DOI:
10.1016/j.cis.2024.103159

Dynamic Covalent Surfactants and Their Uses in the Development of Smart Materials

Fan Min [a, b], Cécile A. Dreiss [c], Zonglin Chu [a, b, *]

[a] State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, China. E-mail: zchu@hnu.edu.cn.

[b] Greater Bay Area Institute for Innovation, Hunan University, Guangzhou 511300, China.

[c] Institute of Pharmaceutical Science, King's College London, Franklin-Wilkins Building, 150 Stamford Street, London, UK SE1 9NH, UK, E-mail: cecile.dreiss@kcl.ac.uk; Tel: +44 (0)207 848 4800

ABSTRACT: Dynamic covalent chemistry, which leverages the dynamic nature of reversible covalent bonds controlled by the conditions of reaction equilibrium, has demonstrated great potential in diverse applications related to both the stability of covalent bonds and the possibility of exchanging building blocks, imparting to the systems the possibility of "error checking" and "proof-reading". By incorporating dynamic covalent bonds into surfactant molecular architectures, combinatorial libraries of surfactants with bespoke functionalities can be readily fabricated through a facile strategy, with minimum effort in organic synthesis. Consequently, a multidisciplinary field of research involving the creation and application of dynamic covalent surfactants has recently emerged, which has aroused great attention in surfactant and colloid science, supramolecular chemistry, self-assembly, smart materials, drug delivery, and

nanotechnology. This review reports results in this field published over recent years, discusses the possibilities presented by dynamic covalent surfactants and their applications in developing smart self-assembled materials, and outlines some future perspectives.

KEYWORDS: Dynamic covalent chemistry, Surfactants, Smart materials, Self-assemblies, Reverse emulsification.

1. Introduction

Surfactants are amphiphilic organic compounds with both a hydrophobic (usually alkyl chain) tail and a hydrophilic head (either a charged or noncharged water-soluble moiety) present on the same molecule (Fig. 1a) [1]. They play an important role in nearly every aspect of our lives from the moment we are born [2]. With the first successful breath at birth, pulmonary surfactants in the lungs thin out the alveolar membrane and increase the surface of the alveoli for gas exchange [3, 4]. They act as powerful cleaners for washing dishes, laundry, cleansing our faces, and so on [5]. They are used in an array of cleaning products for their ability to lower water's surface tension, in essence making the molecules more "slippery", preventing them from sticking together, and promoting interaction with oil and grease. They are key additives in lubricants [6], inks [7], anti-fogging liquids [8], herbicides [9], adhesives [10], emulsifiers [11, 12], and fabric softeners [13]. From a basic research point of view, they are frequently adopted as templates in creating nanoparticles [14] and mesoporous materials [15], micellar catalysts in organic synthesis [16], smart carrier vehicles for drug delivery [17], and even used as models to understand

mechanisms of self-assembly fundamentally [18], resulting from their polymorphic ordered topologies when dispersed in water.

When increasing surfactant concentration in water, these amphiphilic molecules tend to “physically” dimerize, trimerize, oligomerize, and finally “self-polymerize” into well-organized micellar aggregates, owing to van der Waals interactions between their alkyl tails as well as the hydrophobic effect. Concurrently, the interface between water and oil is also steadily occupied by the surfactant tails until a complete monolayer is formed [19]. The concentration of surfactants (Cs) above which micelles form and all additional surfactants added to the system aggregate into micelles is identified as the critical micelle concentration (CMC) [20].

Surfactants are able to organize themselves into various micellar structures: wormlike, vesicular, disk-shaped, or spherical, dependent on the molecular structure of the surfactant as well as the bulk aqueous environment [1]. Using the principle of the "critical packing" parameter p developed by Israelachvili [21], it is possible to predict the shape of self-assembled aggregates based on the effective volume and maximum length of the hydrophobic tail (represented by "v" and "l", respectively) as well as the effective surface area per molecule ("a_0") of the surfactants that make up the aggregate, or the area per molecule at the interface between the surfactants and water: $p = v/a_0 l$. When the ratio is less than one-third, spherical aggregates tend to form, while wormlike micelles are formed with ratios between one-third and one-half, and lamellar structures are observed when the ratio equals one (Fig. 1b). p is primarily influenced by the structure of the surfactant molecule and is also affected by the solution environment: it arises from an intricate interplay between surfactant chemical architecture and external factors, such as concentration of surfactant, and solution pH, temperature, salinity, etc. [22].

Traditional organic molecule synthesis has relied heavily on kinetic control of reactions, resulting in irreversible covalent bonds being formed between the starting materials. In this case, the goal is typically to pursue an energetically more advantageous pathway to form a specific product; for instance, A progresses to C instead of B (Fig. 1c, left). The irreversible nature of the reaction ensures that once the specific product is generated, it cannot be converted into another compound or reconverted back to the starting materials.

In contrast to the classical covalent chemistry described above, dynamic covalent chemistry (DCC) [23-25], in which reversible chemical reactions are conducted under conditions of equilibrium control, has seen a surge of interest in chemistry and materials science due to its unique characteristics, which may find applications in numerous fields. The reactions' reversibility [26] enables the prospect of "proof-reading" and "error checking" of the resulting dynamic combinatorial library of interconverting components, generating the most thermodynamically stable product under specific conditions [27]. That is to say, when DCC is at play (Fig. 1c, right), it is the relative stability of the products (i.e., thermodynamic parameters) that governs the distribution of products instead of each pathway's energy barriers (i.e., kinetic parameters). The reaction outcome therefore mainly depends on and is also affected by the conditions of reaction [28], such as concentration, pressure, temperature, catalyst, as well as external factors, like light and pH. Time also plays a crucial role since the kinetic parameters dictate how long an equilibrium takes to establish. In these reactions, covalent bonds are constantly formed and disrupted, resulting in a dynamic equilibrium that allows the reaction outcome to alternate between different molecular structures. A significant proportion of reversible covalent bonds falls under the category of dynamic polar reactions, characterized by the formation of charged reactive intermediates during the exchange process. These dynamic

covalent reactions can be classified based on the primary bond type established or broken during the exchange, encompassing C-N bonds (imines, Schiff bases, enamines), C-C bonds (aldol reaction, alkyne/olefin metathesis), C-O bonds (nucleophilic additions to C=O bonds, ester exchange), C-S bonds (thioester exchange, thiazolium-Michael additions), S-S bonds (disulfide chemistry), and B-O bonds (boronic esters).[29] For example, imine exchange reactions involve the dynamic interchange of imine functional groups, which consists of a double bond between a carbon and a nitrogen atom. These reactions play a crucial role in dynamic combinatorial chemistry, enabling the generation and screening of diverse libraries of compounds to identify specific properties (Fig. 1d). In addition, orthogonal dynamic covalent bonds have found utility in the construction of orthogonal dynamic combinatorial libraries (DCLs), wherein two or more reversible covalent bonds are activated under distinct conditions. This orthogonal combination of diverse dynamic covalent bonds empowers the creation of a wider spectrum of covalent self-assembled structures, serving as a foundational framework for investigating novel functions and properties.[30] Besides, covalent bond formation and breaking usually displays slow kinetics. These characteristics make DCC crucial in creating complex individual molecular architectures and sophisticated self-assembled nanostructures.

Upon incorporating dynamic covalent bonds into surfactant molecular architectures, combinatorial libraries of versatile surfactants with varied functionalities can be readily obtained through a very simple, handy, and cost-effective strategy with minimum, or even without any, effort in organic synthesis, which is a challenging task for those who are not synthetic chemists by training. Indeed, the multidisciplinary research field of dynamic covalent surfactant (DCS) is now emerging, arousing interest from a range of areas, including surfactant and colloid science, supramolecular chemistry, self-assembly, smart materials, drug delivery, and nanotechnology.

In addition to reducing the burden required to synthesize surfactants, the incorporation of dynamic covalent chemistry into surfactants is revolutionizing the field by imparting them with unprecedented responsiveness to changes in the surrounding environment, a route towards elaborate materials with on-demand functionalities. DCS design relies on tailoring two precursors to react into thermodynamically stable structures with desired properties (such as the hydrophilic-lipophilic balance (HLB) and "critical stacking" parameter (p)) under specific environmental conditions. These smart surfactants, like traditional ones, can form specific-shaped micelles or stabilize emulsions on demand. What sets them apart is their remarkable reversibility and responsiveness to external stimuli like pH, temperature, or chemical triggers. Upon environmental shifts, they readily revert to their precursor state, allowing disassembly/reassembly into different micelle shapes or resulting in emulsion breakdown (Scheme 1). This dynamic behavior enables the manipulation of the system at will by simply tuning the environment, instead of being confined to the static functionality of traditional surfactants. "Smart" materials, which dynamically alter their structures and functionalities based on environmental stimuli, especially those capable of switching between an 'on' and 'off' state, are indeed a highly topical research field [1]. The ability of DCS to dynamically adapt ensures efficient performance, stability, and tunability—making them ideal building blocks for smart materials, drug delivery systems, and other cutting-edge technologies. Dynamic covalent chemistry is thus paving the way for the design of highly advanced surfactants which can meet the evolving demands of modern applications.

2. Dynamic covalent surfactants for the reversible manipulation of self-assemblies

Reversible dynamic covalent bond formation provides a powerful strategy for the in-situ synthesis and decomposition of surfactant molecules. Based on the amphiphiles' composition

and molecular architectures, surfactants dispersed in aqueous solution can self-assemble into various micellar structures. Since dynamic covalent chemistry offers a facile means not only to manipulate the formation/destruction of surfactant molecules but also to alter composition (particularly for mixed surfactant systems), it is possible to achieve a reversible switch between a given self-assembled structure and its building blocks, or between different types of self-assembled structures.

2.1. Reversible switch between self-assemblies and building block molecules

Non-amphiphilic precursors have been used for the in-situ synthesis of amphiphilic dynamic covalent surfactants through reversible covalent bond formation. These intelligent dynamic surfactants can be applied to the creation of smart assemblies such as wormlike micelles, vesicular aggregates, and spherical micelles, which could be reversibly switched between the self-organized form and the disassociated building blocks.

2.1.1 Switch between spherical micelles and building block molecules

Utilizing dynamic imine chemistry as a tool, van Esch and coworkers [31] have reported DCSs which can be used for the development of smart self-assembly. DCSs were prepared from an aqueous solution of simple nonamphiphilic precursors of an aromatic aldehyde and various aliphatic amines through the formation of reversible imine bonds (Fig. 2a). The reversible character of imine bonds allows the tuning of surfactant concentration by simply shifting the equilibrium in favor of the amphiphiles by varying temperature and pH. A combination of aromatic aldehydes with aliphatic amines was adopted, because generally the equilibrium constant of imine generation in these conditions is the highest. Following the combination of equimolar quantities of both building blocks dispersed in water with a pH of 11.8 at room temperature, the formation of imine was verified via ^{1}H NMR spectroscopy. Observation of

distinctive signals for both aldehyde and imine reveals that the equilibrium between them shifts relatively slowly in comparison to the time frame of an NMR measurement. In contrast, above a critical concentration, the imine proton peak at 8.35 ppm gradually shifted upfield. This implies that the self-assembly process is fast compared to the time frame of NMR analysis. The critical concentration where the imine proton peaks displayed a remarkable upfield shift was deemed to be the CMC. This phenomenon was further confirmed by dynamic light scattering and surface tension analysis. Surface tension results demonstrated that the imine products are indeed capable of reducing surface tension (e.g., surface tensions of 37 mN m^{-1} at Cs > CMC).

Fluorescence emission spectroscopy was employed to investigate the demicellization induced by a reduction in pH, using the imine bearing a heptyl tail as a model surfactant and Nile Red as a fluorescent indicator of hydrophobicity. In buffer, the emission of Nile Red was recorded at 654 nm; however, a blue-shifted peak of 645 nm was detected upon addition of the surfactant at concentrations above the CMC. This indicated that Nile Red became encapsulated within the micelles' interior, surrounded by a predominantly hydrophobic milieu. Upon titration with acid, the imine micelles underwent dissociation, leading to a red-shifted fluorescence, which resulted from the liberation of Nile Red from the hydrophobic region inside the micelles (Fig. 2b). The demicellization process was fully reversible, allowing the system to transition between spherical micelles and dissociated building blocks by a straightforward adjustment of the pH of the solution (Fig. 2c). The switchable demicellization and micellization could also be accomplished by increasing and decreasing the temperature, respectively.

Zhang's team [32] prepared a bola-type DCS through dynamic benzoic imine bond formation (Fig. 3a), which demonstrated a reversible transformation between spherical micellar assembly and dissociated building blocks, with potential applications in controlled release. In a subsequent

work [33], the authors fabricated an array of bolaform DCSs with varying symmetries (Fig. 3b), and observed that the degree of imine bond formation differed among these DCSs, namely, DCSs with a lower symmetry always gave reduced imine formation. This result implies that the aggregation of bola-type DCSs is influenced by molecular symmetry.

