being excited to higher energy levels and then returning to lower energies. Due to high sensitivity, selectivity, reproducibility, simplicity, non-invasion, and ease of integration, fluorescence labeling is widely used in molecular imaging, detection of biomolecules, chemical analysis, and quality control [30–35]. In the microfluidic droplet domain, fluorescence plays a crucial role. Incorporating fluorescent dyes into droplets, either internally or on their surfaces, imparts unique properties, rendering them invaluable tools for real-time monitoring, molecular detection, and high-throughput screening in microfluidic systems [36]. Specific fluorescent labels enable the tracking of droplet position, concentration, and chemical composition, facilitating various biomedical research applications such as single-cell analysis, drug screening, and disease diagnosis. Moreover, fluorescence technology holds promise in chemical synthesis and microreactors, enabling the simultaneous tracking of multiple reaction pathways or the analysis of multiple compounds concurrently. Utilizing fluorescent labels aids researchers in comprehending flow and mixing processes within droplets, which is essential for optimizing the performance of microfluidic systems.

It has been shown that fluorescent droplets can be applied to a variety of fields, especially the preparation of functional materials, including controlled drug delivery systems (DDSs), stimulus-responsive color-changing inks, up-conversion luminescent materials, and tunable structural coloration droplets. And other important applications in biological systems, including simulating the behavior of cellular communication, analyzing single cells, screening drugs, and diagnosing diseases, *etc.* [37,38]. This emergence of fluorescent droplet-based applications can primarily be attributed to the unique properties of fluorescent droplets, such as high specificity and sensitivity, non-invasive and real-time imaging without destroying the droplet structure, easy integration with other detecting technologies without complex manufacturing costs, and a combination of multiple wavelength ranges allows flux detection to be improved by simultaneously generating multiple information [39,40]. Hence, this review comprehensively discusses the application of fluorescence to different types of droplets and addresses the challenges associated with droplet preparation and operation to enable broader applications to be achieved. Generally, droplets can be classified into the following categories based on their morphological diversity: single-emulsion droplets, high-order hierarchical emulsion droplets, multiple-core droplets, multicompartmental droplets, and nonspherical droplets [41]. Due to space limitations, we have selected the three most widely studied types of fluorescent droplets for discussion, including simple emulsion droplets, multilayered droplets, and multicompartmental droplets. Representative examples are provided to facilitate readers' understanding of the advancements, challenges, and existing issues (Fig. 1b). Finally, we offer a detailed overview of future research directions in microfluidic droplets.

2. Simple emulsion droplets

Simple emulsion droplets consist of a dispersed phase and a continuous phase, and they can be categorized into oil-in-water (O/W) emulsion and water-in-oil (W/O) emulsion. Microdroplets prepared by traditional homogenizers or high-speed jets lack control over the distribution of their inner and outer surfaces, making it challenging to modify their interface and encapsulate drug efficiently. Microcapsules, which are microscale particles or vesicles characterized by distinctive structures typically composed of polymers, lipids, or other materials, find extensive use in various fields, including drug delivery, biosensing, and catalysis for encapsulating and protecting internal substances [42–44]. Hence, precise control over the polymerization behavior of the shell is crucial for loading and releasing internal content. Traditionally, layer-by-layer encapsulation is performed after nanoparticle formation, resulting in low loading efficiency [45,46]. The use of microfluidic technology is gaining popularity as a method for precisely tailoring the preparation of microcapsules due to its ability to control fluid manipulation accurately.

In 2012, Abell and coworkers developed a one-step microcapsule synthesis method utilizing a microfluidic chip, which seamlessly integrated the formation of microdroplets with supramolecular interactions among host and guest molecules [10]. Employing a straightforward T-junction geometry on the microfluidic chip, the aqueous phase consisted of three key components: aqueous CB[8], polyethylene glycol (**1**)/methyl viologen (**2**)-modified Au nanoparticles (AuNPs), and a naphthalene-based co-polymer (**3**) (Figs. 2a and b). At the T-junction, the fluorous oil phase and the aqueous phase converged, giving rise to the formation of droplets. Subsequently, a meticulous mixing and assembly process occurred within serpentine channels, yielding highly dispersed microdroplets with a diameter averaging approximately 59.6 micrometers and a coefficient of variation of about 1.3% (Fig. 2c). Notably, the host-guest interactions between CB[8] and viologen/naphthalene led to the formation of ternary complexes, culminating in a continuous network of cross-links. As dehydration ensued, the oil-encapsulated water droplets underwent gradual size reduction, eventually collapsing to form microcapsules (Fig. 2d).

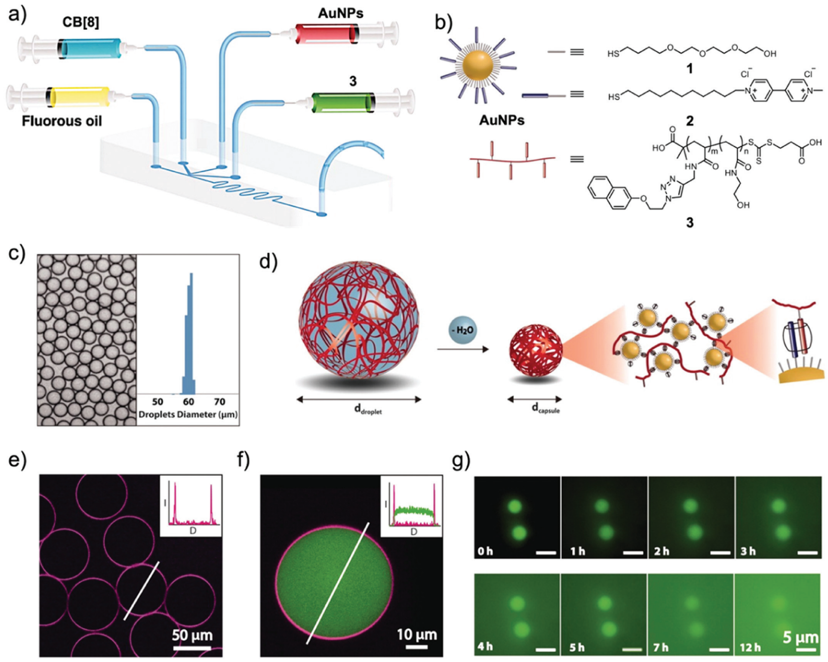

Fig. 2. (a) Diagram of a four-channel T-shaped microfluidic chip. (b) Schematic representation of AuNPs, and chemical structures of compounds **1**, **2** and **3**. (c) Transmission electron microscope (TEM) image and dynamic light scattering (DLS) curve of the resultant droplets. (d) Diagram of microdroplets dehydrated to form microcapsules. CLSM images (e) at the interface of and (f) the inside the fluorescent droplets. (g) Time-dependent CLSM images of droplets in the presence of $Na_2S_2O_4$ solution. Reproduced with permission [10]. Copyright 2012, American Association for the Advancement of Science (AAAS).

