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1 Dynamic Covalent Surfactants and Their Uses in the

2 Development of Smart Materials

3 Fan Min ^{a, b}, Cécile A. Dreiss ^c, Zonglin Chu ^{a, b, *}

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

6 ^b Greater Bay Area Institute for Innovation, Hunan University, Guangzhou 511300, China.

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

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

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

4
5 **KEYWORDS:** Dynamic covalent chemistry, Surfactants, Smart materials, Self-assemblies,
6 Reverse emulsification.

8 **1. Introduction**

9 Surfactants are amphiphilic organic compounds with both a hydrophobic (usually alkyl chain)
10 tail and a hydrophilic head (either a charged or noncharged water-soluble moiety) present on the
11 same molecule (Fig. 1a) [1]. They play an important role in nearly every aspect of our lives from
12 the moment we are born [2]. With the first successful breath at birth, pulmonary surfactants in
13 the lungs thin out the alveolar membrane and increase the surface of the alveoli for gas exchange
14 [3, 4]. They act as powerful cleaners for washing dishes, laundry, cleansing our faces, and so on
15 [5]. They are used in an array of cleaning products for their ability to lower water's surface
16 tension, in essence making the molecules more “slippery”, preventing them from sticking
17 together, and promoting interaction with oil and grease. They are key additives in lubricants [6],
18 inks [7], anti-fogging liquids [8], herbicides [9], adhesives [10], emulsifiers [11, 12], and fabric
19 softeners [13]. From a basic research point of view, they are frequently adopted as templates in
20 creating nanoparticles [14] and mesoporous materials [15], micellar catalysts in organic synthesis
21 [16], smart carrier vehicles for drug delivery [17], and even used as models to understand

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

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

10 Surfactants are able to organize themselves into various micellar structures: wormlike,
11 vesicular, disk-shaped, or spherical, dependent on the molecular structure of the surfactant as
12 well as the bulk aqueous environment [1]. Using the principle of the "critical packing" parameter
13 p developed by Israelachvili [21], it is possible to predict the shape of self-assembled aggregates
14 based on the effective volume and maximum length of the hydrophobic tail (represented by " v "
15 and " l ", respectively) as well as the effective surface area per molecule (" a_0 ") of the surfactants
16 that make up the aggregate, or the area per molecule at the interface between the surfactants and
17 water: $p = v/a_0l$. When the ratio is less than one-third, spherical aggregates tend to form, while
18 wormlike micelles are formed with ratios between one-third and one-half, and lamellar structures
19 are observed when the ratio equals one (Fig. 1b). p is primarily influenced by the structure of the
20 surfactant molecule and is also affected by the solution environment: it arises from an intricate
21 interplay between surfactant chemical architecture and external factors, such as concentration of
22 surfactant, and solution pH, temperature, salinity, etc. [22].

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

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

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

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

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

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

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

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

7 2.1. Reversible switch between self-assemblies and building block molecules

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

13 2.1.1 Switch between spherical micelles and building block molecules

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

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

9 Fluorescence emission spectroscopy was employed to investigate the demicellization induced
10 by a reduction in pH, using the imine bearing a heptyl tail as a model surfactant and Nile Red as
11 a fluorescent indicator of hydrophobicity. In buffer, the emission of Nile Red was recorded at
12 654 nm; however, a blue-shifted peak of 645 nm was detected upon addition of the surfactant at
13 concentrations above the CMC. This indicated that Nile Red became encapsulated within the
14 micelles' interior, surrounded by a predominantly hydrophobic milieu. Upon titration with acid,
15 the imine micelles underwent dissociation, leading to a red-shifted fluorescence, which resulted
16 from the liberation of Nile Red from the hydrophobic region inside the micelles (Fig. 2b). The
17 demicellization process was fully reversible, allowing the system to transition between spherical
18 micelles and dissociated building blocks by a straightforward adjustment of the pH of the
19 solution (Fig. 2c). The switchable demicellization and micellization could also be accomplished
20 by increasing and decreasing the temperature, respectively.