The same group also developed H-shaped bola-type DCSs (Fig. 3c) by binding two bolaform amphiphiles (each bearing an aldehyde group in the centre) with one spacer (bearing one amino group in each end) through the formation of one dynamic benzoic imine bond in both terminals [34]. Compared with the former studies, these DCSs show a lower CMC and are more sensitive to pH changes, i.e., the reversible disassembly process can be achieved by tuning the pH from basic to slightly acidic. Measurements of the surface tension isotherms for H-shaped DCSs featuring varying spacers suggest a "twisted" molecular arrangement at the interface between air and water. This study on H-shaped DCSs enriches the repertoire of DCSs and their unique pH-responsiveness holds potential for applications for targeted drug delivery in biological environments.

Wang et al. [35] prepared dynamic covalent surfactants by mixing 4-formyl-*N,N,N*-trimethylbenzenaminium iodide and alkylamines (heptylamine or octylamine). These dynamic covalent surfactants can spontaneously form micelles in alkaline environments and demonstrate coacervation with hydrolyzed polyacrylamide. It has been shown that coacervates with a polymer-network structure can effectively remove negatively charged dyes like Congo Red. Under acidic conditions, the imine bonds were hydrolyzed, resulting in the transition of the coacervates into a clear solution, and the release of the trapped dyes. This indicates that the trapping and liberation of dye molecules can be achieved with dynamic covalent surfactant/polymer network systems, which has great potential in wastewater treatment.

Utilizing a dynamic supra-amphiphile formed by dodecyl[2-(4-formylphenoxy) ethyl] dimethylammonium bromide in the presence of a pharmaceutical agent (isonicotinic acid hydrazide) in alkaline conditions, Zheng's team developed dynamic self-assembling systems responsive to changing pH values for targeted drug delivery [36]. Through hierarchical assembly, the resulting supra-amphiphile can form highly ordered micelles, enhancing its suitability for drug delivery. Importantly, the dynamic products can disintegrate upon encountering acidic environments, allowing for the controlled release of drug molecules. Therefore, the dynamic surfactant-drug system opens up avenues for pH-triggered targeted drug release.

2.1.2. Reversible switch between wormlike micelles and building block molecules

Wormlike micelles (WLMs) are elongated and flexible structures that arise from the spontaneous organization of surfactant molecules in aqueous solutions [37]. When the surfactant concentration surpasses a critical threshold known as the overlapping concentration (C*), WLMs become entangled in a constantly breaking and reforming dynamic reversible network, earning them the descriptors of "living" or "equilibrium" polymers. The intertwining of WLMs gives the solution exceptional viscoelastic properties, crucial to many industrial and technological sectors like enhanced oil recovery, rheology control, drag reduction, personal care, and everyday uses [38].

Dynamic Imine Chemistry offers a powerful approach for constructing smart wormlike micelles, where these solution properties can be tuned by altering solution pH. For example, van Esch and coworkers [39] reported the spontaneous formation of dynamic covalent wormlike micelles using imine-based Gemini surfactants. This formation occurred through the straightforward combination of two complementary non-surface-active species. Due to the

reversible nature of imine bond formation, the wormlike micelles can transition between an isotropic solution and assembled state, influenced by temperature and pH. Thermodynamic modelling of the reaction equilibria reveals that despite the formation of single- and double-tailed surfactants mixtures, wormlike micelle formation is primarily governed by the double-tailed amphiphilic products (Fig. 4a).

Wang et al. [40] prepared pH-sensitive wormlike micelles based on a dynamic covalent surfactant formed by mixing hexylamine (HA) and 4-formylbenzoic acid (FA)in a 1:1 molar ratio (Fig. 4b) with cetyltrimethylammonium bromide (CTAB) present. The dynamic system's solution properties were assessed through visual observation, rheological measurements, ^{1}H NMR, and cryo-TEM analysis. Upon increasing the solution pH to 12.07 from 6.01, the mixed solution was switched from a low viscous Newtonian fluid to a viscoelastic solution before eventually becoming hydrogels, with the zero-shear viscosity showing a ~ 6000-fold increase (Fig. 4c). Besides, the viscoelasticity of these dynamic systems could be reversibly switched through adjusting the pH of solution (Fig. 4d). The remarkable change in rheological characteristics was ascribed to the pH-controlled imine product generation between FA and HA, which displays increased hydrophobicity and thus enables hydrotrope molecules to move from the water phase into the micelle's interior. Such a structural transformation favors the increase in the critical packing parameter from a value below one-third, to around one-third, then one-half, and thus prompts the micellar aggregates to grow from spherical to wormlike (Fig. 4e). In contrast, when replacing 4-formylbenzoic acid with *p*-phthalic acid (*p*-PA), the solutions obtained did not show any change in viscosity when altering the pH (Fig. 4c), since the transfer of the hydrotropes cannot occur due to the hydrophilicity of disodium phthalate.

2.1.3. Reversible switch between vesicles and building block molecules

In addition to the dynamic wormlike micellar system discussed above, van Esch et al. [41] also prepared responsive vesicles by using dynamic covalent imine chemistry, where the bilayer membrane's responsiveness can be controlled through tuning the formation of amphiphilic surfactants reversibly (Fig. 5a). Specifically, the authors created a double-tailed surfactant which is readily obtained from two non-surface-active starting materials, namely, a cationic bisaldehyde A and an alkylamine with a relatively short chain, e.g., hexylamine B.

Cationic surfactant was synthesized in situ from the water-soluble reactants via reversible imine bond generation. One can expect that both single-tailed AB_1 and double-tailed AB_2 surfactants are obtained, which exists in dynamic equilibrium with each other and with the precursors (Fig. 5b). After mixing the precursors as aqueous solution, vesicles formed within minutes, verified via increased scattering intensity, and an accompanying blue-shifted emission of Nile Red, implying the formation of hydrophobic regions. The morphology of micellar aggregates was studied by cryo-transmission electron microscopy (Cryo-TEM) and confocal laser scanning microscopy (CLSM). CLSM analysis unveiled vesicles varying in size from 2 to 5 μm, while Cryo-TEM observations showed the existence of unilamellar vesicles measuring 50 to 100 nm. In fact, dynamic light scattering (DLS) measurements displayed a bimodal distribution with hydrodynamic sizes of (95±11) nm and (5.2±1.6) μm. As the vesicles form through the reversible interaction between their non-amphiphilic reactants, it is anticipated that an alteration in the relative abundance of imine products will induce a rapid response of the vesicle bilayer. The authors demonstrated the tuning of the vesicle formation by controlling solution concentration and pH.

It is suggested that the concentration of vesicle-forming surfactant AB_2 monomers in the aqueous phase is negligible, and that the exchange between bulk phase and bilayer occurs at an

exceptionally slow rate. The dynamic surfactants undergo dissociation as a consequence of dilution-induced reduction in the concentration of the surfactant precursors within the bulk. Due to the slow transition rates between AB_2 monomers and the self-assembled bilayer, it seems likely that AB_2 within the bilayer initially revert back to the starting agent. Subsequently, the freed surfactant precursors diffuse out from the bilayer, potentially starting with those in the outermost layer. Therefore, the stability of the bilayer may experience a further decline due to a greater disparity between the outer and inner layers, resulting in increased permeability, and ultimately shrinkage of the vesicles. Alternatively, reversible formation of the vesicles can also be realized by modulation of the pH. The stability of the vesicles was observed to persist up to a pH of 7.1 ± 0.2, as confirmed by fluorescence spectroscopy and DLS. However, upon decreasing pH values to 4 and below the vesicles dissociated completely. It is worth noting that the dissociation of vesicles is entirely reversible, as verified by a notable rise in scattering as well as the restoration of the initial vesicle diameter while tuning the solution back to an alkaline environment.

This research demonstrates how dynamic imine chemistry can create promising smart vesicular architectures for encapsulation and release applications, thanks to facile synthesis methods, fast disassembly rates, and controllable morphological transitions.

By coupling dynamic covalent imine chemistry with sophisticated self-assembled supramolecular structures, Giuseppone et al. demonstrated that a self-replicating selection can happen at two length scales, exhibiting an interesting sigmoidal relationship between concentration and time profiles [42]. By using dynamic amphiphilic compounds, in which a hydrophilic headgroup is reversibly linked to a hydrophobic tail through a dynamic imine bond (Fig. 5c), the micelles display autopoietic growth in aqueous solution (Fig. 5d). Moreover,

competition for access to the same hydrophobic tail in situations where various hydrophilic units engage in intertwined equilibria may influence the final outcome, as more efficient replicators or more stable intermediates will outcompete weaker counterparts and reduce their representation in the end product. The separate reactions involving benzylic, aromatic, aliphatic, and hydroxy amines featuring variable lengths of polyethylene oxide segments, and p-substituted benzaldehydes terminated with octanoyl groups - lead to dynamic covalent surfactants. These amphiphilic products show varying hydrophilic/hydrophobic ratios which are related to surfactant structural parameters. The imine condensation process is contingent upon the nucleophilicity of the amine reacting moieties following the order: hydroxy amine >> aliphatic amine >> benzylic amine >> aromatic amine. The molecular components compete at the sub-nanometer scale for the reversible formation of dynamic surfactants with varying hydrophilic/hydrophobic ratios, which, in conjunction with the stacking effect, primarily governs the self-organization and the thermodynamics of the bound structures at the scale of tens of nanometers. These supramolecular aggregates exhibit sigmoidal concentration-time profiles and fit the definition of autopoiesis because they replicate themselves through accelerated imine condensation within their original catalyst-rich loop. More importantly, in the subsequent thermodynamic loop, these self-assembled aggregates exhibit selectivity towards the integrated dynamic building blocks and thereby promoting the selective generation of their own components. This system demonstrates a general concept of integrating cooperative processes across various size scales within networks of equilibria, featuring autocatalysis in dynamic covalent libraries, and offers valuable insights into the development of spontaneously organized collective properties.

Jiang et al. [43] developed a smart system also based on vesicles, where the generation of imine products occurs to a limited extent in the absence of a bound substrate. However, it experiences significant and specific amplification when glucose binds to an aldehyde group through boronate ester bonds, resulting in the formation of glucose-associated supramolecular aggregates (Fig. 6). The dynamic covalent surfactant molecules synthesized from glucose, octylamine, and 4-formylphenylboronic acid spontaneously organize into vesicles in water, which enables the detection of glucose through the mere combination of readily available compounds.

2.2. Reversible switch between different types of self-assemblies

As discussed in the above section, precursors can be used for the in-situ synthesis of dynamic covalent surfactants through reversible covalent bond formation, and thus provide a facile way for the reversible manipulation of the formation/destruction of surfactant assemblies. In addition, dynamic covalent surfactants can also be utilized to build smart self-assemblies, in which the micellar aggregates can be switched between different morphologies.

2.2.1. Reversible switch between wormlike micelles and spherical micelles

Kang and coworkers [44] constructed a new pH-responsive wormlike micelle system by combining cetyltrimethylammonium bromide (CTAB), *p*-toluidine (MB) and 4-hydroxybenzaldehyde (HB) at a concentration of 60, 40, and 40 mM, respectively. The creation of the dynamic covalent bond hydrotropes and the morphology as well as rheological behavior of the resulting micellar aggregates were studied by means of ^{1}H NMR spectroscopy, rheology, and cryo-TEM. The findings indicate that with an increase in pH, the solution's viscosity initially experiences a slight decrease followed by a substantial increase. The micellar aggregates in the aqueous solution show a sphere-to-wormlike transition; as a result, the solution transforms from

a water-like low viscous fluid to a hydrogel capable of supporting its own weight. The alteration in the self-assembled aggregates and their rheological response can be ascribed to the creation and equilibrium of MB-HB products, a type of hydrotrope bearing a dynamic covalent bond. Furthermore, this system exhibits complete reversibility in its transition from spherical aggregates to wormlike micelles.

2.2.2. Reversible switch between spherical micelles and vesicles

Chen et al. [45] prepared pH-responsive vesicles from a mixture of 1-methyl-3-(10-(4-formyl-phenoxy) decyl) imidazolium (FDI) or 1-(10-(4-formyl-phenoxy) decyl)-pyridinium (FDP) with 1-octyl amine under basic conditions in equal proportions. The micellar structures and morphologies were examined using TEM with the sample prepared through freeze-fracture or negative staining. Dynamic covalent surfactants from amine in the presence of FDP and FDI yielded spherical unilamellar vesicles, measuring 71 and 107 nm in diameter, respectively. The vesicles demonstrated their ability to encapsulate Nile Red and rapidly release it at low pH. The evolution of the supra-amphiphile composition was tracked through ^{1}H NMR and fluorescence spectroscopic assays, revealing superior CMC values and aldehyde conversion yields for the FDI-derived products over those generated from FDP. The advantages of ease of formation, quick dissociation, and changeable morphologies make such systems ideal candidates for the construction of advanced smart supra-amphiphile systems which could potentially be used in controlled drug delivery.