Subsequently, to evaluate the controlled delivery capability of the microcapsules, naphthalene copolymers were covalently modified with the fluorescent dye rhodamine B (RB). Additionally, water-soluble fluorescein isothiocyanate (FITC)-dextran was introduced as a carrier. Confocal laser scanning microscopy (CLSM) revealed the purple fluorescence of RB at the interface of the microdroplets, indicating successful modification. FITC-dextran, a water-soluble green dye, was predominantly localized within the droplets, signifying the establishment of host-guest interaction at the oil-water interface (Figs. 2e and f). Subsequent treatment with a solution of $Na_2S_2O_4$ led to the cleavage of the trithiocarbonate moiety in the polymer, disrupting the interfacial structure of the droplets. This disruption facilitated the slow diffusion of FITC-dextran from the interior to the exterior of the microcapsules (Fig. 2g). By integrating microdroplet preparation with supramolecular self-assembly at the interface, this study demonstrated the rapid formation of internally hollow, monodisperse microcapsules with high uniformity. This approach offers a straightforward and efficient method for microcapsule preparation, as well as for the encapsulation and delivery of pharmaceuticals. Furthermore, the interface resulting from pace-confined self-assembly exhibits inherent defect-free uniformity, with its morphology controllable *via* adjustments in monomer concentration and solvent type. Thus, the method of self-assembly in confined interfaces demonstrated in this study holds promise for the preparation of various functional materials, including ultrathin films, capsules, and nanofibers [41,47,48].

While disrupting microcapsules through reduction-based methods effectively achieves drug release, it often lacks reversibility, thus rendering on-demand controlled drug release unattainable. An alternative approach involves photochromism, wherein light triggers structural changes in fluorescent molecules, altering their fluorescence from the initial state. Azobenzene serves as a prime example of a photochromic compound capable of undergoing photoinduced *cis-trans* isomerization. This process not only affects the absorption and emission spectrum, but also alters the molecular arrangement. Consequently, azobenzene represents a promising candidate for facilitating drug delivery under photocontrolled conditions [49–52].

In order to achieve this objective, Scherman and colleagues employed microfluidic techniques to fabricate microdroplets containing photochromic components (Fig. 3a) [53]. Initially, they synthesized two viologen/naphthalene-modified polymer molecules (**4** and **5**) with different luminescent units (RB and fluorescein), capable of forming supramolecular ternary complexes with CB[8] (Fig. 3b). Self-assembly took place at the interface of microdroplets, leading to the formation of a nanoscale network of cross-linked polymers. Water-soluble **4** is labeled with green fluorescein, while oil-soluble **5** was labeled with red rhodamine B. An intriguing aspect of water-in-oil microdroplet formation was that their interiors appeared red, while their exteriors appeared green (Fig. 3c). In oil-in-water microdroplets, the colors of the interior and exterior were reversed (Fig. 3d). The results of these experiments demonstrated that polymer redistribution within aqueous or oil phases did not disrupt the assembly occurring at the microdroplet interface.

The drug loading study indicates that when polymers assemble at the interface, water-soluble Congo Red (CR) is encapsulated within the microdroplet. These microdroplets further shrink upon dehydration, forming microcapsules, where CR is successfully encapsulated, suggesting their potential for drug delivery (Figs. 3e and f). Upon replacing the naphthyl part with the photochromic azobenzene (AB) moiety, microdroplets release internal CR when exposed to 365 nm light, achieving on-demand cargo delivery in a light-controlled manner (Figs. 3g and h). In this study, photochromism and microdroplet interface assembly are combined to develop a method for interface drug encapsulation. Besides carrying other drug molecules, microdroplets potentially offer controlled and synergistic delivery of multiple drugs simultaneously. This approach holds promise for enhancing drug efficacy, reducing medication dosage, minimizing side effects, and cutting costs.

In microfluidics, the stability of common microdroplets depends on the compatibility of interfacial tensions at the interface be-

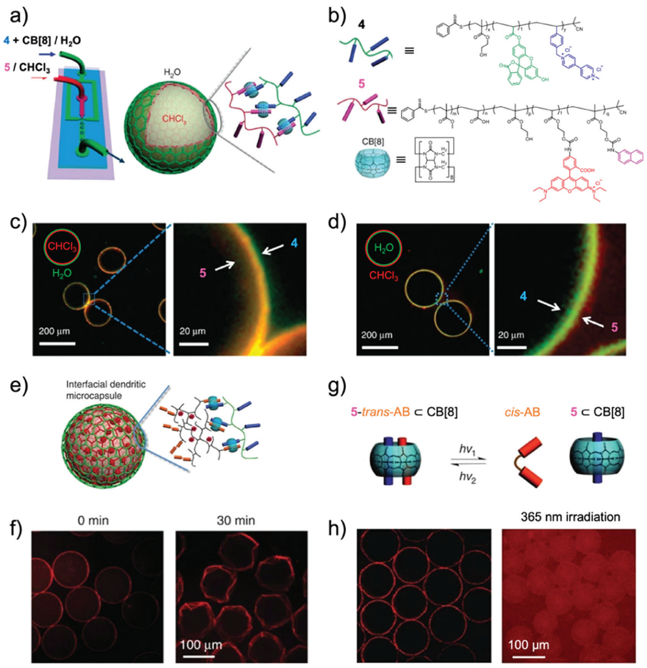

Fig. 3. (a) Schematic illustration of microfluidic chip and the principles of interfacial assembly. (b) Chemical structures and cartoon representation of compound CB[8], **4** and **5**. (c) CLSM image of W/O emulsion. (d) CLSM image of O/W emulsion. (e) Schematic illustration of the encapsulation of CR within capsules *via* interfacial assembly. (f) CLSM images before and after dehydration of liquid droplets. (g) Schematic illustration of the interfacial assembly system with the introduction of azobenzene. (h) CLSM image before and after 365 nm ultraviolet light irradiation. Reproduced with permission [53]. Copyright 2014, Springer Nature.