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

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

5 The same group also developed H-shaped bola-type DCSs (Fig. 3c) by binding two bolaform
6 amphiphiles (each bearing an aldehyde group in the centre) with one spacer (bearing one amino
7 group in each end) through the formation of one dynamic benzoic imine bond in both terminals
8 [34]. Compared with the former studies, these DCSs show a lower CMC and are more sensitive
9 to pH changes, i.e., the reversible disassembly process can be achieved by tuning the pH from
10 basic to slightly acidic. Measurements of the surface tension isotherms for H-shaped DCSs
11 featuring varying spacers suggest a “twisted” molecular arrangement at the interface between air
12 and water. This study on H-shaped DCSs enriches the repertoire of DCSs and their unique pH-
13 responsiveness holds potential for applications for targeted drug delivery in biological
14 environments.

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

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

10 2.1.2. Reversible switch between wormlike micelles and building block molecules

11 Wormlike micelles (WLMs) are elongated and flexible structures that arise from the
12 spontaneous organization of surfactant molecules in aqueous solutions [37]. When the surfactant
13 concentration surpasses a critical threshold known as the overlapping concentration (C^*), WLMs
14 become entangled in a constantly breaking and reforming dynamic reversible network, earning
15 them the descriptors of "living" or "equilibrium" polymers. The intertwining of WLMs gives the
16 solution exceptional viscoelastic properties, crucial to many industrial and technological sectors
17 like enhanced oil recovery, rheology control, drag reduction, personal care, and everyday uses
18 [38].

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

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

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

23 2.1.3. Reversible switch between vesicles and building block molecules

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

7 Cationic surfactant was synthesized in situ from the water-soluble reactants via reversible
8 imine bond generation. One can expect that both single-tailed AB_1 and double-tailed AB_2
9 surfactants are obtained, which exists in dynamic equilibrium with each other and with the
10 precursors (Fig. 5b). After mixing the precursors as aqueous solution, vesicles formed within
11 minutes, verified via increased scattering intensity, and an accompanying blue-shifted emission
12 of Nile Red, implying the formation of hydrophobic regions. The morphology of micellar
13 aggregates was studied by cryo-transmission electron microscopy (Cryo-TEM) and confocal
14 laser scanning microscopy (CLSM). CLSM analysis unveiled vesicles varying in size from 2 to 5
15 μm , while Cryo-TEM observations showed the existence of unilamellar vesicles measuring 50 to
16 100 nm. In fact, dynamic light scattering (DLS) measurements displayed a bimodal distribution
17 with hydrodynamic sizes of (95 ± 11) nm and (5.2 ± 1.6) μm . As the vesicles form through the
18 reversible interaction between their non-amphiphilic reactants, it is anticipated that an alteration
19 in the relative abundance of imine products will induce a rapid response of the vesicle bilayer.
20 The authors demonstrated the tuning of the vesicle formation by controlling solution
21 concentration and pH.

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

1 exceptionally slow rate. The dynamic surfactants undergo dissociation as a consequence of
2 dilution-induced reduction in the concentration of the surfactant precursors within the bulk. Due
3 to the slow transition rates between AB₂ monomers and the self-assembled bilayer, it seems
4 likely that AB₂ within the bilayer initially revert back to the starting agent. Subsequently, the
5 freed surfactant precursors diffuse out from the bilayer, potentially starting with those in the
6 outermost layer. Therefore, the stability of the bilayer may experience a further decline due to a
7 greater disparity between the outer and inner layers, resulting in increased permeability, and
8 ultimately shrinkage of the vesicles. Alternatively, reversible formation of the vesicles can also
9 be realized by modulation of the pH. The stability of the vesicles was observed to persist up to a
10 pH of 7.1 ± 0.2 , as confirmed by fluorescence spectroscopy and DLS. However, upon decreasing
11 pH values to 4 and below the vesicles dissociated completely. It is worth noting that the
12 dissociation of vesicles is entirely reversible, as verified by a notable rise in scattering as well as
13 the restoration of the initial vesicle diameter while tuning the solution back to an alkaline
14 environment.