Zhang and coworkers [46] prepared a selenium-containing imine-based dynamic covalent surfactant (HOBAB−BSeEA) by mixing an asymmetric double-chain cationic surfactant with a formyl group at the end of one hydrophobic tail and a Se-containing amine (2-(benzylselanyl)ethan-1-amine), as shown in Fig. 7a. The imine bond of HOBAB−BSeEA can be

controlled by adjusting the pH or through oxidation (Fig. 7a). The imine bond formation is largely dependent on the level of oxidation and solution pH. Full oxidation led to a reduction in conversion efficiency from 87% to 48%. Similar results were obtained by altering the solution pH to 7.0 from 10.0. Due to the generation and disassociation of imine products, the resulting amphiphilic compounds could be toggled reversibly between symmetric and asymmetric structures (Fig. 7b). Such a structural change can induce a morphological transformation of the self-assemblies between vesicles and spherical micelles. Oxidation cannot break all imine bonds, which means the full transformation of vesicles into spherical micelles is still possible. This can be attributed to the increased polarity of the micellar microenvironment by the oxidation of selenium. Nile red encapsulated within HOBAB−BSeEA vesicles was promptly, precisely, and incrementally released in response to oxidation. This novel work provides a starting point to understand how oxidation triggers imine bond breakage and vesicle disruption, which will be very helpful in creating redox-responsive, imine-based carriers capable of releasing drugs in response to local reactive oxygen species levels within biological environments.

2.2.3. Reversible switch between wormlike micelles and vesicles

Kang et al. [47] created a dynamic surfactant system responsive to pH shifts using CTAB in the presence of two non-amphiphilic precursors, octylamine (OA) and 4-hydroxybenzaldehyde (HB) with a concentration of 100, 60, and 60 mM for CTAB, OA and HB, respectively. The morphology transformation of the solution was accessed through macroscopic observation, ^{1}H NMR, Fourier transform infrared spectroscopy, dynamic light scattering, rheology, and cryo-TEM. Upon increasing the pH, the mixed system displays a transition from a liquid resembling water to a clear hydrogel and finally a translucent solution with low viscosity. When the pH rises to 7.99 from 4.93, the micellar aggregates show a sphere-to-worm structural transformation. At

pH = 12.02 and above, the wormlike micelles gradually disappear while vesicles are also present. This result demonstrates that a morphology transition from spherical-to-wormlike-to-vesicular aggregates can be triggered by altering solution pH. Such significant change in morphological can be ascribed to the pH-triggered ionization and generation of the dynamic anionic surfactant HB-OA$^-$. Moreover, this system shows excellent reversibility.

2.2.4. Reversible switch between vesicles and nanofibers

Hao's team [48] developed a fascinating type of self-assembled system relying on dynamic covalent bonds in which the micellar aggregates can be reversibly controlled between vesicles and nanofibers (Fig. 8a). Under alkaline conditions, the aldehyde group in benzaldehyde (BA) or 1-naphthaledhyde (NA) can react with the amine group in 11-aminoundecanoic acid (AUA) to produce a small organic building block concurrently triggering a morphological shift from vesicles to nanofibers. At neutral pH, the dynamic covalent imine bonds can be hydrolyzed, leading to the dissociation of the nanofibers and appearance of vesicular aggregates. The transition was reversible as fibers reappeared as the pH was reverted to basic condition. Besides, reversible control over the hydrogel state was achieved via nanofiber assembly. By Introducing NaCl, which substantially increases nanofiber density and the number of cross-links, a free-standing gel was induced to form from a previously flowable solution of nanofibers; the gel obtained was confirmed to be pH-switchable.

In order to create a novel supramolecular structure with multi-stimuli responsiveness, Li et al. [49] developed the strategy of connecting the hydrophilic and hydrophobic components together with a bi-functional linker utilizing more than one type of interaction, namely, the creation of a dynamic inclusion complex between azobenzene and α-cyclodextrins (α-CD) bearing an aldehyde moiety, as well as in situ-generated dynamic imine bonds between the dodecylamine

and aldehyde to produce a surfactant, referred to as PPBI (Fig. 8b). TEM, DLS, and X-ray diffraction (XRD) were employed for self-assembled structure analysis. ^{1}H NMR studies and UV-vis spectroscopy revealed that the amphiphile was constructed from host-guest interaction and dynamic covalent bond formation. Light exposure and pH adjustments can activate or deactivate the amphiphile, demonstrating its ability (Fig. 8c). The responsiveness imparts well-controlled self-assembly for this supra-amphiphile, and it can also encapsulate and deliver drug molecules (rhodamine B as a typical model).

3. Dynamic covalent surfactants for reversible emulsification

Dynamic covalent chemistry opens an avenue for the effective control of interfacial properties since the hydrophilic-lipophilic balance (HLB) of the amphiphilic products is precisely tuned with solution conditions. The use of reversible bonding dynamics allows for on-demand emulsion formation by breaking the existing equilibrium. In this section, reversible emulsification utilizing dynamic covalent surfactants will be discussed.

3.1. pH-switchable emulsions

Researchers have devoted great efforts to the development of smart emulsions that react to external stimuli like light [50], temperature [51], pH [52], magnetic field [53], redox reactions [54], etc. The introduction of stimulus-responsive properties to emulsions not only enables controlled demulsification but also allows the retrieval and reuse of the emulsifiers. Amongst the various triggers utilized towards controllable emulsification/demulsification, pH is the most facile and economical trigger, with great potential for industrial uses.

By mixing polyethylenimine (PEI) and benzaldehyde (B), dynamic covalent surfactants PEI-B were obtained and used for the fabrication of pH-switchable emulsions [55]. Stable emulsions with different water/paraffin oil ratios were successfully fabricated at a pH of 7.8 with

ultrasonication, using PEI-B as the emulsifier. A reduction in pH to 3.5 triggers complete demixing as the dynamic covalent imine bond broke down. By returning the pH to 7.8, the dynamic imine bond reforms and surface-active PEI-B regains stability, resulting in a robust emulsion again. Emulsification and demulsification were determined by the establishment and decomposition of the dynamic imine bond of PEI-B, which can be controlled by a variation in pH. This work by Ren et al. [55] opens up a new avenue for the creation of smart emulsions.

In a subsequent investigation [56], the same authors prepared a dynamic covalent surfactant (T-DBA) utilizing a mixture of taurine (T) and p-decyloxybenzaldehyde (DBA). Nanoemulsions were obtained using paraffin, water and T-DBA as the dispersed phase, continuous phase, and emulsifier, respectively. The dynamic nature of T-DBA allows it to switch between surface active and inactive states responding to pH changes, enabling the nanoemulsions to toggle between "on" and "off" states. The adoption of dynamic covalent bonds to turn nanoemulsion stability allows smart control that can be extended to many industrial processes, for instance, enhanced oil recovery.

3.2. pH-switchable Pickering and non-Pickering emulsions

In 1907, Pickering [57] made the discovery that particles could act as stabilizers for emulsions, in which water and oil wettability of the particles is of crucial importance to the emulsion's structure and stability. Since that time, a wide range of studies have shown that particles can absorb at interfaces and decrease the interfacial tension to form stable Pickering emulsions. The combination of both particles and surfactants has also been investigated in numerous studies and is present in many commercial emulsion formulations [58]. However, the production of such emulsions, in general, requires a high concentration of particles [59].

Binks et al. [60] created a new pH-responsive Bola type surfactant through a dynamic imine bond utilizing 4-formylbenzoic acid (FA) and 12-aminolauric acid (AA), which can not only lead to the reversible emulsification of Pickering emulsions but also reduce the required concentration of silica particles. In acidic aqueous media with a pH below 4.1, the C=N bond breaks, liberating positively charged HAA surfactants that can make Pickering emulsions stable in combination with negative-charged silica nanoparticles. Instead, in alkaline aqueous environments with a pH above 10, FA-AA act as poor emulsifiers, leading to the destabilization of the Pickering emulsion. FA-AA and nanoparticle composites can lead to pH-sensitive Pickering emulsions at relatively low concentrations. Given its high hydrophilicity, when demulsification occurs, both FA-AA and the charged nanoparticles revert to the aqueous phase without polluting the oil phase. This innovative method for creating a recyclable dynamic covalent surfactant allows the entire aqueous phase to be recycled and reused multiple times.

Emulsions can also be stabilized through the synergy of particles and surfactants where the particles and surfactants carry the same type of charge, and the particles no longer adhere to the oil/water interface. Instead, the bulk continuous phase contains dispersed particles due to repulsive forces with the surfactants. These are referred to as “non-Pickering” emulsions.

Liu and his team [61] created a cutting-edge stimuli-responsive system using a silica nanoparticle-stabilized “non-Pickering” emulsion. A dynamic covalent surfactant was synthesized by combining equal molar quantities of hexylamine and 4-formylbenzoic acid under pH = 12.55. A stable emulsion was obtained even at low concentrations of surfactant (< CMC) and silica nanoparticles (0.5%, w/w). Silica particles do not accumulate at the oil-water interface but instead reside within the continuous phase. The generation/de-composition of the dynamic covalent surfactants governs the emulsification/demulsification through altering the pH. It was

demonstrated that the “non-Pickering” emulsion could serve as microreactors in chemical transformations.

3.3. pH-switchable double emulsions

Double emulsions play a crucial role in food applications and cell-encapsulation drug delivery. Thermally-induced phase separation is a typical method toward the preparation of double emulsions [11]. In this case, the dispersed phase containing a hydrocarbon (HC) and a fluorocarbon (FC) oil, which are immiscible with each other, is heated beyond its upper critical temperature so as to afford a single-phase mixture. Subsequently, the homogeneous mixture is emulsified in water containing the surfactants with an appropriate hydrophilic–lipophilic balance (HLB). Upon cooling, the HC and FC oils separate from each other, forming a double emulsion with consistent composition and a structure governed by the surfactant molecular architecture. Precise tuning of the interfacial tensions between the different phases through a suitable choice of surfactant - a challenging task - is key to the emulsion structure and composition as well as its stability.

Using dynamic covalent chemistry as a potent method, the fabrication of dynamic surfactants from precursors through in situ interfacial synthesis during droplet formation avoids extra manufacturing steps with synthetic complexity and grants access to versatile surfactants with appropriate HLB. Swager, Thayumanavan and colleagues [62] marked the first demonstration of fast manufacturing and immediate use of surfactants in double emulsions via instant imine bond construction within oil-water interfaces (Fig. 9). Imine products formation significantly streamlines the preparation of intricate double emulsions, replacing several steps with just one straightforward process.

In principle, surfactants bearing a hydrocarbon (HC-surfactant) and a fluorocarbon tail (FC-surfactant) stabilize HC/water (HC/W) and FC/water (FC/W) interfaces, respectively. Tuning the interfacial tension (γ) at the HC/water ($\gamma_{HC/W}$) and FC/water ($\gamma_{HC/W}$) interfaces using HC-surfactant and FC-surfactant, respectively, generates different morphologies, such as encapsulated and Janus droplets. If $\gamma_{HC/W} \gg \gamma_{FC/W}$, a larger surface area at the FC/W interface compared to the HC/W exists, resulting in encapsulated droplets with HC-in-FC-in-water (HC/FC/W) structure, whereas the opposite conditions are required to achieve FC-in-HC-in-water morphology (FC/HC/W). Perfect Janus morphology with structure of equal hemispheres can be obtained while $\gamma_{HC/W} = \gamma_{FC/W}$. Adjusting the equilibrium of the dynamic system alters the ratio of $\gamma_{HC/W}$ and $\gamma_{FC/W}$, consequently influencing the transformation in morphology of the droplet.

Double emulsions incorporating dynamic imine surfactants as emulsifiers remain intact under neutral/basic environments and exhibit dynamic behaviors through acid-induced hydrolysis and exchange of imine. This smart system's dynamic nature enables the handling of oil-water interfaces by adjusting the pH as well as related imine exchange. The authors have also shown how creating complex surfactants with biomolecules like antibodies through in situ imine surfactant formation can be highly beneficial for biosensing applications. Moreover, forming imine at the emulsion-solid interfaces triggers a payload release mechanism. This work illustrates that facile, dynamic interfacial imine formation can affect macroscale phenomena.

4. Other functions of dynamic covalent surfactants

Having reviewed the principles of shape transition and switching between different states that DCSs make possible, this final section considers concrete applications facilitated by this technology.

4.1 Functional perfumery

The controlled release of functional molecules is of critical importance for the fragrance and flavor industries. Surfactant profragrances that can be cleaved, useful in functional perfumery have been synthesized by condensing a water-repelling fragrance aldehyde and a water-soluble amine which is the derivation of a diblock copolymer of poly(ethylene oxide) and poly(propylene oxide)[63]. Such cleavable surfactants can self-assemble into micellar aggregates which contain perfume oils, either covalently attached or unbonded, inside the hydrophobic core. It has been demonstrated that solubilized perfumes with cleavable surfactants and their non-cleavable counterparts present similar evaporation behaviors. For practical applications, the cleavable imine surfactant can be hydrolyzed to release fragrance aldehydes that are dynamically bonded to the surfactant. The profragrances in aqueous formulations show excellent stability during storage, which is a significant benefit for their intended use in functional perfumery. Surprisingly, dilution can induce an efficient imine hydrolysis product and thus the release of the bonded fragrance aldehyde, displaying a blooming effect. The use of cleavable imine surfactants enables a more even evaporation of the dissolved perfumes upon dilution by decreasing concentrations of headspace for highly volatile fragrances and raising them for less volatile ones.

4.2 Agrochemicals

Pesticides play a key role in modern agriculture; however, traditional pesticide formulations easily drift, run off, and seep into the environment, and the active ingredients are decomposed and leached because of inadequate encapsulation. It is estimated that less than 1% of the pesticides reach the biological targets and take effect [64]. The wasted toxic pesticides and organic solvents in pesticide formulations have resulted in serious environmental and ecological problems. Consequently, sustainable agriculture not only demands an improvement of pesticide

efficiency but also requires the elimination of organic solvents. Sustainable pesticide formulations should satisfy the following requirements: [65] (1) water should be used as a green solvent; (2) pesticides must be well encapsulated; (3) be completely deposited on the surface of biological targets after being sprayed; (4) firmly stick to the target surfaces; (5) and be precisely released in order to reduce the dosage and application frequency.