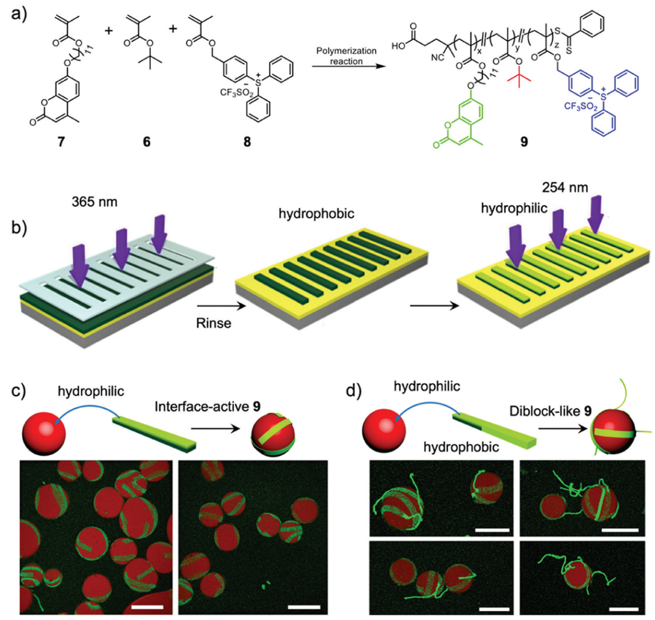

Fig. 4. (a) Synthetic route of co-polymer **9** through a free radical polymerization of compounds **6**, **7** and **8**. (b) Schematic representation of the formation of ribbon-like polymer and surface modification process *via* photopolymerization and deprotection steps. Schematic representation and CLSM images of droplets incubated with (c) hydrophilic **9** or (d) diblock-like **9** (hydrophilic and hydrophobic), the scale bar (10 μm) is suitable for all images. Reproduced with permission [54]. Copyright 2022, American Chemical Society.

tween immiscible phases. In simple emulsion droplets, this stability is primarily governed by the presence of surfactants or colloidal nanoparticles, the former in O/W or W/O systems, and the latter in Pickering emulsions. Manipulating interfacial behaviors of microdroplets, such as fusion, fission, and adhesion, becomes challenging in the presence of surfactants and colloidal particles. Hence, developing uniform and stable microdroplets without the reliance on surfactants or colloidal particles is critical for advancing novel microdroplet technologies.

In 2022, Emrick and coworkers reported a microfluidic chip for stabilizing microdroplets by utilizing ribbon-like polymers as an interfacial stabilizer [54]. The core of this study involves the synthesis of ribbon-like polymers (**9**) endowed with surfactant-like properties. The polymer is a copolymer of *tert*–butyl methacrylate (**6**), coumarin-substituted methacrylate (**7**), and triphenylsulfonium-substituted methacrylate (**8**) (Fig. 4a). Subsequently, a ribbon-like polymer layer is formed through [2 + 2] photodimerization of the coumarin moieties under 365 nm ultraviolet light irradiation. Upon 365 nm ultraviolet light irradiation, the photoacid generator (triphenylsulfonium triflate) is activated and release protons, causing the *tert*–butyl groups to separate, resulting in hydrophilic carboxylic acid groups. Following the aforementioned photopolymerization and deprotection steps, the polymer film is transformed into a ribbon-like polymer that exhibits hydrophobic and hydrophilic properties (Fig. 4b).

When these hydrophilic-modified ribbon-like polymer are mixed with microdroplets, the ribbon can adsorb onto the droplet surfaces, effecting the surface tension of the microdroplets (Fig. 4c). Furthermore, localized hydrophilic modifications may be performed on the polymer ribbons. CLSM images demonstrate that hydrophilic ribbons are entangled around the droplets, while hydrophobic segments of the ribbons remain free around the edges (Fig. 4d). This study demonstrates a photolithographic technique for creating hydrophobic/hydrophilic polymer strips, which can stabilize microdroplets differently from traditional methods. It facilitates easy modification of microdroplet interfaces, contributing to the enhancement of their functionality. Moreover, the hydrophobic polymer ribbons can be further crosslinked to congregate microdroplets, resulting in the formation of phase-transitioned multiphase microinterfaces between liquid and solid, which may be useful for separating particles and contaminants from solutions. Moreover, the unique modification method developed in this study assists in the construction of smart droplets, such as inter-droplet communication (aggregation, fusion and division), and driving droplet motion [55].

Microdroplets of ink are utilized in inkjet printers to print images and text on paper. Microfluidics provides precise control over these ingredients, ensuring uniform dispersion and stability of inks, which comprise pigments, dyes, solvents, binders, and additives. Microdroplets have emerged as an extremely effective method for processing inks due to their ease of preparation and modularity. Color-changing inks provide advanced security features for anti-counterfeiting technology, as they can alter their optical properties in response to external stimuli. Traditional color-changing inks rely on structural changes induced by external stimuli, such as light, heat, or acidity, but they often cannot be reused more than once. Additionally, apart from conventional photo-induced fluorescence, some materials can reflect or refract light to generate structural color due to their microstructure or physical arrangement, which differs from the traditional pigment-based color [16,25,56]. When combined with fluorescence and structural color, microfluidic technology can significantly enhance the security level of labels by arranging molecules within droplets in an ordered manner [57,58].

In 2021, Yu and coworkers developed a method for continuously producing monodisperse microdroplets with radially aligned helical structures using capillary microfluidics [59]. These microdroplets comprised fluorescent molecule **10**, chiral dopants de-