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

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

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

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

9 2.2. Reversible switch between different types of self-assemblies

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

15 2.2.1. Reversible switch between wormlike micelles and spherical micelles

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

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

6 2.2.2. Reversible switch between spherical micelles and vesicles

7 Chen et al. [45] prepared pH-responsive vesicles from a mixture of 1-methyl-3-(10-(4-formyl-
8 phenoxy) decyl) imidazolium (FDI) or 1-(10-(4-formyl-phenoxy) decyl)-pyridinium (FDP) with
9 1-octyl amine under basic conditions in equal proportions. The micellar structures and
10 morphologies were examined using TEM with the sample prepared through freeze-fracture or
11 negative staining. Dynamic covalent surfactants from amine in the presence of FDP and FDI
12 yielded spherical unilamellar vesicles, measuring 71 and 107 nm in diameter, respectively. The
13 vesicles demonstrated their ability to encapsulate Nile Red and rapidly release it at low pH. The
14 evolution of the supra-amphiphile composition was tracked through ^1H NMR and fluorescence
15 spectroscopic assays, revealing superior CMC values and aldehyde conversion yields for the
16 FDI-derived products over those generated from FDP. The advantages of ease of formation,
17 quick dissociation, and changeable morphologies make such systems ideal candidates for the
18 construction of advanced smart supra-amphiphile systems which could potentially be used in
19 controlled drug delivery.

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

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

15 2.2.3. Reversible switch between wormlike micelles and vesicles

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

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

6 2.2.4. Reversible switch between vesicles and nanofibers

7 Hao's team [48] developed a fascinating type of self-assembled system relying on dynamic
8 covalent bonds in which the micellar aggregates can be reversibly controlled between vesicles
9 and nanofibers (Fig. 8a). Under alkaline conditions, the aldehyde group in benzaldehyde (BA) or
10 1-naphthaldehyde (NA) can react with the amine group in 11-aminoundecanoic acid (AUA) to
11 produce a small organic building block concurrently triggering a morphological shift from
12 vesicles to nanofibers. At neutral pH, the dynamic covalent imine bonds can be hydrolyzed,
13 leading to the dissociation of the nanofibers and appearance of vesicular aggregates. The
14 transition was reversible as fibers reappeared as the pH was reverted to basic condition. Besides,
15 reversible control over the hydrogel state was achieved via nanofiber assembly. By introducing
16 NaCl, which substantially increases nanofiber density and the number of cross-links, a free-
17 standing gel was induced to form from a previously flowable solution of nanofibers; the gel
18 obtained was confirmed to be pH-switchable.

19 In order to create a novel supramolecular structure with multi-stimuli responsiveness, Li et al.
20 [49] developed the strategy of connecting the hydrophilic and hydrophobic components together
21 with a bi-functional linker utilizing more than one type of interaction, namely, the creation of a
22 dynamic inclusion complex between azobenzene and α -cyclodextrins (α -CD) bearing an
23 aldehyde moiety, as well as in situ-generated dynamic imine bonds between the dodecylamine

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

8 **3. Dynamic covalent surfactants for reversible emulsification**

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

14 **3.1. pH-switchable emulsions**

15 Researchers have devoted great efforts to the development of smart emulsions that react to
16 external stimuli like light [50], temperature [51], pH [52], magnetic field [53], redox reactions
17 [54], etc. The introduction of stimulus-responsive properties to emulsions not only enables
18 controlled demulsification but also allows the retrieval and reuse of the emulsifiers. Amongst the
19 various triggers utilized towards controllable emulsification/demulsification, pH is the most
20 facile and economical trigger, with great potential for industrial uses.