Jiang and coworkers [65] have developed a comprehensive strategy grounded in a precise design for the entire pesticide application process, which would significantly improve pesticide efficiency. To enhance encapsulation, adhesion, sustained retention, and controlled release on hydrophobic plant surfaces, they designed a water-based coacervate with dynamic covalent trimers acting as surfactants. The coacervate composed of nanoscale networks of wormlike micelles and large amounts of water fixed by the nanonetwork, accounts for an effective encapsulation of pesticide molecules (Fig. 10). Moreover, the network structures interact with superhydrophobic plant micro/nanosurfaces, which enables the complete deposition of the pesticides on super-repellent plants following high-speed contact and prevention of wind/rainwater washing. In addition, this green pesticide formula possesses characteristics of CO_2-triggered release: CO_2 induces the degradation of the surfactant and thereby the precise release of the pesticides. This innovative pesticide formulation based on these dynamic coacervates paves the way to advanced pesticide applications and will likely contribute to promoting a more sustainable agriculture.

4.3 Orthogonal functionalization of graphene

So far, dynamic covalent surfactants based on small amphiphilic molecules that can be reversibly formed/decomposed, depending on solution conditions, have been discussed. Recently, amphiphilic Janus nanomaterials bearing hydrophilic groups on one side and lipophilic

moieties on the other - the structure resembling that of surfactants - have been reported. These display better performances (e.g., improved surface and interfacial activity, extremely low aggregation number of the micelles—micelles can be formed by only a few nanoparticles-, and improved emulsification ability, etc.) than classical surfactants. We here refer to these novel nanostructured amphiphilic materials, which resemble that of surfactants both in terms of their structures and functionalities, as "nanosurfactants". In addition to nanosurfactants, dynamic covalent nanosurfactants based on reversible bond formation/decomposition have also appeared very recently. For example, Swager et al. [66] described a new class of dynamic covalent nanosurfactants using 2D Janus graphenes, which will be discussed in detail in the following. The authors successfully accomplished the dynamic covalent functionalization of graphene through Meisenheimer complexes made from reactions between primary amines and pre-attached dinitroaromatic moieties that were pre-bonded to graphene.

Strong π–π attraction always occurs between pristine graphene sheets, which normally results in stacking between different sheets. However, once modified with 3,5-dinitrophenyl moieties, the resulting functionalized graphenes (FGs) display reduced inter-sheet interactions and a decreased tendency to stacking. It was found that water–ethyl acetate interface can effectively trap such modified graphenes and induce the spontaneous formation of lateral self-assembly of individual sheets, which enables the creation of 2D Janus graphenes (JGs) through differential functionalization at the liquid-liquid interface. Such functionalization was achieved by selectively adding amine to the electron-withdrawing 3,5-dinitrophenyl groups on one side of the graphene basal plane, controlled by the extremely different solubilities of the relative amine in the two immiscible liquids. Consequently, asymmetric functionalization of 3,5-dinitrophenyl-modified graphenes with hydrophilic ethylene oxide chains, hydrophobic hydrocarbon chains,

and/ or amphiphobic fluorocarbon chain can be accomplished in a controllable manner (Fig. 11a). Furthermore, the connections between 3,5-dinitrophenyl groups and amines involve reversible covalent bonds formation via Meisenheimer complexes.

When the FGs are assembled at an oil/water interface, they can react with NH_2-bearing species that are solubilized in the corresponding oil and water phases, offering an opportunity for the asymmetric functionalization of FG. For instance, n-octylamine (H) or 1H,1H,2H,2H-perfluorooctylamine (F) solubilized in ethyl acetate can react with FG from the upper side of the oil/water interface, leading to the fabrication of 2D graphenes bearing hydrophobic tails (H-chain or F-chain) in one side (H-FG or H-FG). Subsequently, water-soluble 4,7,10-trioxa-1,13-tridecanediamine (W) reacted with the H-FG or H-FG from the lower side. Finally, amphiphilic Janus 2D graphene (H-FG-W or F-FG-W), bearing hydrophobic hydrocarbon-chain or fluorocarbon-chain on one face and hydrophilic moieties on the reverse, was generated (Fig. 11a). Propelled by Marangoni force, the hydrophilic side of the amphiphilic Janus 2D graphene moved up the hydrophilic wall of a glass vial (covered by a thin water layer) and spread its hydrophobic side in nonpolar solvents such as hexane (Fig. 11b). Interestingly, nearly all H-FG-W and F-FG-W remained at the interface, demonstrating strong adsorption of such graphenes at interfaces. Similarly, amphiphilic Janus 2D graphenes hydrocarbon-chain on one side and fluorocarbon-chain on the other (H-FG-F) can also be produced. The asymmetrical functionalities on the two different sides of the 2D graphene nanosheets created novel 2D nanostructured “super-surfactants” that are very interesting for interfacial applications. These “super-surfactants” featuring two chemically different sections display excellent performance at oil/water interfaces.

Non-spherical emulsions were obtained when total H-FG-W surfactant coverage surpassed liquid interfacial areas, forcing jammed assemblies to retain the unique Hexane-Droplet-In-Water shapes at equilibrium. Water droplets introduced to the oil phase can slide freely on the hydrophobic side of the H-FG-W assembly (Fig. 11c). The "super-surfactant" stops the underlying water reservoir's merger with water droplets, providing mechanically robust isolation of the water droplets with these hydrophobic coatings. Amphiphilic Janus 2D graphene H-FG-W may also find applications in enhanced oil recovery (EOR). Performance analysis for H-FG-W in EOR was done using a microfluidics-based reservoir model for visualizing micropore-fluid movement as well as studying oil-water-rock interactions (Fig. 11d). The oil distribution after flooding with aqueous solution of H-FG-W with a low concentration of 91 μg mL^{-1} is illustrated in Fig. 4c. Compared to pure water, oil recovery improved by 14%.

In brief, an approach for synthesizing versatile amphiphilic Janus 2D graphene with various functionalities that are general and scalable and may be applied to other 2D solid materials such as MoS_2, layered double hydroxide (LDH) and 2D metal-organic frameworks, was demonstrated.

5. Conclusions

Conventional surfactants face substantial drawbacks, including limited adaptability to dynamic environments, difficulties in tailoring properties for specific applications, environmental concerns associated with their production and disposal, and a lack of recyclability and self-healing capabilities. In marked contrast, the unique characteristics of surfactants based on dynamic covalent chemistry offer promising solutions to these challenges. The incorporation of dynamic covalent bonds endows these surfactants with an exceptional ability to adapt to variations in pH, temperature, or other external stimuli, bestowing them with unparalleled versatility. Precise control over surfactant properties can be achieved through a careful selection

of building blocks and modulation of reaction parameters. The reversible nature of bond formation within dynamic covalent surfactants not only facilitates recyclability but also contributes significantly to waste reduction. Additionally, the integration of self-healing mechanisms enhances surfactant performance and longevity, effectively addressing the key shortcomings of conventional surfactant technologies.

In this review, we first introduced basic concepts about surfactants and their self-assembly, as well as principles of dynamic covalent chemistry. Next, we showed how the incorporation of dynamic covalent bonds into surfactant molecular structures can benefit the tuning of the micromorphology of the surfactant self-assemblies, and consequently their macroscopic properties. Using dynamic covalent chemistry as a powerful tool, dynamic covalent surfactants have demonstrated their efficiency and potential in the creation of smart self-assemblies. Then, the advantages of precisely tuning HLB through the introduction of a dynamic covalent bond into a surfactant were presented. The convenient and effective control of the interfacial properties provided by the dynamic nature of the reversible surfactant with tuneable HLB undoubtedly facilitates both emulsification and demulsification processes, and thus offers a completely new method for the fabrication of smart emulsions with switchability. This will certainly benefit many industries, including enhanced oil recovery where the underground crude oils are first emulsified by the flooding fluids containing surfactant during the production process and then demulsified so as to ensure effective oil-water separation. Last but not least, applications of dynamic covalent surfactants in perfumery, agriculture, and graphene functionalization were also presented.

Currently, the vast majority of studies in this field rely on dynamic imine bonds and the systems obtained only show responsiveness to pH changes. Future trends in this area could

involve expanding to the developments of multi-stimuli-responsive materials through the incorporation of two or more different types of dynamic covalent bonds. For example, the combination of dynamic imine bonds and dynamic disulfide bonds would enable dual-responsive properties of surfactant solutions to the stimuli of both pH and redox reaction.

Overall, small molecules of reversible surfactant bearing a dynamic covalent bond offer a versatile toolkit for creating adaptable structures. Essential research is crucial to understand the link between dynamic behavior and micromorphology, guiding the development of formulation strategies for future practical applications.

CRediT authorship contribution statement

Fan Min: Writing – original draft. **Cécile A. Dreiss**: Writing – review & editing. **Zonglin Chu**: Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Acknowledgements

This work was funded by National Natural Science Foundation of China (Grant No.: 22172046).

References

[1] Chu Z, Dreiss CA, Feng Y. Smart wormlike micelles. Chem Soc Rev 2013;42:7174-203.

[2] Chakraborty M, Kotecha S. Pulmonary surfactant in newborn infants and children. Breathe 2013;9:476-88.

[3] Halliday HL. Surfactants: past, present and future. J Perinatol 2008;28:S47-S56.

[4] Stachowicz-Kuśnierz A, Korchowiec B, Rogalska E, Korchowiec J. The lung surfactant activity probed with molecular dynamics simulations. Adv Colloid Interface Sci 2022;304:102659.

[5] Seweryn A. Interactions between surfactants and the skin – theory and practice. Adv Colloid Interface Sci 2018;256:242-55.

[6] Peng Y, Hu Y, Wang H. Tribological behaviors of surfactant-functionalized carbon nanotubes as lubricant additive in water. Tribol Lett 2007;25:247-53.

[7] Liu ZX, Chen AP, Qian JJ, Shen H. Effect of surfactant on the properties of gel ink. Advanced Materials Research 2009;66:143-6.

[8] Lee Y, Chung Y-W, Park J, Park K, Seo Y, Hong S-N, et al. Lubricant-infused directly engraved nano-microstructures for mechanically durable endoscope lens with anti-biofouling and anti-fogging properties. Sci Rep 2020;10:17454.

[9] Sieverding E, Humble GD, Fleute-Schlachter I. A new herbicide adjuvant based on a non-super spreading trisiloxane surfactant. J Plant Dis Protect 2006:2005-11.

[10] Brandão R, Borges CSP, Marques EAS, Carbas RJC, Akhavan-Safar A, Nunes PDP, et al. Effect of surfactant contamination on the properties of aluminum/silicone adhesive joints. Mech Adv Mater Struct 2023;30:1875-88.

[11] Zarzar LD, Sresht V, Sletten EM, Kalow JA, Blankschtein D, Swager TM. Dynamically reconfigurable complex emulsions via tunable interfacial tensions. Nature 2015;518:520-4.

[12] Hosseinpour S, Götz V, Peukert W. Effect of surfactants on the molecular structure of the buried oil/water interface. Angew Chem Int Ed 2021;60:25143-50.

[13] Oikonomou EK, Christov N, Cristobal G, Bourgaux C, Heux L, Boucenna I, et al. Design of eco-friendly fabric softeners: structure, rheology and interaction with cellulose nanocrystals. J Colloid Interface Sci 2018;525:206-15.

[14] Guerrero-Martínez A, Pérez-Juste J, Carbó-Argibay E, Tardajos G, Liz-Marzán LM. Gemini-surfactant-directed self-assembly of monodisperse gold nanorods into standing superlattices. Angew Chem Int Ed 2009;48:9484-8.

[15] Tsai C-H, Vivero-Escoto JL, Slowing II, Fang IJ, Trewyn BG, Lin VSY. Surfactant-assisted controlled release of hydrophobic drugs using anionic surfactant templated mesoporous silica nanoparticles. Biomaterials 2011;32:6234-44.

[16] Huang X, Dong Z, Liu J, Mao S, Xu J, Luo G, et al. Selenium-mediated micellar catalyst: an efficient enzyme model for glutathione peroxidase-like catalysis. Langmuir 2007;23:1518-22.

[17] Rajera R, Nagpal K, Singh SK, Mishra DN. Niosomes: A controlled and novel drug delivery system. Biol Pharm Bull 2011;34:945-53.

[18] Hill JP, Shrestha LK, Ishihara S, Ji Q, Ariga K. Self-assembly: from amphiphiles to chromophores and beyond. Molecules 2014;19:8589-609.

[19] Hoffmann H. Fascinating phenomena in surfactant chemistry. Adv Mater 1994;6:116-29.

[20] Fisher LR, Oakenfull DG. Micelles in aqueous solution. Chem Soc Rev 1977;6:25-42.

[21] Israelachvili JN. Intermolecular and surfaces forces: Academic Press, London, 2nd edition; 1992.

[22] Oda R. Safin gels with amphiphilic molecules. In: Weiss RG, Terech P (eds). Molecular gels: materials with self-assembled fibrillar networks. Springer, Dordrecht, 2006; pp 577–609.