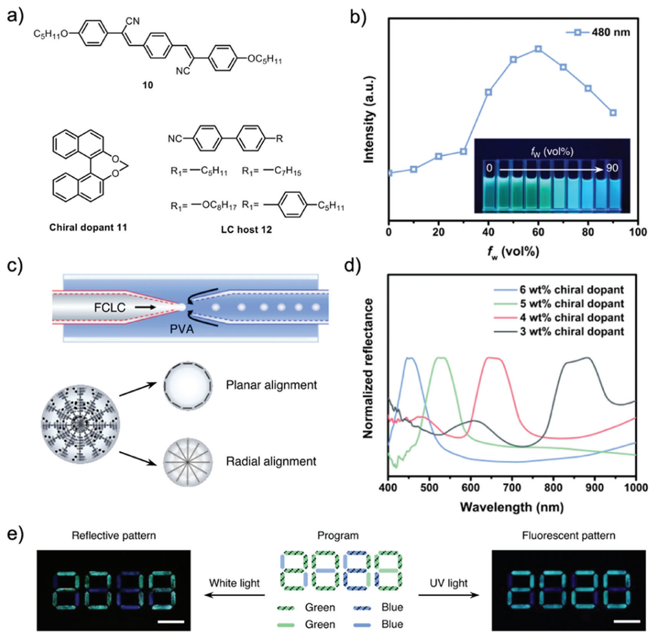

Fig. 5. (a) Chemical structures of fluorescent molecule **10**, chiral dopant **11** and liquid crystal host **12**. (b) Fluorescence intensity of **10** in the different ratio mixture of THF and H_2O (0%–90%, v/v) at the excited wavelength of 380 nm. (c) Schematic representation of flow-focused microfluidic chip. LC **12** is arranged in a planar arrangement at the interface and in a radial arrangement along the spiral axis in the microdroplet. (d) Normalized reflectance of microdroplet consisting of **10**, **12** and different content chiral dopant **11** (3–6 wt%). (e) Schematic illustration and digital photographs of the label with dual-fluorescent and structural color under the UV or white light irritation, where the left fluorescence information is 2019 and represented in green, the right structural color information is 2020 and represented in blue. Reproduced with permission [59]. Copyright 2021, Springer Nature.

rived from (*S*)-binaphthyls **11**, and the host molecule **12**, possessing liquid crystal (LC) properties (Fig. 5a). To improve the solubility of **10** in liquid crystal **12**, flexible *n*-pentyloxy groups (-OC_5H_{11}) was introduced into the structure, resulting in high photoluminescence efficiency. Following modification, compound **10** exhibited clear aggregation-induced emission properties in a mixed solvent of tetrahydrofuran and water, with fluorescence quantum yields of 85.7% in tetrahydrofuran (THF) solution and 100% in solid state, rendering it an excellent luminescent material (Fig. 5b).

Aside from the photoluminescence efficiency of fluorescent molecules, the uniformity of microdroplets and the arrangement of liquid crystal molecules within them are also critical factors in determining the structural color of security labels. A glass capillary microfluidic device with flow focusing has been used to obtain uniformly sized microdroplets with a coefficient of variation of less than 0.87%. This device comprises two coaxial glass capillaries, with the mixture (**10**, **11** and **12**) injected from the left and 5 wt% aqueous solution of poly (vinyl alcohol) (PVA) injected from the right, resulting in the generation of microdroplets (Fig. 5c). By employing PVA as a surfactant with the continuous phase, compound **10** could be arranged in an orderly manner within the microdroplets, producing structural color beyond that of fluorescence. Additionally, the content of chiral substances **11** could be adjusted to tune the structural color of microdroplets, thus enabling emission across the entire visible to near-infrared spectrum (Fig. 5d). By integrating microdroplets containing structural color and cyan fluorescence onto a digitally etched interface, dual-information retrieval based on structural and fluorescent color was achieved (Fig. 5e). In this study, researchers applied microfluidics to control the size of microdroplets and molecular arrangements within them, resulting in a dual-color ink that combines fluorescence and structural color, providing a novel means to encrypt information. The ink can be used to encode messages that can only be read using a special microscope, which has the potential to revolutionize the field of secure communication.

3. Multilayered droplets

Compared to monolayer droplets, multilayered microdroplets exhibit a superior capacity for encapsulating substances within their interiors and across multiple layers. However, as the number of layers increases, the significant interactions between these layers exert a more pronounced effect on the stability of multilayer droplets. Microfluidics, a precision liquid manipulation technique, has emerged as a highly effective method for preparing stable and controlled multilayer droplets [60–62]. Typically, multilayered droplets are formed by encapsulating them stepwise as they traverse T-shaped junctions, necessitating the use of two or more such junctions. This approach poses challenges in controlling droplet size and interlayer distance (Fig. 6a). Moreover, the stepwise formation process hampers efficient encapsulation of contents, resulting in a low payload rate.

In 2017, Reichmanis and coworkers developed a microfluidic chip featuring a flow-focusing design for preparing three-layer droplets in one step [63]. The microfluidic chip comprises two coaxial glass capillaries that are responsible for forming and collecting droplets. It orchestrates four different flow phases: a hydrocarbon oil-based microliquid core, two internal layers containing water with glycerol, and an outer layer containing PVA (Fig. 6b). This configuration enables the generation of triple emulsions (O/W/O/W) droplets by guiding the four components through the microfluidic chip. These resulting droplets are multilayered and well-suited for encapsulating materials with varying solubilities. Leveraging the stability of these multilayered droplets, the researchers proceeded to encapsulate upconversion luminescent materials (**13** and **14**), as shown as (Fig. 6c). Notably, within multilayered droplets, the layers act as a barrier against oxygen, thereby enhancing the stability and longevity of the upconversion

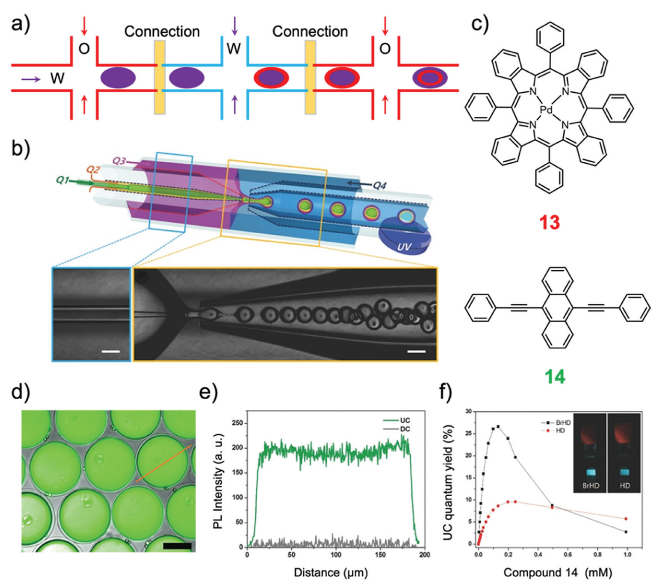

Fig. 6. (a) Schematic representation of a traditional multiple T-junctions for multilayered droplets generation. (b) Diagram of a coaxial glass capillary. (c) Chemical structures of the upconversion sensitizer **13** and emitter **14**. (d) CLSM images of multilayer droplets encapsulating upconversion luminescent material. (e) Quantification data of PL intensity in Fig. 6d on orange line. (f) Upconversion efficiency in various solvent phases, BrHD and HD. Reproduced with permission [63]. Copyright 2017, Wiley-VCH.

process. Additionally, the ordered structure within these droplets improves the diffusion efficiency of triple excitons (Figs. 6d–f).