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

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

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

15 3.2. pH-switchable Pickering and non-Pickering emulsions

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

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

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

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

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

3 3.3. pH-switchable double emulsions

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

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

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

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

20 **4. Other functions of dynamic covalent surfactants**

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

1 4.1 Functional perfumery

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

17 4.2 Agrochemicals

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

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

6 Jiang and coworkers [65] have developed a comprehensive strategy grounded in a precise
7 design for the entire pesticide application process, which would significantly improve pesticide
8 efficiency. To enhance encapsulation, adhesion, sustained retention, and controlled release on
9 hydrophobic plant surfaces, they designed a water-based coacervate with dynamic covalent
10 trimers acting as surfactants. The coacervate composed of nanoscale networks of wormlike
11 micelles and large amounts of water fixed by the nanonetwork, accounts for an effective
12 encapsulation of pesticide molecules (Fig. 10). Moreover, the network structures interact with
13 superhydrophobic plant micro/nanosurfaces, which enables the complete deposition of the
14 pesticides on super-repellent plants following high-speed contact and prevention of
15 wind/rainwater washing. In addition, this green pesticide formula possesses characteristics of
16 CO₂-triggered release: CO₂ induces the degradation of the surfactant and thereby the precise
17 release of the pesticides. This innovative pesticide formulation based on these dynamic
18 coacervates paves the way to advanced pesticide applications and will likely contribute to
19 promoting a more sustainable agriculture.

20 4.3 Orthogonal functionalization of graphene

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

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

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

1 and/ or amphiphobic fluorocarbon chain can be accomplished in a controllable manner (Fig.
2 11a). Furthermore, the connections between 3,5-dinitrophenyl groups and amines involve
3 reversible covalent bonds formation via Meisenheimer complexes.

4 When the FGs are assembled at an oil/water interface, they can react with NH₂-bearing species
5 that are solubilized in the corresponding oil and water phases, offering an opportunity for the
6 asymmetric functionalization of FG. For instance, n-octylamine (H) or 1H,1H,2H,2H-
7 perfluorooctylamine (F) solubilized in ethyl acetate can react with FG from the upper side of the
8 oil/water interface, leading to the fabrication of 2D graphenes bearing hydrophobic tails (H-chain
9 or F-chain) in one side (H-FG or H-FG). Subsequently, water-soluble 4,7,10-trioxa-1,13-
10 tridecanediamine (W) reacted with the H-FG or H-FG from the lower side. Finally, amphiphilic
11 Janus 2D graphene (H-FG-W or F-FG-W), bearing hydrophobic hydrocarbon-chain or
12 fluorocarbon-chain on one face and hydrophilic moieties on the reverse, was generated (Fig.
13 11a). Propelled by Marangoni force, the hydrophilic side of the amphiphilic Janus 2D graphene
14 moved up the hydrophilic wall of a glass vial (covered by a thin water layer) and spread its
15 hydrophobic side in nonpolar solvents such as hexane (Fig. 11b). Interestingly, nearly all H-FG-
16 W and F-FG-W remained at the interface, demonstrating strong adsorption of such graphenes at
17 interfaces. Similarly, amphiphilic Janus 2D graphenes hydrocarbon-chain on one side and
18 fluorocarbon-chain on the other (H-FG-F) can also be produced. The asymmetrical
19 functionalities on the two different sides of the 2D graphene nanosheets created novel 2D
20 nanostructured “super-surfactants” that are very interesting for interfacial applications. These
21 “super-surfactants” featuring two chemically different sections display excellent performance at
22 oil/water interfaces.

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

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

15 **5. Conclusions**

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

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

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

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

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

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

9

10 **CRedit authorship contribution statement**

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

13

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18 **References**

19

20 [1] Chu Z, Dreiss CA, Feng Y. Smart wormlike micelles. *Chem Soc Rev* 2013;42:7174-203.

21 [2] Chakraborty M, Kotecha S. Pulmonary surfactant in newborn infants and children. *Breathe*
22 2013;9:476-88.

23 [3] Halliday HL. Surfactants: past, present and future. *J Perinatol* 2008;28:S47-S56.