[23] Rowan SJ, Cantrill SJ, Cousins GRL, Sanders JKM, Stoddart JF. Dynamic covalent chemistry. Angew Chem Int Ed 2002;41:898-952.

[24] Zheng N, Xu Y, Zhao Q, Xie T. Dynamic covalent polymer networks: a molecular platform for designing functions beyond chemical recycling and self-healing. Chem Rev 2021;121:1716-45.

[25] Jin Y, Yu C, Denman RJ, Zhang W. Recent advances in dynamic covalent chemistry. Chem Soc Rev 2013;42:6634-54.

[26] Zhang W, Chen L, Dai S, Zhao C, Ma C, Wei L, et al. Reconstructed covalent organic frameworks. Nature 2022;604:72-9.

[27] Belowich ME, Stoddart JF. Dynamic imine chemistry. Chem Soc Rev 2012;41:2003-24.

[28] Corbett PT, Leclaire J, Vial L, West KR, Wietor J-L, Sanders JKM, et al. Dynamic combinatorial chemistry. Chem Rev 2006;106:3652-711.

[29] Schaufelberger F, Timmer BJJ, Ramström O. Principles of dynamic covalent chemistry. In: Zhang W, Jin Y (eds). Dynamic covalent chemistry. Weinheim:Wiley-VCH, 2017. p. 1-30.

[30] Zhang D-W, Li Z-T. Orthogonal dynamic covalent and non-covalent reactions. In: Zhang W, Jin Y (eds). Dynamic covalent chemistry. Weinheim:Wiley-VCH, 2017. p. 207-51.

[31] Minkenberg CB, Florusse L, Eelkema R, Koper GJM, van Esch JH. Triggered self-assembly of simple dynamic covalent surfactants. J Am Chem Soc 2009;131:11274-5.

[32] Wang G, Wang C, Wang Z, Zhang X. Bolaform superamphiphile based on a dynamic covalent bond and its self-assembly in water. Langmuir 2011;27:12375-80.

[33] Wang G, Wu G, Wang Z, Zhang X. Asymmetric and symmetric bolaform supra-amphiphiles: formation of imine bond influenced by aggregation. Langmuir 2014;30:1531-5.

[34] Wang G, Wang C, Wang Z, Zhang X. H-shaped supra-amphiphiles based on a dynamic covalent bond. Langmuir 2012;28:14567-72.

[35] Zhao W, Wang H, Wang Y. Coacervation of dynamic covalent surfactants with polyacrylamides: properties and applications. Soft Matter 2018;14:4178-84.

[36] Sun P, Lu F, Wu A, Yin Y, Shi L, Zheng L. Construction of pH-responsive supramolecular assemblies based on dynamic covalent bonds for tunable drug release. J Surfactants Deterg 2018;21:593-600.

[37] Chu Z, Feng Y, Su X, Han Y. Wormlike micelles and solution properties of a C22-tailed amidosulfobetaine surfactant. Langmuir 2010;26:7783-91.

[38] Chu Z, Feng Y, Sun H, Li Z, Song X, Han Y, et al. Aging mechanism of unsaturated long-chain amidosulfobetaine worm fluids at high temperature. Soft Matter 2011;7:4485-9.

[39] Minkenberg CB, Homan B, Boekhoven J, Norder B, Koper GJM, Eelkema R, et al. Responsive wormlike micelles from dynamic covalent surfactants. Langmuir 2012;28:13570-6.

[40] Wang P, Zhu T, Hou X, Zhao Y, Zhang X, Wang T, et al. Responsive wormlike micelle with pH-induced transition of hydrotrope based on dynamic covalent bond. J Mol Liq 2019;286:110935.

[41] Minkenberg CB, Li F, van Rijn P, Florusse L, Boekhoven J, Stuart MCA, et al. Responsive vesicles from dynamic covalent surfactants. Angew Chem Int Ed 2011;50:3421-4.

[42] Nguyen R, Allouche L, Buhler E, Giuseppone N. Dynamic combinatorial evolution within self-replicating supramolecular assemblies. Angew Chem Int Ed 2009;48:1093-6.

[43] Wu X, Chen X-X, Zhang M, Li Z, Gale PA, Jiang Y-B. Self-assembly of a “double dynamic covalent” amphiphile featuring a glucose-responsive imine bond. Chem Commun 2016;52:6981-4.

[44] Kang X, Kang W, Yang H, Hou X, Zhu T, Wang P, et al. pH-responsive aggregates transition from spherical micelles to WLMs induced by hydrotropes based on the dynamic imine bond. Soft Matter 2020;16:9705-11.

[45] Wang J, Chen X, Cui W, Yi S. pH-responsive vesicles from supra-amphiphiles based on dynamic imine bond. Colloids Surf A 2015;484:28-36.

[46] Lu P, He S, Zhou Y, Zhang Y. Oxidation-induced breakage of the imine bond and aggregate transition in a Se-containing dynamic covalent surfactant. Langmuir 2021;37:2833-42.

[47] Wang P, Zhu T, Hou X, Zhao Y, Zhang X, Yang H, et al. Responsive morphology transition from micelles to vesicles based on dynamic covalent surfactants. Soft Matter 2019;15:2703-10.

[48] Wang Y, Xing P, Li S, Ma M, Yang M, Zhang Y, et al. Facile stimuli-responsive transformation of vesicle to nanofiber to supramolecular gel via ω-amino acid-based dynamic covalent chemistry. Langmuir 2016;32:10705-11.

[49] Li S, Hao A, Shen J, Shang N, Wang C. UV and pH-responsive supra-amphiphiles driven by combined interactions for controlled self-assembly behaviors. Soft Matter 2018;14:2112-7.

[50] Li Z, Shi Y, Zhu A, Zhao Y, Wang H, Binks BP, et al. Light-responsive, reversible emulsification and demulsification of oil-in-water Pickering emulsions for catalysis. Angew Chem Int Ed 2021;60:3928-33.

[51] Rajbanshi A, da Silva MA, Murnane D, Porcar L, Dreiss CA, Cook MT. Polymer architecture dictates thermoreversible gelation in engineered emulsions stabilised with branched copolymer surfactants. Polym Chem 2022;13:5730-44.

[52] Wu H, Chen X, Tan R, Luo Y, Hu Y, Li Y, et al. Controllable regulation of emulsion stability by a pH-responsive zwitterionic/anionic surfactant system. Fuel 2022;312:122921.

[53] Zhang H, Ge L, Ding C, Guo R. Magnetic response Janus emulsions stabilized by Mangeto-surfactant. J Mol Liq 2022;349:118416.

[54] Zhu P, Liu D, Dai S, Wang B, Lu H, Huang Z. Redox and pH dual-responsive emulsion using ferrocenecarboxylic acid and N,N-dimethyldodecylamine. Langmuir 2020;36:2368-74.

[55] Ren G, Wang L, Chen Q, Xu Z, Xu J, Sun D. pH switchable emulsions based on dynamic covalent surfactants. Langmuir 2017;33:3040-6.

[56] Ren G, Li B, Ren L, Lu D, Zhang P, Tian L, et al. pH-responsive nanoemulsions based on a dynamic covalent surfactant. Nanomaterials 2021;11:1390.

[57] Pickering SU. CXCVI.—Emulsions. J Chem Soc Trans 1907;91:2001-21.

[58] Binks BP, Rodrigues JA, Frith WJ. Synergistic interaction in emulsions stabilized by a mixture of silica nanoparticles and cationic surfactant. Langmuir 2007;23:3626-36.

[59] Frelichowska J, Bolzinger M-A, Chevalier Y. Effects of solid particle content on properties of o/w Pickering emulsions. J Colloid Interface Sci 2010;351:348-56.

[60] Liu P, Wu J, Pei X, Cui Z, Jiang J, Song B, et al. Recyclable surfactant containing a dynamic covalent bond and relevant smart emulsions. Green Chem 2022;24:7612-21.

[61] Zhang Y, Lu H, Wang B, Wang N, Liu D. pH-responsive non-Pickering emulsion stabilized by dynamic covalent bond surfactants and nano-SiO_2 particles. Langmuir 2020;36:15230-9.

[62] Zentner CA, Anson F, Thayumanavan S, Swager TM. Dynamic imine chemistry at complex double emulsion interfaces. J Am Chem Soc 2019;141:18048-55.

[63] Tchakalova V, Lutz E, Lamboley S, Moulin E, Benczédi D, Giuseppone N, et al. Design of stimuli-responsive dynamic covalent delivery systems for volatile compounds (part 2): fragrance-releasing cleavable surfactants in functional perfumery applications. Chem Eur J 2021;27:13468-76.

[64] Lamberth C, Jeanmart S, Luksch T, Plant A. Current challenges and trends in the discovery of agrochemicals. Science 2013;341:742-6.

[65] Liu B, Fan Y, Li H, Zhao W, Luo S, Wang H, et al. Control the entire journey of pesticide application on superhydrophobic plant surface by dynamic covalent trimeric surfactant coacervation. Adv Funct Mater 2021;31:2006606.

[66] Jeon I, Peeks MD, Savagatrup S, Zeininger L, Chang S, Thomas G, et al. Janus graphene: scalable self-assembly and solution-phase orthogonal functionalization. Adv Mater 2019;31:1900438.

Fig. 1. Model and examples of surfactants: sodium undecyl (anionic surfactants), sulfatehexadecyltrimethylammonium bromide (cationic surfactants), *N*-Dodecyl-*N,N*-dimethyl-3-ammonio-1-propanesulfonate (amphoteric surfactants), D-Glucitol (non-ionic surfactants) (a). Relationship between the packing parameter *p* and the morphology of surfactant aggregates (b). Free energy profiles illustrating kinetically (left) and thermodynamically (right) controlled reactions (c). Schematic illustration of dynamic covalent chemistry (DCC) and a typical type of DCC based on dynamic imine bonds (d). Fig. 1b is reprinted with permission from ref 1.

Copyright (2013) The Royal Society of Chemistry. Fig. 1c is adapted from ref. 23. Copyright © 2002 WILEY-VCH Verlag GmbH, Weinheim, Fed. Rep. of Germany.

Fig. 2. Reversible spherical micelles formed by a dynamic imine surfactant. Dynamic formation of imine surfactants and spherical micelles based on water-soluble nonamphiphilic precursors of short-chain alkylamines and an aromatic aldehyde bearing a cationic ammonium bromide group (a). The dependency of Nile Red maximum emission wavelength on pH (b). pH-reversible Nile Red encapsulation (c). Fig. 2b and 2c are reproduced with permission from ref. 28. Copyright © 2009 American Chemical Society.

Fig. 3. Bola-type DCSs developed by Zhang's group. A simple bolaform DCS based on benzoic imine bond (a). DCSs with different symmetries (b). H-shaped bola-type DCSs (c).

Fig. 4. pH-switchable wormlike micelles based on dynamic imine chemistry. pH-responsive wormlike micelles generated from reversible imine-based Gemini surfactant (a). The diagram of FA-HA$^-$ formation (b). Zero-shear viscosity (η_0) for solutions of CTAB/FA/HA and CTAB/*p*-PA/HA against pH at 25 °C temperature (c). CTAB/FA/HA solution's viscosity with pH-reversible characteristic at 25 °C (d). Schematic diagram of the mechanism for pH-responsiveness in CTAB/FA/HA solution. Fig.4c, 4d, and 4e are reprinted and adapted with permission from ref. 37. Copyright © 2019 Elsevier B.V.

Fig. 5. Dynamic vesicles formed by the cationic bisaldehyde A and hexylamine B. Reversible formation of imine vesicles (a). Proposed mechanism of vesicle dissociation upon dilution (b). Dynablocks generated by the reactions between hydrophilic amines 1–8 and hydrophobic aldehyde A (c). Synergistic constitutional relationships within a model minimal self-replicating dynamic combinatorial library (d). Fig. 5a and 5b are reprinted with permission from ref. 38.

Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. Fig. 5c and 5d are reproduced with permission from ref. 39. Copyright © 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Fig. 6. The proposed mechanism suggests aggregation of amphiphiles synthesized in-situ triggered by glucose, involving the formation of 2 orthogonal dynamic covalent bonds. Reprinted with permission from ref. 40. Copyright © The Royal Society of Chemistry 2016.

Fig. 7. Diagram illustrating the responsive properties of the Se-containing dynamic covalent surfactant (a) and its assemblies in response to redox and pH stimuli (b). Fig. 7b is reproduced with permission from ref. 43. Copyright © 2021 American Chemical Society.

Fig. 8. Dynamic covalent surfactants formed by benzaldehyde (BA) or 1-naphthaledhyde (NA) with 11-aminoundecanoic acid (AUA) and the morphological transformation from vesicles to nanofibers controlled by pH (a). Schematic illustration of the chemical structures of the components and the formation of the supramolecular amphiphile PPBI (b). TEM images and schematic representation of the assembly behaviours of the α-CD/PPBI samples subject to pH variation and UV irradiation (c). Fig. 8a is reprinted with permission from ref. 45. Copyright © 2016 American Chemical Society. Fig. 8b and 8c are reproduced and adapted with permission from ref. 46. Copyright © The Royal Society of Chemistry 2018.