Compared to hexadecane (HD), 1-bromohexadecane (BrHD) exhibits a higher heavy atom effect, which increases spin-orbit coupling between monomers and triplet states, and thereby strengthening intersystem crossing and leading to higher upconversion quantum yields. As a result, BrHD-based microdroplets exhibit a threefold increase in luminescence efficiency (Fig. 6f). Moreover, these droplets have the capability to undergo further cross-linking under illumination, resulting in the formation of microcapsules that facilitate the upconversion of luminescence in the solid phase. This study provides a practical solution for a rational control of components between layers, promising the advancement of high-performance luminescent materials.

A cholesteric liquid crystal (CLC) constitutes a soft photonic crystal characterized by a periodic helical structure capable of reflecting light at different wavelengths, thereby producing structural colors [64–66]. In cholesteric phase liquid crystals, the periodic helical superstructure imparts unique optical properties, notably the selective reflection of circularly polarized light in correspondence with their intrinsic helical structure. Following Bragg's law, $\lambda = np$ (where n is the average refractive index of the liquid crystal matrix), the reflected wavelength (λ) is directly proportional to the pitch (p) of the helical superstructure [67,68]. Bright structural colors emerge when the reflected wavelength falls within the visible light spectrum.

Using this principle, Reichmanis and coworkers employed the same capillary microfluidic chip to fabricate multilayered droplets containing CLC (Fig. 7a) [69]. The core oil phase comprised a hydrocarbon solution and a pair of upconversion (UC) sensitizers based on TTA emitter chromophores. A relatively low-viscosity medium, 1-bromohexane, was selected for its support of the external heavy-atom effect, which facilitates inter-system crossing. By adjusting the concentration of chiral dopants, the chiral pitch of the CLC could be modified. The core exhibited a pale yellow-green color due to the absorption of red and blue upconversion spectra (Fig. 7b). Owing to its narrow stopband, the microcapsules remained transparent across nearly all visible light wavelengths. Cross-polarized microscopy revealed a Maltese cross pattern in the refraction of liquid crystals (Figs. 7c and d). The spherical symmetry of the capsules led to local variations in the degree of resonant enhancement at normal incidence, amplifying the delayed fluorescence emission at the stopband edge (Fig. 7e).

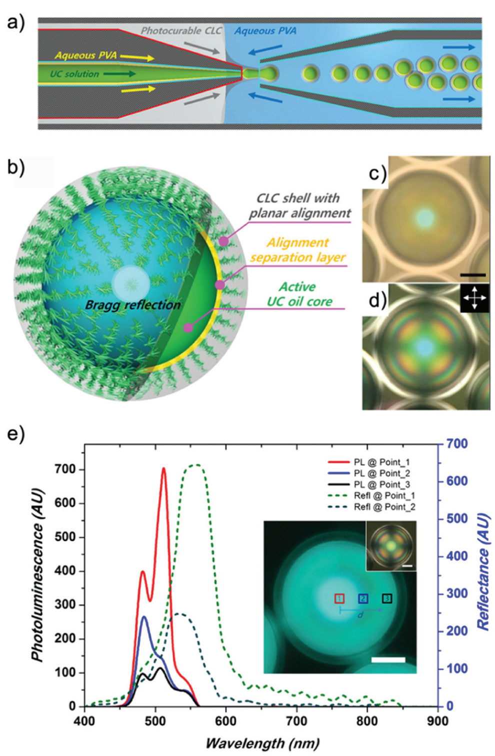

Fig. 7. (a) Diagram of capillary microfluidic chip for the formation of multilayered droplets containing CLC, and (b) the arrangement of liquid crystal molecules in multilayered droplets. (c) Optical transmittance and (d) cross-polarized microscopy imaging of the multilayered droplets. (e) Fluorescence spectra, optical reflection spectra and cross-polarized microscopy images of multilayered droplets at different points from the center. Reproduced with permission [69]. Copyright 2017, American Chemical Society.

Furthermore, this triple emulsion can undergo photopolymerization to stabilize the internal upconversion dye, rendering it suitable for diverse applications including heterogeneous catalysis and bioimaging. Given the unique luminescent and transparency properties of liquid crystal, the light emitted by the internal upconversion luminescence can uniformly disperse in all directions, rendering it an excellent light-emitting unit for microlasers. This article introduces structural colors within multiple emulsion droplets and achieves upconversion luminescence enhancement through modulation of edge structural colors. This not only broadens the application scope of multiple emulsion droplets, but also provides a practical method for utilizing upconversion luminescent materials in real-world scenarios.

Structural color, stemming from the microscopic composition of materials and interference effects, is closely tied to the surface texture and structure of objects. Offering numerous advantages over chemical pigments such as heightened stability, full spectral emission, increased saturation, and enhanced variability, structured colors are highly sought after. Leveraging microfluidic technology allows for the manipulation of multilayered microdroplets in terms of layer number and spacing, thereby affecting microscale concave interfaces. Commonly employed in the creation of artificial structural colors, this method relies on total internal reflection and interference at these interfaces. However, prevalent techniques predominantly rely on oil-water or solid-oil interfaces, constraining their suitability for aqueous-based biological systems, such as sensors and diagnostic kits [70,71]. To tackle these limitations, Deng and coworkers have successfully used a microfluidic chip to create a water-in-oil-in-water (W/O/W) multilayered droplets, which displays prominent rainbow-like colors in eccentric droplets [72]. Structural colors become apparent solely in eccentric thin-shell W/O/W droplets when a crescent-shaped oil film serves as the intermediate shell. Droplets possessing thicker shells lack discernible structural colors (Fig. 8a).