- 1 [4] Stachowicz-Kuśnierz A, Korchowiec B, Rogalska E, Korchowiec J. The lung surfactant
2 activity probed with molecular dynamics simulations. *Adv Colloid Interface Sci*
3 2022;304:102659.
- 4 [5] Seweryn A. Interactions between surfactants and the skin – theory and practice. *Adv Colloid*
5 *Interface Sci* 2018;256:242-55.
- 6 [6] Peng Y, Hu Y, Wang H. Tribological behaviors of surfactant-functionalized carbon
7 nanotubes as lubricant additive in water. *Tribol Lett* 2007;25:247-53.
- 8 [7] Liu ZX, Chen AP, Qian JJ, Shen H. Effect of surfactant on the properties of gel ink.
9 *Advanced Materials Research* 2009;66:143-6.
- 10 [8] Lee Y, Chung Y-W, Park J, Park K, Seo Y, Hong S-N, et al. Lubricant-infused directly
11 engraved nano-microstructures for mechanically durable endoscope lens with anti-
12 biofouling and anti-fogging properties. *Sci Rep* 2020;10:17454.
- 13 [9] Sieverding E, Humble GD, Fleute-Schlachter I. A new herbicide adjuvant based on a non-
14 super spreading trisiloxane surfactant. *J Plant Dis Protect* 2006:2005-11.
- 15 [10] Brandão R, Borges CSP, Marques EAS, Carbas RJC, Akhavan-Safar A, Nunes PDP, et al.
16 Effect of surfactant contamination on the properties of aluminum/silicone adhesive joints.
17 *Mech Adv Mater Struct* 2023;30:1875-88.
- 18 [11] Zarzar LD, Sresht V, Sletten EM, Kalow JA, Blankschtein D, Swager TM. Dynamically
19 reconfigurable complex emulsions via tunable interfacial tensions. *Nature* 2015;518:520-4.
- 20 [12] Hosseinpour S, Götz V, Peukert W. Effect of surfactants on the molecular structure of the
21 buried oil/water interface. *Angew Chem Int Ed* 2021;60:25143-50.

- 1 [13] Oikonomou EK, Christov N, Cristobal G, Bourgaux C, Heux L, Boucenna I, et al. Design of
2 eco-friendly fabric softeners: structure, rheology and interaction with cellulose nanocrystals.
3 *J Colloid Interface Sci* 2018;525:206-15.
- 4 [14] Guerrero-Martínez A, Pérez-Juste J, Carbó-Argibay E, Tardajos G, Liz-Marzán LM.
5 Gemini-surfactant-directed self-assembly of monodisperse gold nanorods into standing
6 superlattices. *Angew Chem Int Ed* 2009;48:9484-8.
- 7 [15] Tsai C-H, Vivero-Escoto JL, Slowing II, Fang IJ, Trewyn BG, Lin VSY. Surfactant-assisted
8 controlled release of hydrophobic drugs using anionic surfactant templated mesoporous
9 silica nanoparticles. *Biomaterials* 2011;32:6234-44.
- 10 [16] Huang X, Dong Z, Liu J, Mao S, Xu J, Luo G, et al. Selenium-mediated micellar catalyst:
11 an efficient enzyme model for glutathione peroxidase-like catalysis. *Langmuir*
12 2007;23:1518-22.
- 13 [17] Rajera R, Nagpal K, Singh SK, Mishra DN. Niosomes: A controlled and novel drug
14 delivery system. *Biol Pharm Bull* 2011;34:945-53.
- 15 [18] Hill JP, Shrestha LK, Ishihara S, Ji Q, Ariga K. Self-assembly: from amphiphiles to
16 chromophores and beyond. *Molecules* 2014;19:8589-609.
- 17 [19] Hoffmann H. Fascinating phenomena in surfactant chemistry. *Adv Mater* 1994;6:116-29.
- 18 [20] Fisher LR, Oakenfull DG. Micelles in aqueous solution. *Chem Soc Rev* 1977;6:25-42.
- 19 [21] Israelachvili JN. Intermolecular and surfaces forces: Academic Press, London, 2nd edition;
20 1992.
- 21 [22] Oda R. Safin gels with amphiphilic molecules. In: Weiss RG, Terech P (eds). *Molecular*
22 *gels: materials with self-assembled fibrillar networks*. Springer, Dordrecht, 2006; pp 577–
23 609.