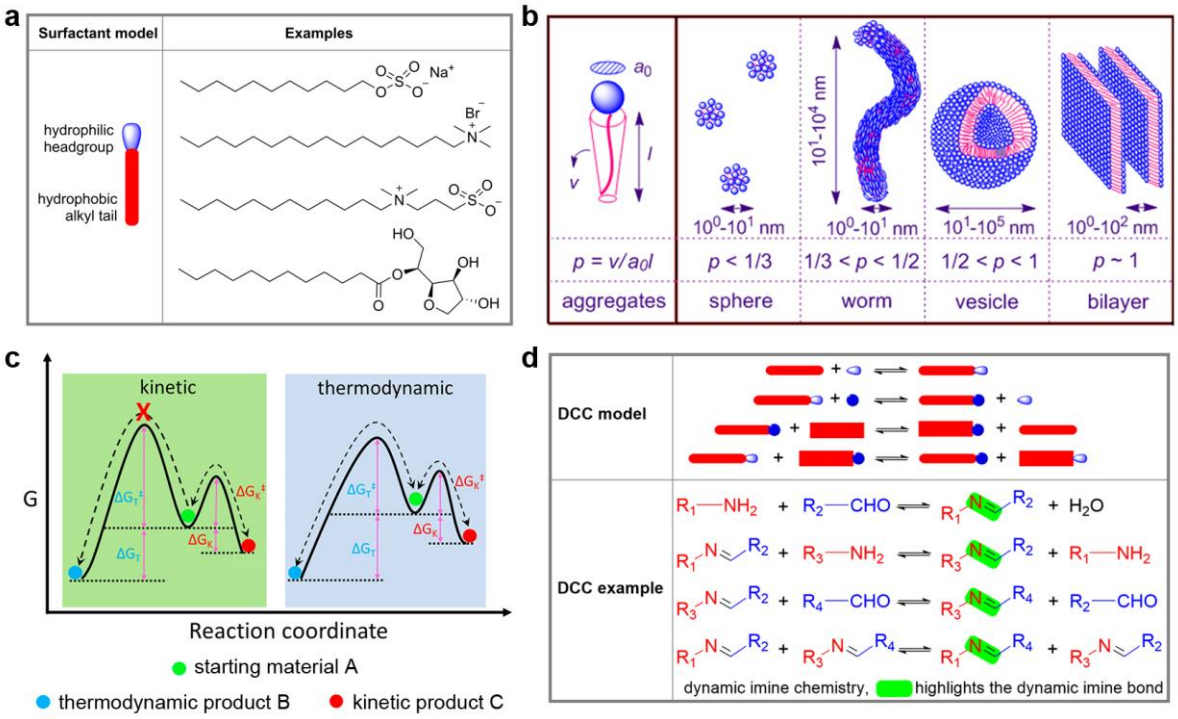
Fig. 9. Changes in double emulsion morphologies (HC-red, FC-white) are observed through alterations in γ balance (a). Diagram representation of the generations of imine surfactants and double emulsions (b). Interfacial imine formation scope and the corresponding emulsification performance (c). Imine surfactant 8 and Zonyl stabilize droplets containing toluene/HFE-7500 and FC-43 (9:1) (d left). Imine surfactant 6 and Tween 20 stabilize Diethylbenzene/HFE-7500

droplets (d right). Reproduced with permission from ref. 59. Copyright © 2019 American Chemical Society. Adapted with permission from ref. 46. Copyright © The Royal Society of Chemistry 2018.

Fig. 10. Illustration outlining the approach to oversee the complete pesticide application process on superhydrophobic plant surface. (a). Formation pathway of the covalent trimeric surfactants based on imine chemistry. (b). Schematic illustration of the encapsulation of the pesticides (c). Reproduced with permission from ref. 62. Copyright © 2020 Wiley-VCH GmbH.

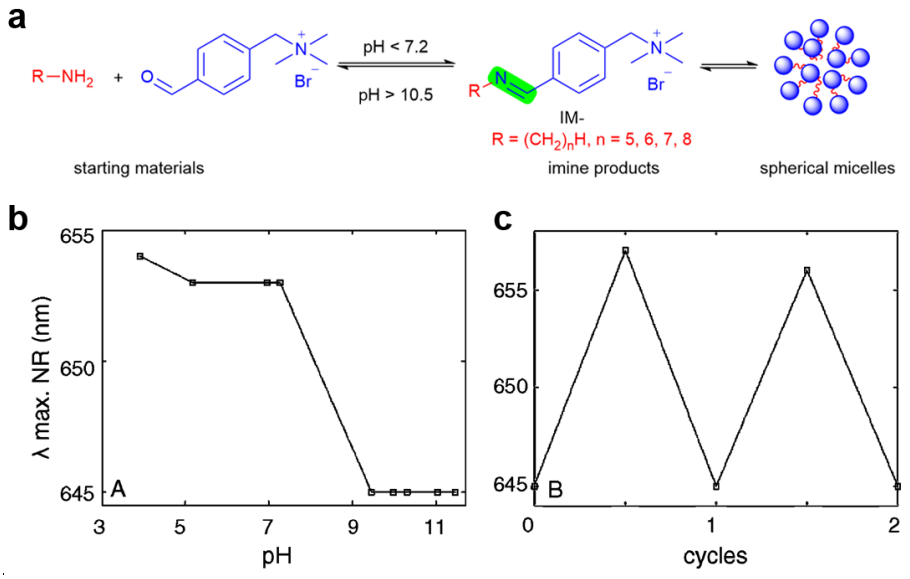
Fig. 11. Diagram outlining the process for preparing FG-H, FG-F, JG-1, JG-2, and JG-3 (a). JG-1 ascends from the water-hexane interface to the air-glass interface along the glass vial surface, propelled by hexane-induced Marangoni flow (b, left). The interfacial jamming of the JG-1 surfactants (b, right). Water droplets slide on the hydrophobic surface of the 2D JG-1 assembly (c). Injection of 2D JG-1 into the microfluidic system designed to mimic oil in a carbonate mineral formation. (d). Left: Following flooding with green-dyed water, 39 ± 2% of crude oil (red) remained. Right: After flooding with a JG-1 water solution, 25 ± 1% of crude oil remained. Reprinted with permission from ref. 63. Copyright © 2019 WILEY-VCH Verlag GmbH & Co. KGaA.

1 **Fig. 1.**



2

3 **Fig. 2.**



4

Fig. 3.

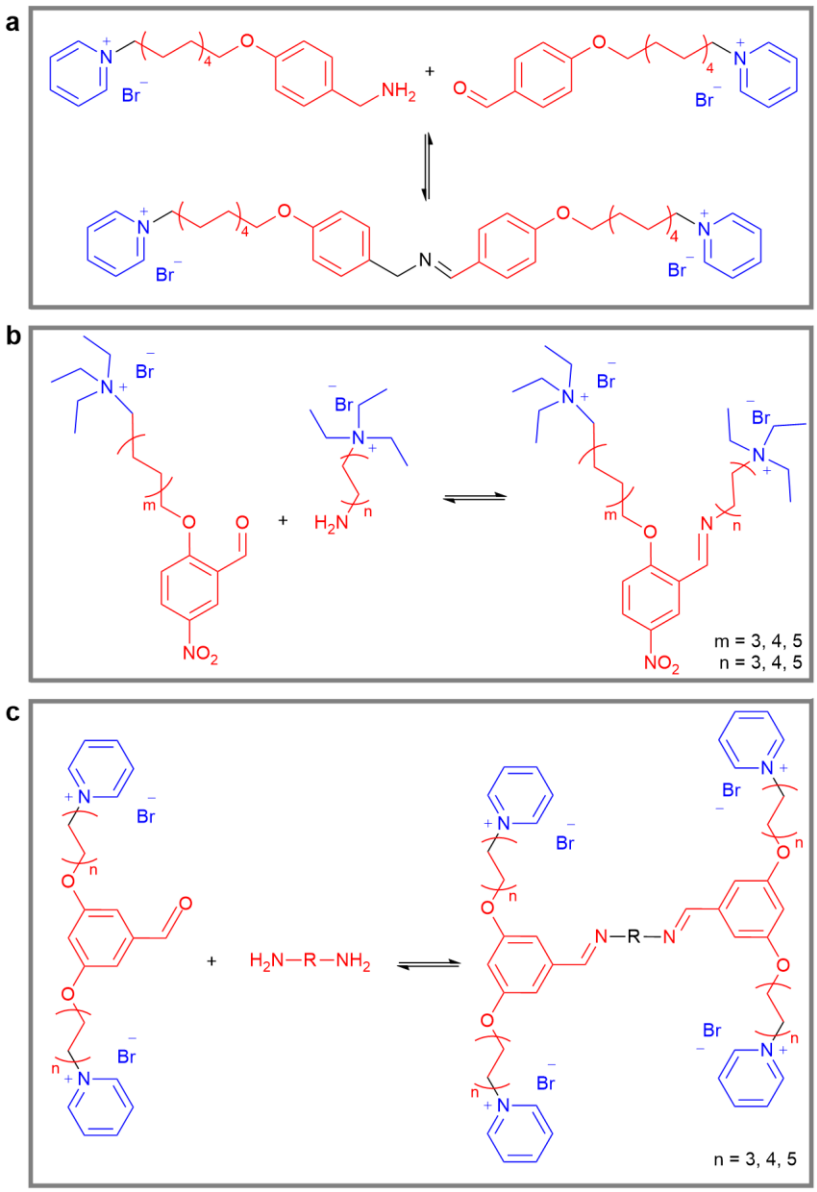
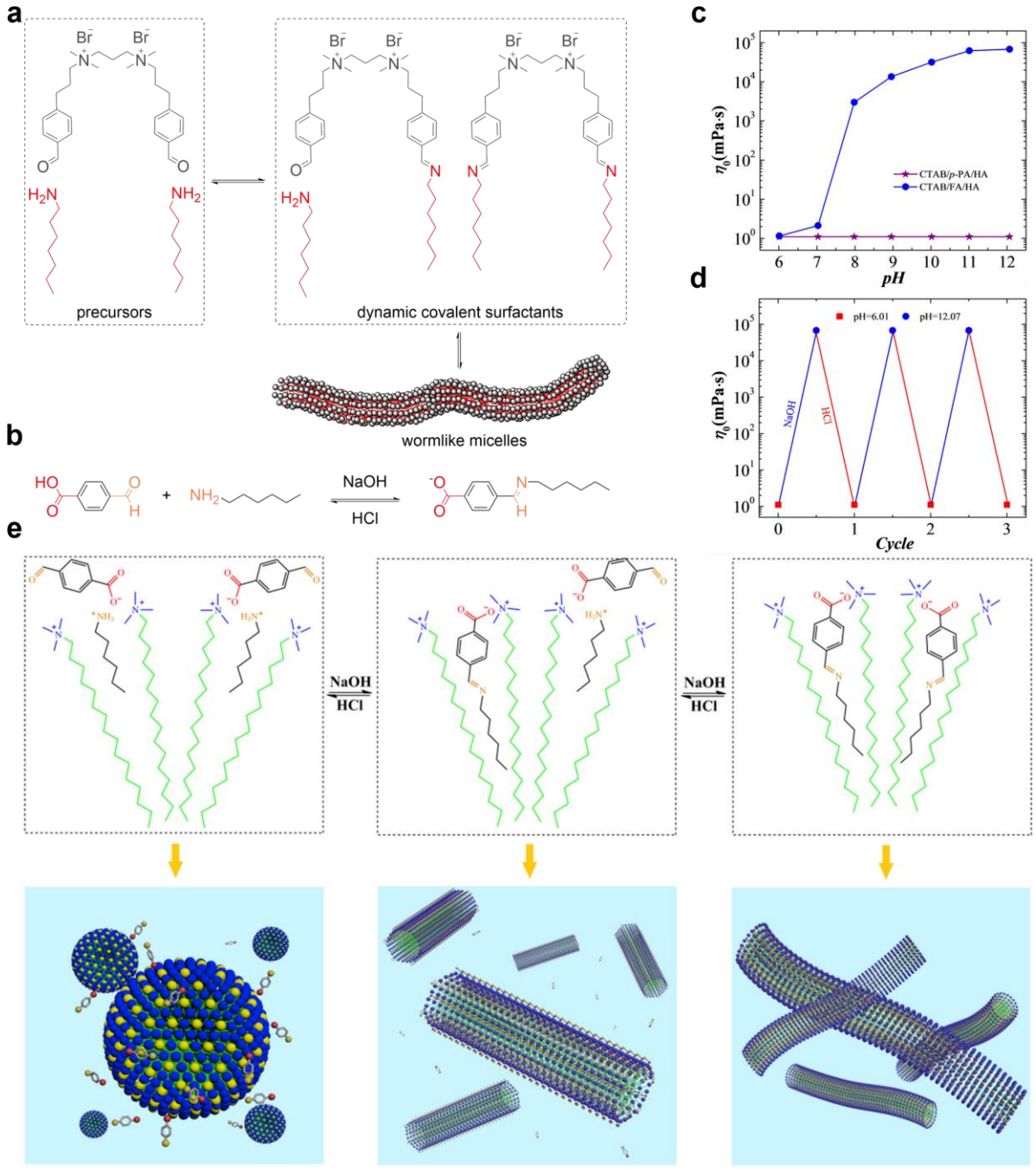
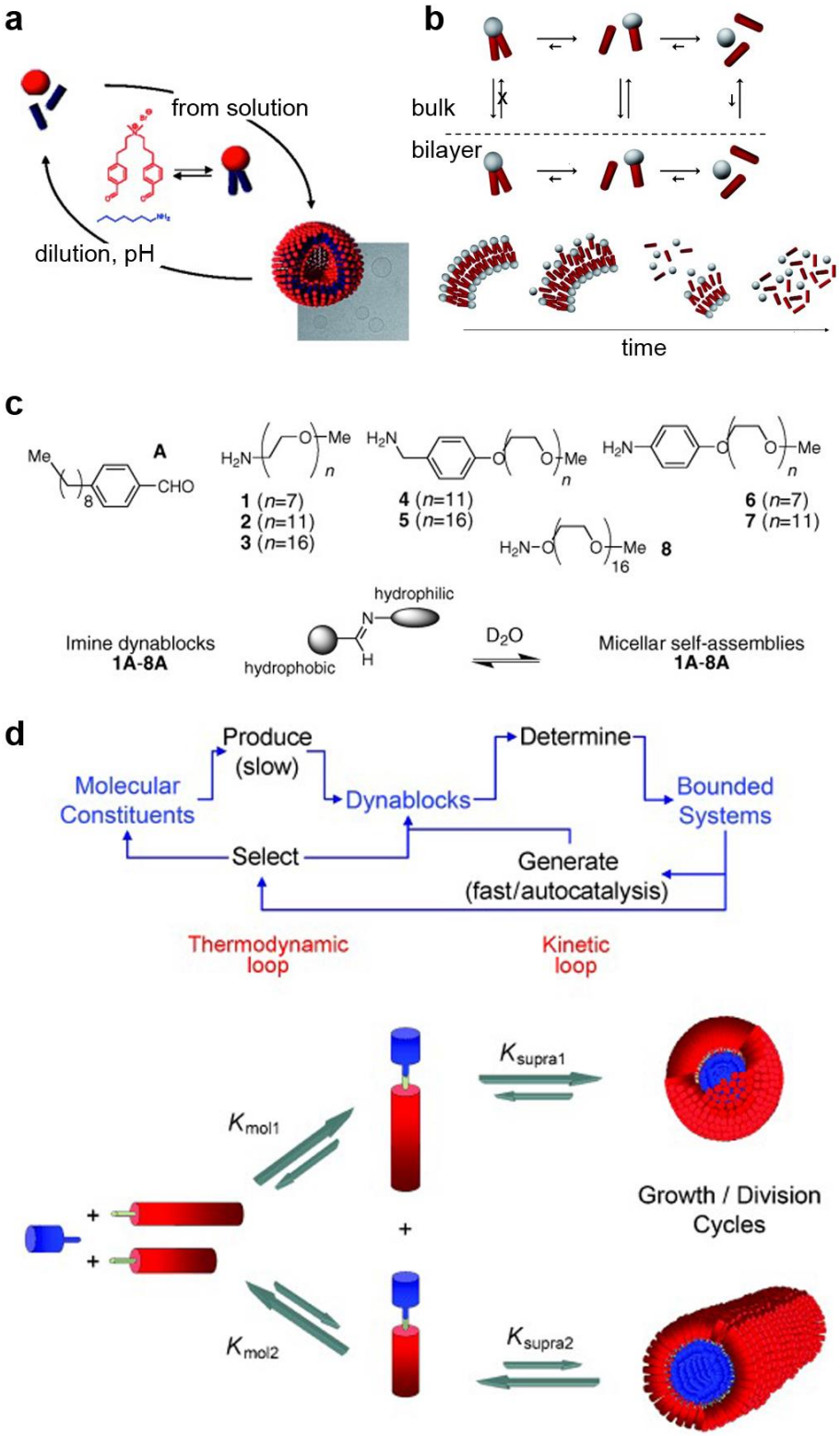