Coaxial capillaries are used in this microfluidic chip, which consist of poly(vinyl alcohol) (PVA) in an aqueous medium as the outer phase, *n*-octanol as the oil phase, and a mixture of PVA and Pluronic F-68 in an aqueous solution as the inner phase (Fig. 8b). It is noted that droplets of varying sizes exhibit diverse structural colors (Fig. 8c). In order to elucidate the significance of the difference in radii between the outer oil droplet and the inner water droplet in determining droplet structural colors, the authors introduced a high salt sodium chloride solution to the external environment to induce shrinkage of the inner water droplet, observing resultant changes in the structural colors. With the gradual increase in radius difference, the structural colors transition from purple to light green, pink, and ultimately cyan (Fig. 8d). Additionally, these droplets exhibit temperature-dependent color alterations, potentially attributable to the distinct thermal expansion coefficients between the oil shell and the inner water droplet (Fig. 8e). This study presents a representative example of adjusting structural color by varying the distance between the water and oil interfaces. Moreover, the manipulation of colors through osmotic pressure and

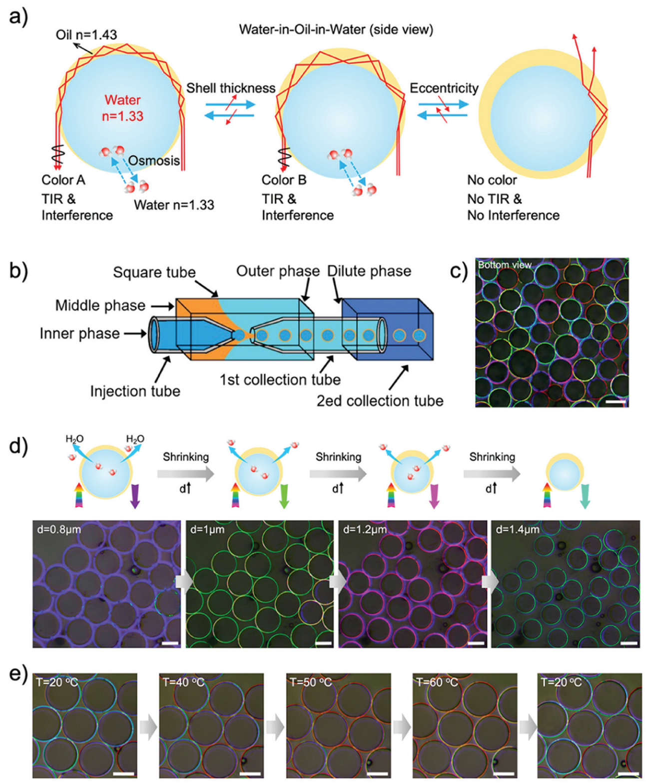

Fig. 8. (a) Schematic illustration of the principle of eccentric W/O/W multilayered droplets for structural colors, and (b) capillary microfluidic chip. (c) reflective optical micrographs of W/O/W droplets of varying sizes. (d) Structural color changes in droplets upon contraction in high osmolarity solutions. (e) Reflective optical microscopy images of multilayer droplets at different temperatures. Reproduced with permission [72]. Copyright 2023, American Chemical Society.

temperature holds promise for further advancements in sensor and diagnostic development utilizing structural color droplets, thereby establishing a solid foundation for the exploration of multilayered droplet structural colors.

4. Multicompartmental droplets

Microfluidic technology can be employed not only for the preparation of multilayered droplets but also for the production of multicompartmental droplets, which contain two or more compartments, each containing different liquids or gasses [73]. These multicompartmental droplets encompass multiple non-miscible cores within a single droplet, serving as carriers for various functional molecules such as pharmaceuticals, reagents, or catalysts. Each core, residing within its own distinct liquid phase, minimizes cross-contamination and interference between different cores, thereby enabling the simultaneous testing of multiple conditions in a single experiment, facilitating high-throughput screening. Multicompartmental droplets provide an effective way to simulate the dynamics and interactions of suborganelles, such as mitochondria and endoplasmic reticulum in a cell. Due to these unique advantages, multicompartmental droplets exhibit extensive applications in controlled compound synthesis, fluorescence-encoded microspheres, and multi-channel sensing.

In 2010, Weitz and Cowrkers reported the use of a T-shaped chip with dual inlets to prepare multicompartmental droplets (Fig. 9a) [74]. In order to prevent fusion between multiple cores, they used poly(*N*-isopropylacrylamide) (pNIPAAm) capable of polymerizing under ultraviolet (UV) exposure for the production of multicompartmental droplets (Fig. 9b). The number of cores contained within each droplet could be accurately regulated by controlling the ratio of the polymer phase to the external oil phase. In order to differentiate between the oil phase externally and the core internally, fluorescent dyes fluorescein and rhodamine were used to label them, respectively. With an increase in polymer concentration, there was a rise in the number of cores within the droplets, resulting in the formation of non-miscible subspaces following photocrosslinking (Fig. 9c). This study represents a typical example of using a microfluidic chip to prepare multicompartmental droplets, greatly advancing the development of multi-core liquid droplet production techniques. This technology has been used in various fields, including pharmaceuticals, chemistry, and biology, revolutionizing the way researchers study complex interactions in liquid systems.

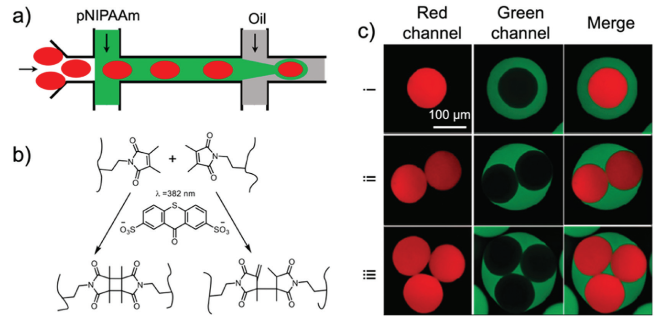

Fig. 9. (a) Schematic diagram of a microfluidic chip for the preparation of multicompartmental droplets. The internal polymer core is injected into the microfluidic chip following the formation of polymer microspheres, and the concentration can be adjusted in order to obtain a desired number of multi-core droplets. (b) The dimerization of dimethylmaleimide (DMMI) groups on the side chain of pNIPAAm. (c) CLSM images of multicompartmental droplets containing different numbers of polymer cores. Reproduced with permission [74]. Copyright 2010, American Chemical Society.

Microfluidics is commonly employed not only for producing polymeric multicompartmental droplets but also for generating multicompartmental liposome droplets [75–77]. Liposomes are highly suitable for simulating multi-chambered cellular environments owing to their resemblance to cell membranes and widespread application as drug carriers [78–80]. They offer a valuable platform for studying intricate biological processes such as cell division and migration, thereby providing insights into cellular behavior and interactions [2,81,82]. Huck and coworkers reported a multistep microfluidic approach for fabricating multicompartmental liposome droplets [19]. Initially, mononuclear liposome droplets were prepared and subsequently reintroduced as internal phases into the microfluidic device (Fig. 10a). During the generation of liposome-containing microdroplets, the volatile nature of chloroform in the oil phase led to phase separation between the liposomes and the oil droplets, resulting in liposome droplets devoid of oil. Moreover, the concentration and flow rate can be precisely adjusted to control the number of vesicles in the core.

In order to characterize the structures of multicompartmental droplets, fluorescent-labeled dextran was incorporated into different phases to generate fluorescent droplets, as depicted in Fig. 10b. CLSM images showed that FITC-dextran emitted green fluorescence in the interior of multicompartmental droplets, while FITC-dextran emitted red fluorescence on the exterior. The multicompartmental droplets displayed a coefficient of variation of less than 5%, with respective inner and outer diameters of 43 and 102 μm (Fig. 10c). In addition to producing multicompartmental droplets containing similar liposome cores, various vesicles were introduced into the microfluidic chip (Figs. 10d and e), enabling the synthesis of multicore liposome droplets capable of encapsulating diverse molecules, thereby facilitating intercore signal transmission. This study offers

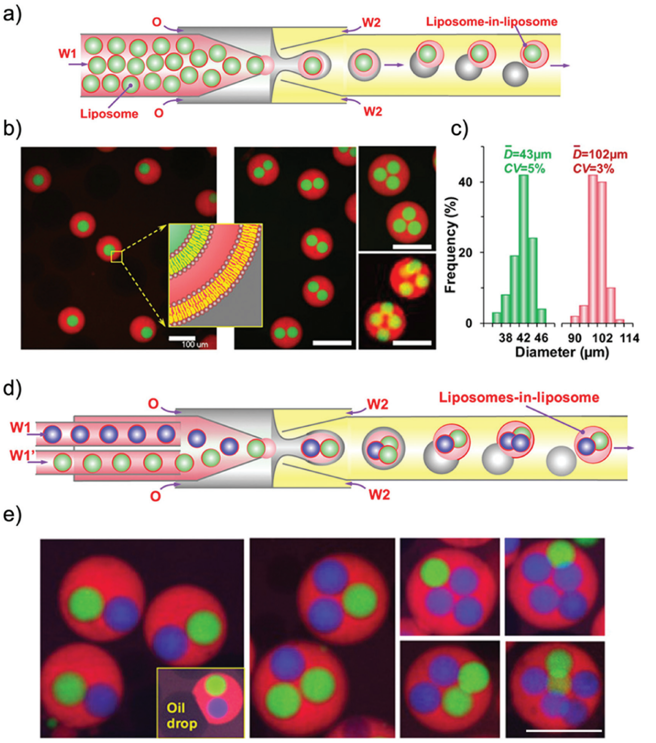

Fig. 10. (a) Schematic diagram of microfluidic chip for the fabrication of multicompartmental liposome droplets, and the phase separation of oil and vesicles induced by solvent evaporation. (b) CLSM images of liposome droplets with varied internal core numbers. (c) Particle size distributions of droplets and internal core vesicles. (d) Schematic diagram of microfluidic chip in generating liposome droplets with multiple distinct cores. (e) CLSM images of liposome droplets with varied distinct core. Reproduced with permission [19]. Copyright 2017, American Chemical Society.

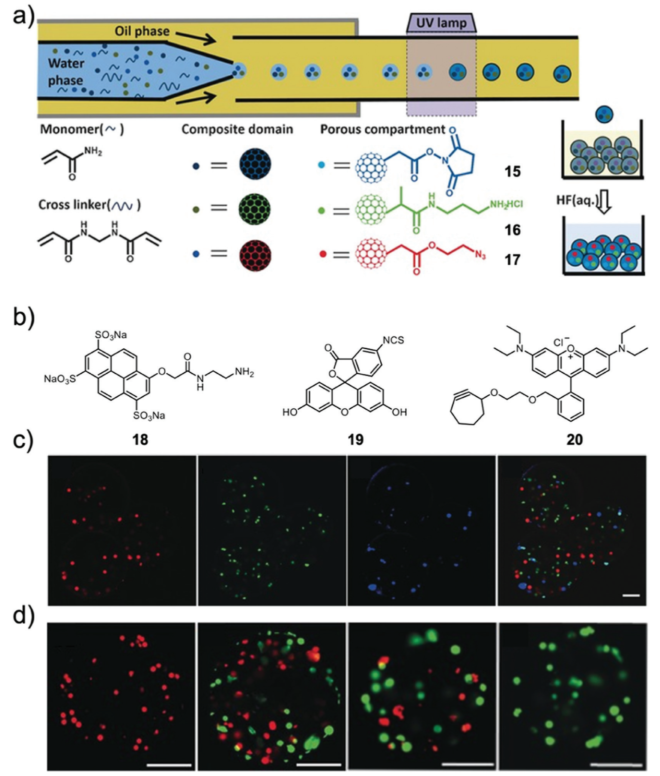

Fig. 11. (a) Schematic diagram of the microfluidic chip for the preparation of porous systems with multiple stable, independent compartments with a reactive multidomain configuration, polymerization of acrylamide and *N,N'*-methylene bis(acrylamide) under ultraviolet irradiation, silica microspheres coated with three orthogonally ligand (**15**, **16** and **17**) and removing the silica microsphere template in HF solution. (b) Chemical structures of three orthogonal ligand (N1–N3). (c) CLSM images of multicompartmental hydrogel spheres after reaction with three orthogonal ligand (**18**, **19** and **20**). (d) CLSM images of multicompartmental hydrogel spheres after reaction with increasing N1. The scale bar (150 μm) is suitable for all images. Reproduced with permission [83]. Copyright 2017, Wiley-VCH.

a feasible approach for simulating intricate subcellular organelles and holds promise for advancing studies in artificial cells. It can aid in investigating phenomena such as cell fusion, division, and recognition, offering insights into how organelles interact within the extracellular environment.