Fig. 4.


a
precursors
dynamic covalent surfactants
wormlike micelles
b
NaOH
HCl
c
CTAB/p-PA/HA
CTAB/FA/HA
pH
d
pH=6.01
pH=12.07
NaOH
HCl
Cycle
e
NaOH
HCl
NaOH
HCl

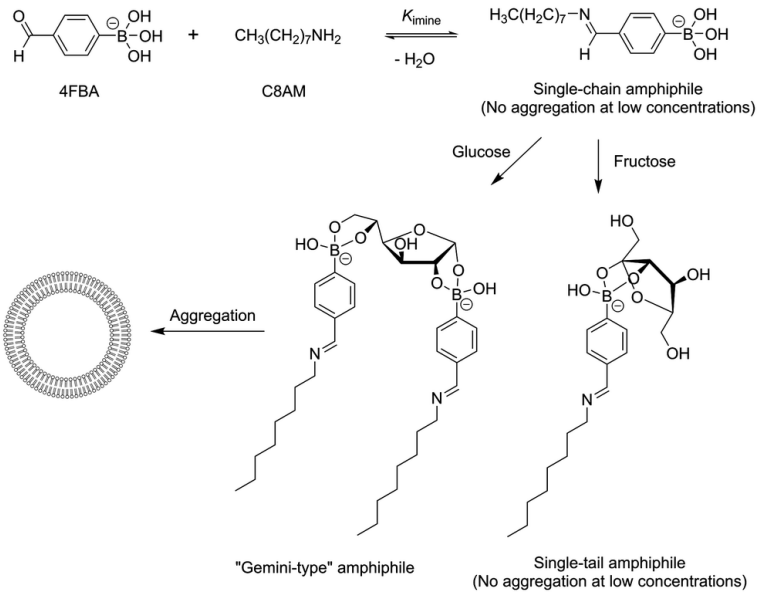
1 **Fig. 5.**


a
from solution
dilution, pH
b
bulk
bilayer
time
c
A
1 (n=7)
2 (n=11)
3 (n=16)
4 (n=11)
5 (n=16)
6 (n=7)
7 (n=11)
8
Imine dynablocks
1A-8A
hydrophilic
hydrophobic
D2O
Micellar self-assemblies
1A-8A
d
Molecular Constituents
Produce (slow)
Dynablocks
Determine
Bounded Systems
Select
Generate (fast/autocatalysis)
Thermodynamic loop
Kinetic loop
Kmol1
Kmol2
Ksupra1
Ksupra2
Growth / Division Cycles

2

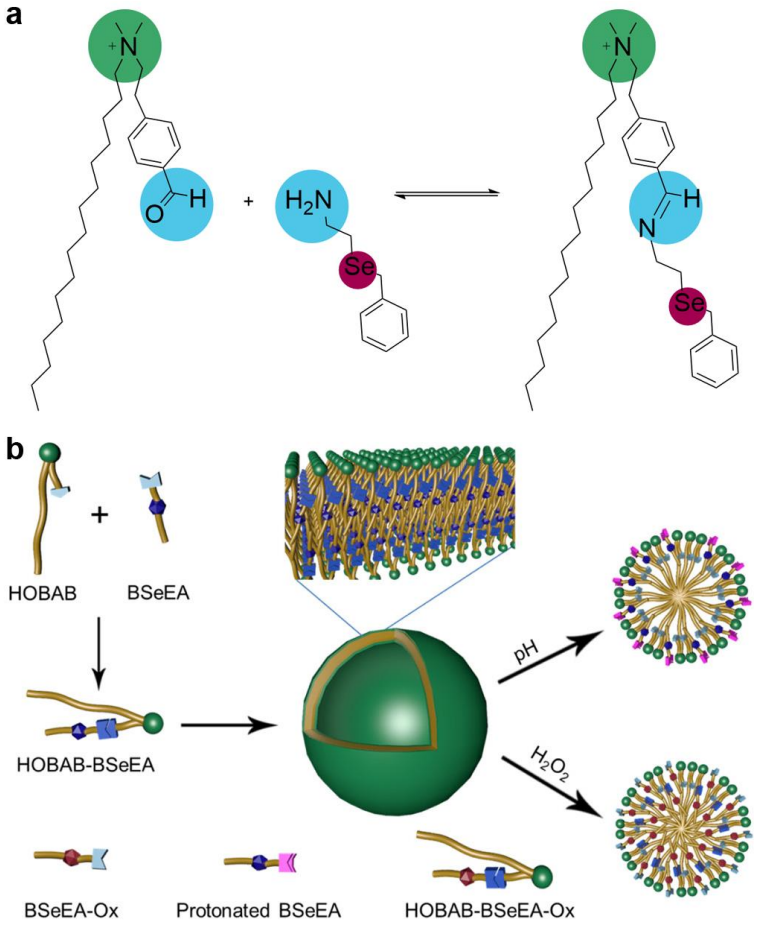
3

1 **Fig. 6.**



2

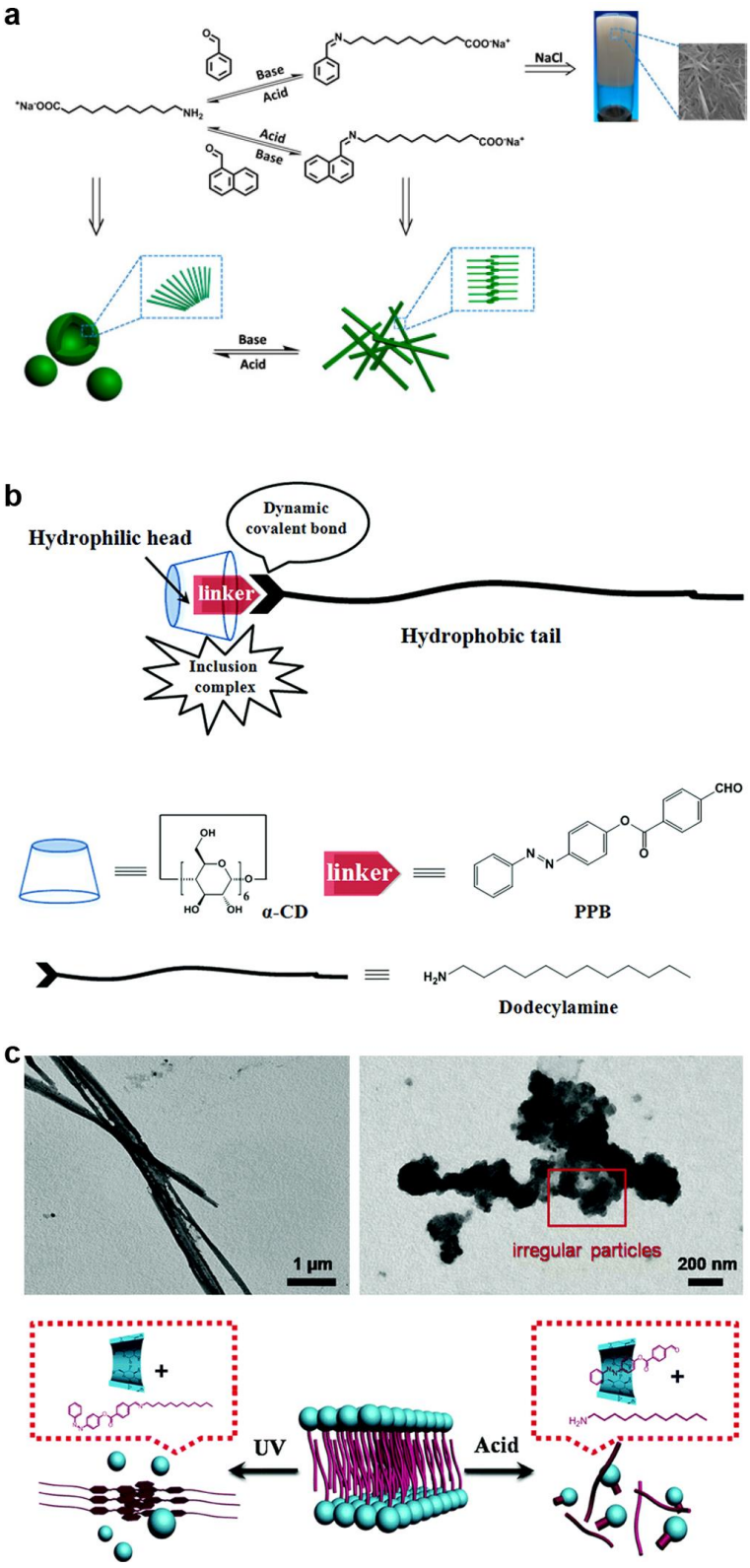
3 **Fig. 7.**



4

5

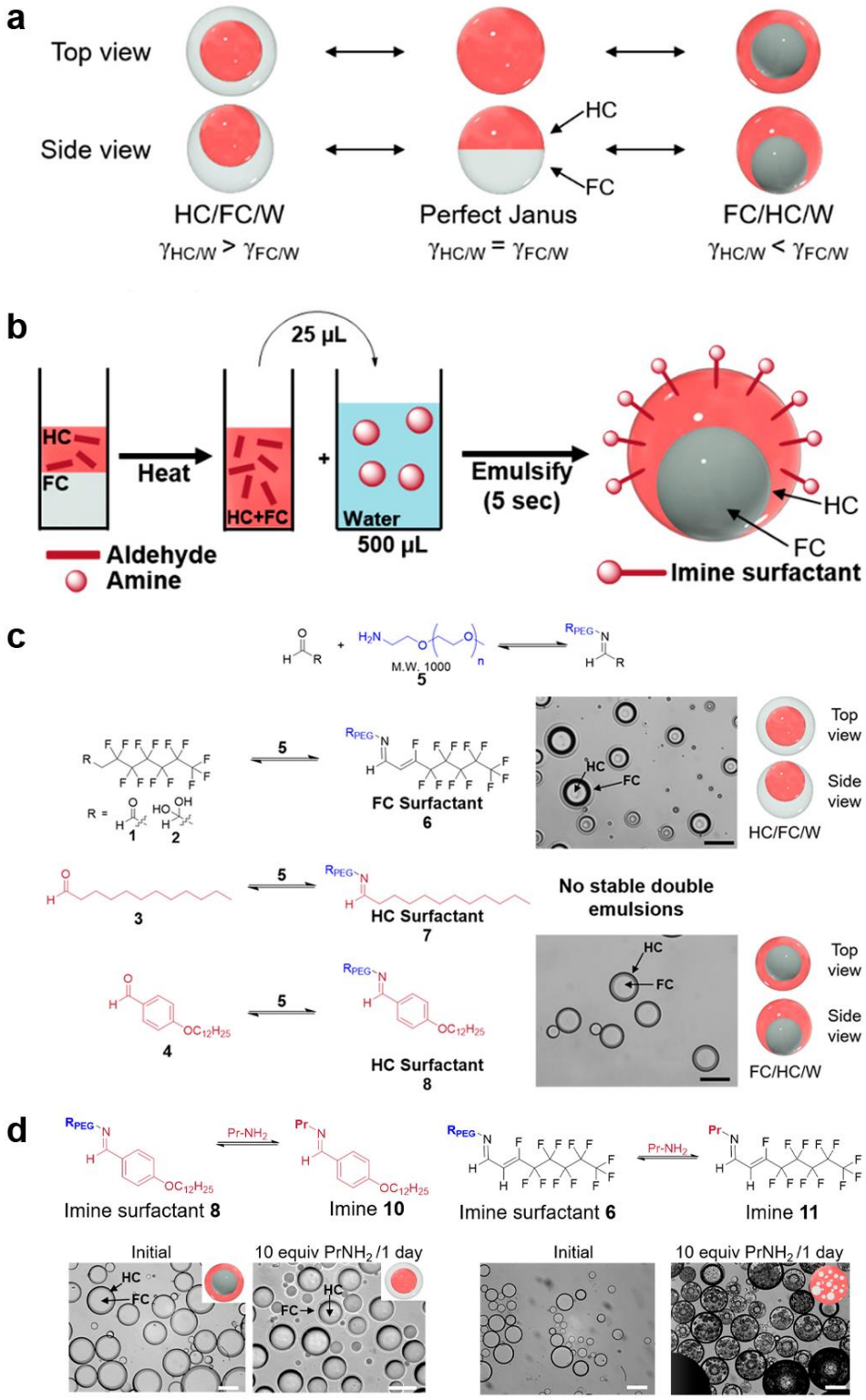
1 **Fig. 8.**


a
Base
Acid
NaCl
Acid
Base
Base
Acid
b
Hydrophilic head
Dynamic covalent bond
linker
Hydrophobic tail
Inclusion complex
α-CD
linker
PPB
Dodecylamine
c
1 μm
irregular particles
200 nm
UV
Acid

2

3

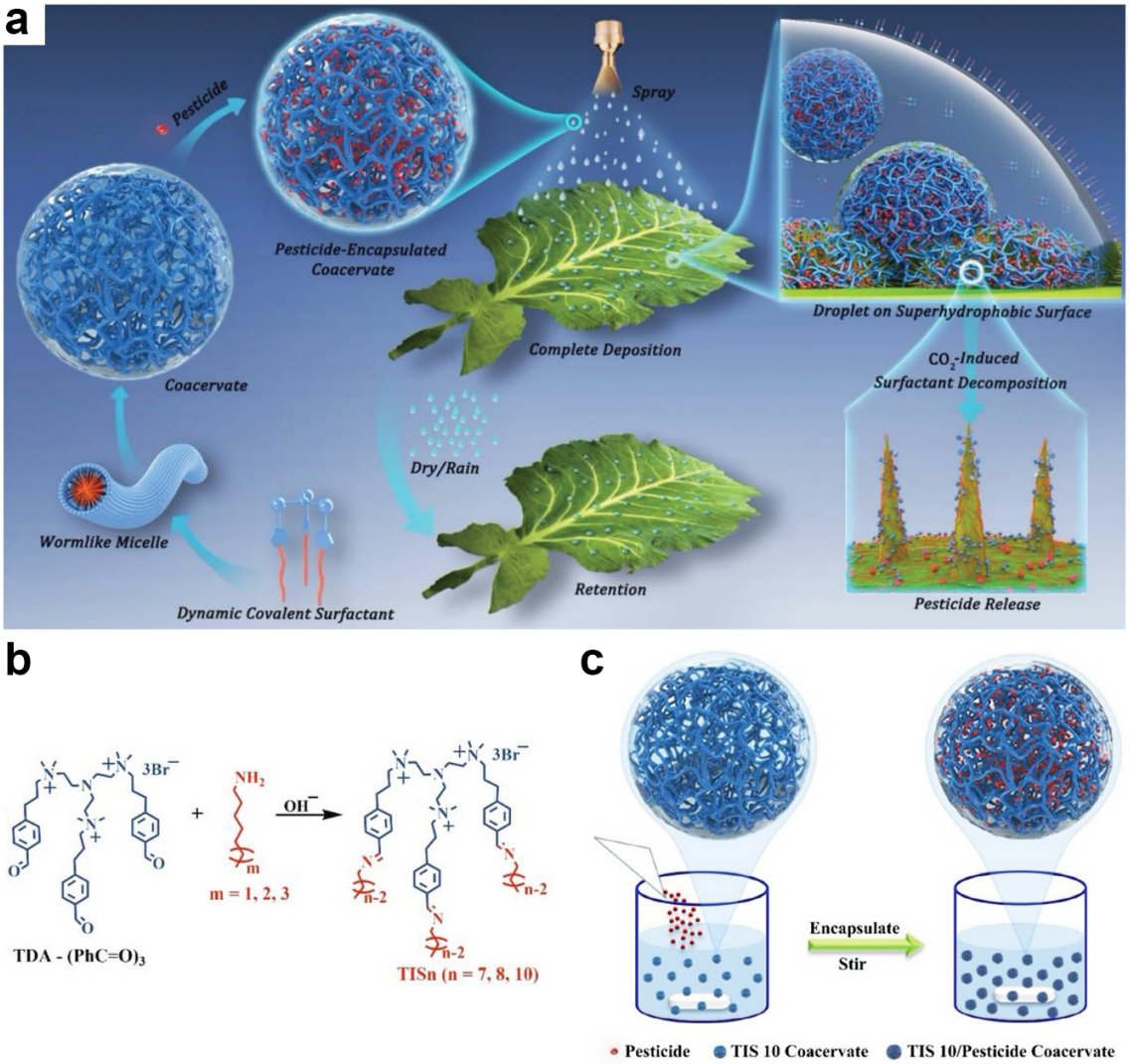
1 **Fig. 9.**


a
Top view
Side view
HC
FC
HC/FC/W
$\gamma_{HC/W} > \gamma_{FC/W}$
Perfect Janus
$\gamma_{HC/W} = \gamma_{FC/W}$
FC/HC/W
$\gamma_{HC/W} < \gamma_{FC/W}$
b
25 µL
HC
FC
Heat
HC+FC
Water
500 µL
Emulsify
(5 sec)
HC
FC
Aldehyde
Amine
Imine surfactant
c
M.W. 1000
5
FC Surfactant
6
Top view
Side view
HC/FC/W
HC Surfactant
7
No stable double emulsions
HC Surfactant
8
FC/HC/W
d
Pr-NH2
Imine surfactant 8
Imine 10
Imine surfactant 6
Imine 11
Initial
10 equiv PrNH2 /1 day
Initial
10 equiv PrNH2 /1 day

2

3

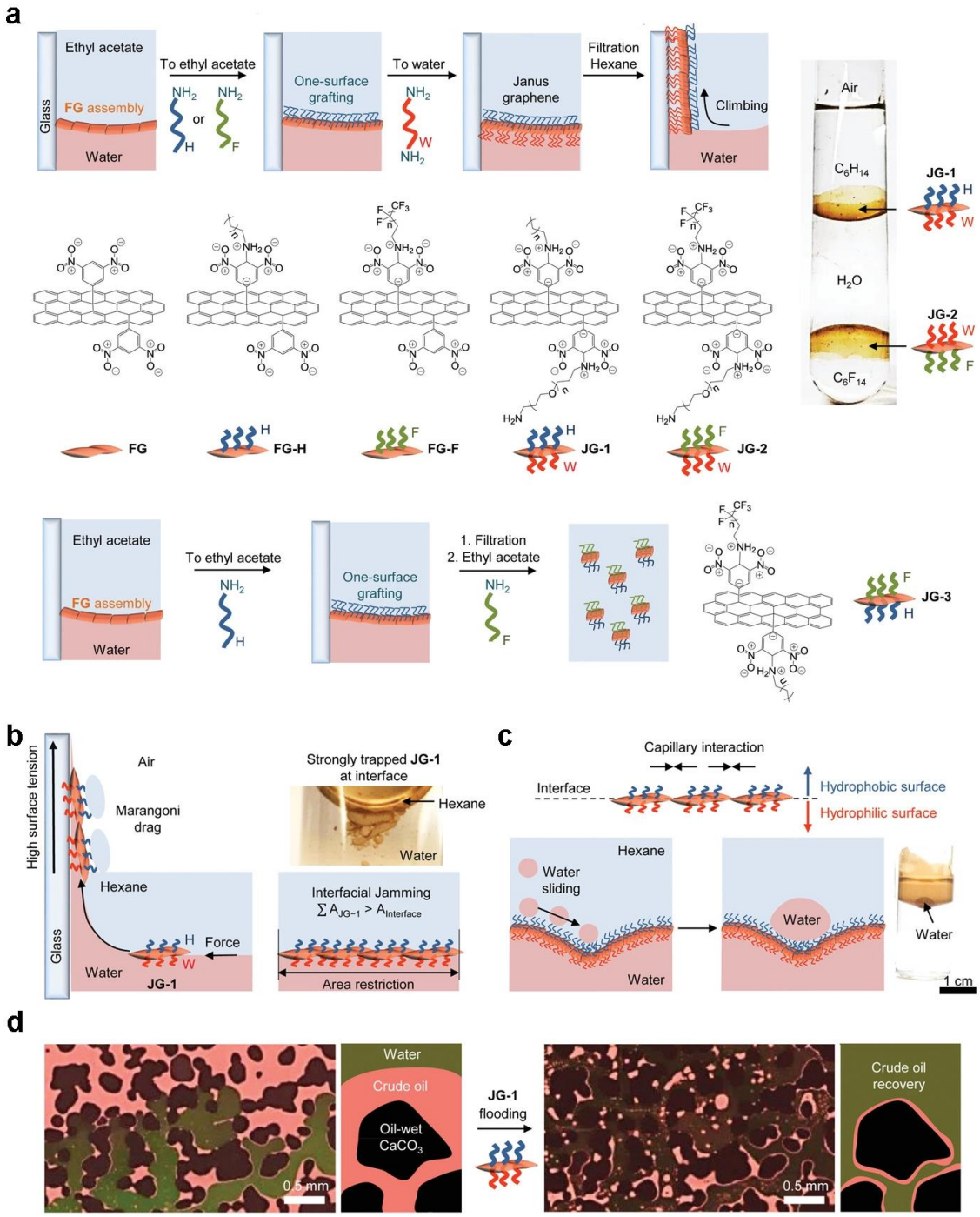
1 **Fig. 10.**


a
Pesticide
Spray
Pesticide-Encapsulated Coacervate
Coacervate
Complete Deposition
Droplet on Superhydrophobic Surface
CO_2-Induced Surfactant Decomposition
Dry/Rain
Wormlike Micelle
Retention
Dynamic Covalent Surfactant
Pesticide Release
b
3Br⁻
NH₂
OH⁻
m = 1, 2, 3
TDA - (PhC=O)₃
TISn (n = 7, 8, 10)
c
Encapsulate
Stir
Pesticide
TIS 10 Coacervate
TIS 10/Pesticide Coacervate

2

3

1 **Fig. 11.**


a
Ethyl acetate
Glass
FG assembly
Water
To ethyl acetate
NH2
or
H
F
One-surface grafting
To water
W
Janus graphene
Filtration
Hexane
Climbing
Air
C6H14
H2O
C6F14
JG-1
JG-2
FG
FG-H
FG-F
JG-3
1. Filtration
2. Ethyl acetate
b
High surface tension
Marangoni drag
Hexane
Force
Strongly trapped JG-1 at interface
Interfacial Jamming
Area restriction
c
Capillary interaction
Interface
Hydrophobic surface
Hydrophilic surface
Water sliding
1 cm
d
Crude oil
Oil-wet CaCO3
0.5 mm
JG-1 flooding
Crude oil recovery

2

3

Scheme 1: Design strategies and principles on dynamic covalent surfactants.