It is worth noting that multicompartmental droplets offer the ability to create multiple independent, non-miscible compartments, similar to subcellular organelles within a cell. Each compartment can serve a unique function without interfering with others. However, the challenge in developing multi-core liquid droplets/capsules arises in subsequently modifying different compartments and introducing various functionalities. This can be achieved by adding different molecules to different compartments, allowing them to interact and form complex networks. Li and coworkers developed a capillary microfluidic chip for producing porous systems with multiple stable, independent compartments featuring a reactive multidomain configuration [83]. These multicompartmental droplets consist of silica microspheres coated with three orthogonally ligands (**15**, **16** and **17**), along with a monomer acrylamide capable of crosslinking and polymerization. In the droplet formation channel, ultraviolet radiation induced polymerization within the droplets, resulting in stable, mesh-like hydrogel microspheres. Subsequently, hydrogen fluoride (HF) solution was introduced to remove the silica microsphere template, exposing the interior compartments and the orthogonal sites available for modification (Fig. 11a).

Then, three fluorescently tagged molecules (**18**, **19** and **20**) were introduced into multicompartmental droplets with orthogonal sites (Fig. 11b). Fluorescence confocal imaging revealed that the hydrogel microspheres contained three distinct fluorescent tags, each emitting non-interfering colors, indicating the independent existence of multiple compartments (Fig. 11c). Furthermore, by varying the precursor ratios, the number of functionally distinct compartments could be adjusted, providing a convenient means to obtain compartments with different degrees of crowding. This enabled the study of catalytic processes in confined environments, similar to those within cellular contexts (Fig. 11d). This study integrated microfluidics with orthogonal reactions to produce multi-reactive sites hydrogel microspheres, significantly simplifying the complexity associated with constructing multi-core compartment microspheres. Furthermore, the technique is capable of creating a variety of microspheres with active sites and compositions, providing a powerful tool for studying the behavior of different molecules. Additionally, this approach offers remarkable flexibility and scalability, providing a feasible solution for investigating confinement-driven catalytic reactions.

In short, fluorophores can be precisely loaded onto the surface or interior of simple emulsion droplets, allowing them to detect and investigate crucial processes within them or at interfaces, like controlled release of drug molecules, visualizing the interfacial assembly processes and surface modification, dual-color inks that use internal fluorescence and structural color together, *etc.* More fluorescent molecules can be loaded into the interior and across multiple layers of multilayered droplets by increasing the number of layers. This can be used to construct a wide variety of luminescent materials, including upconversion luminescent materials created by isolating oxygen, as well as the combination of liquid crystals and upconversion luminescence used for smart display applications. As for multicompartmental droplets, since the droplet core can simultaneously contain multiple incompatible independent compartments, multiple fluorescent molecules can be loaded to produce fluorescently encoded microspheres for the detection of biomarkers in multiple colors. Additionally, their compartments are highly analogous to organelles, making them an ideal model for observing interactions between organelles and the transfer of material information. As a result, with the continuous development of droplet preparation techniques, we believe fluorescent droplets will serve not only as essential tools for real-time monitoring, multicolor imaging, and high-throughput detection, but also provide new opportunities for investigating more complex processes such as cell fusion, division, and migration with fluorescent droplets.

5. Conclusion

Microfluidic technology is capable of manipulating very small volumes of fluids with exceptional precision and accuracy, rendering it a valuable research tool in biomedical science, chemical analysis, and materials science. By virtue of the advantages of microfluidic chip in controllability, high efficiency, and minuscule sample handling capabilities, microdroplets can be tailored in size and composition for specific application [84–86]. Fluorescence imaging offers many advantages [87,88], including high sensitivity, specificity, and real-time images of biological processes. Incorporating fluorescent dyes into these droplets, whether internally or on their surfaces, confers distinctive properties that enable their visualization and tracking in real time. This facilitates the study of their behavior and dynamics, such as droplet locations, concentrations, and chemical compositions, thus making them invaluable tools for microfluidic research. Due to the exceptional features of microfluidic fluorescence droplets, they have emerged as potent tools in various biomedical applications, including single cells analysis, drug screening, and disease diagnosis [89].

Nevertheless, there is considerable untapped potential in microfluidic technology, accompanied by challenges in the preparation and utilization of fluorescent droplets. The preparation of these droplets entails addressing issues such as enhancing the loading efficiency of fluorescent dyes and ensuring their stability. Crucially, achieving optimal proportions of dyes at the interface and within droplets while maintaining stability and preventing leakage is essential, given the diverse application scenarios. Undoubtedly, future research directions will emphasize the controlled construction and diverse application of multicomponent droplets. Advancements in the application and development of fluorescent droplet technology hinge on addressing the complexity and precision requirements of preparation methods to meet diverse application needs. This entails refining fluidic operations and surface modification techniques. Furthermore, promoting the development of new techniques, materials, and reagents, coupled with improved control and understanding of droplet properties, is imperative. This includes optimizing droplet formation protocols and establishing reliable workflows for droplet sorting and detection methods.

Equally important are the applications of droplets in more complex scenarios, such as studying cellular signal transduction, protein aggregation on cell membranes, and compartmentalized reactions within cells [76]. Microfluidic technology, with its modularity and programmability, holds the promise of swiftly acquiring dynamic information about assembly or reaction processes by synergistically combining with other analytical techniques. The integration of fluorescence labeling with other analytical methods shows potential for exploring new frontiers in microfluidic droplet research, addressing a broader range of scientific inquiries and application challenges, especially in biomarker detection, single-cell analysis, and high-throughput screening. In addressing complex biological applications, droplets must maintain stability while performing various functions, necessitating stricter requirements on their structure and formation methods. Additionally, the development of new probes and sensors for fluorescent droplet analysis can mitigate interference from background fluorescence, such as excitation with red or near-infrared wavelengths, and enhance the lifetime of phosphorescence as an output signal [90]. We believe that resolving the controlled preparation issue of multicomponent fluorescent droplets will expedite the advancement of droplets in smart material and biological applications, presenting significant opportunities for organic synthesis, disease diagnosis, targeted treatments, and real-time monitoring of biological processes.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Wei-Tao Dou: Writing – review & editing, Writing – original draft, Conceptualization. **Qing-Wen Zeng:** Conceptualization. **Yan Kang:** Writing – original draft, Conceptualization. **Haidong Jia:** Conceptualization. **Yulian Niu:** Conceptualization. **Jinglong Wang:** Conceptualization. **Lin Xu:** Writing – review & editing, Writing – original draft, Conceptualization.

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