- 1 [23] Rowan SJ, Cantrill SJ, Cousins GRL, Sanders JKM, Stoddart JF. Dynamic covalent
2 chemistry. *Angew Chem Int Ed* 2002;41:898-952.
- 3 [24] Zheng N, Xu Y, Zhao Q, Xie T. Dynamic covalent polymer networks: a molecular platform
4 for designing functions beyond chemical recycling and self-healing. *Chem Rev*
5 2021;121:1716-45.
- 6 [25] Jin Y, Yu C, Denman RJ, Zhang W. Recent advances in dynamic covalent chemistry. *Chem*
7 *Soc Rev* 2013;42:6634-54.
- 8 [26] Zhang W, Chen L, Dai S, Zhao C, Ma C, Wei L, et al. Reconstructed covalent organic
9 frameworks. *Nature* 2022;604:72-9.
- 10 [27] Belowich ME, Stoddart JF. Dynamic imine chemistry. *Chem Soc Rev* 2012;41:2003-24.
- 11 [28] Corbett PT, Leclaire J, Vial L, West KR, Wietor J-L, Sanders JKM, et al. Dynamic
12 combinatorial chemistry. *Chem Rev* 2006;106:3652-711.
- 13 [29] Schaufelberger F, Timmer BJJ, Ramström O. Principles of dynamic covalent chemistry. In:
14 Zhang W, Jin Y (eds). *Dynamic covalent chemistry*. Weinheim:Wiley-VCH, 2017. p. 1-30.
- 15 [30] Zhang D-W, Li Z-T. Orthogonal dynamic covalent and non-covalent reactions. In: Zhang
16 W, Jin Y (eds). *Dynamic covalent chemistry*. Weinheim:Wiley-VCH, 2017. p. 207-51.
- 17 [31] Minkenberg CB, Florusse L, Eelkema R, Koper GJM, van Esch JH. Triggered self-assembly
18 of simple dynamic covalent surfactants. *J Am Chem Soc* 2009;131:11274-5.
- 19 [32] Wang G, Wang C, Wang Z, Zhang X. Bolaform superamphiphile based on a dynamic
20 covalent bond and its self-assembly in water. *Langmuir* 2011;27:12375-80.
- 21 [33] Wang G, Wu G, Wang Z, Zhang X. Asymmetric and symmetric bolaform supra-
22 amphiphiles: formation of imine bond influenced by aggregation. *Langmuir* 2014;30:1531-
23 5.

- 1 [34] Wang G, Wang C, Wang Z, Zhang X. H-shaped supra-amphiphiles based on a dynamic
2 covalent bond. *Langmuir* 2012;28:14567-72.
- 3 [35] Zhao W, Wang H, Wang Y. Coacervation of dynamic covalent surfactants with
4 polyacrylamides: properties and applications. *Soft Matter* 2018;14:4178-84.
- 5 [36] Sun P, Lu F, Wu A, Yin Y, Shi L, Zheng L. Construction of pH-responsive supramolecular
6 assemblies based on dynamic covalent bonds for tunable drug release. *J Surfactants Deterg*
7 2018;21:593-600.
- 8 [37] Chu Z, Feng Y, Su X, Han Y. Wormlike micelles and solution properties of a C22-tailed
9 amidosulfobetaine surfactant. *Langmuir* 2010;26:7783-91.
- 10 [38] Chu Z, Feng Y, Sun H, Li Z, Song X, Han Y, et al. Aging mechanism of unsaturated long-
11 chain amidosulfobetaine worm fluids at high temperature. *Soft Matter* 2011;7:4485-9.
- 12 [39] Minkenberg CB, Homan B, Boekhoven J, Norder B, Koper GJM, Eelkema R, et al.
13 Responsive wormlike micelles from dynamic covalent surfactants. *Langmuir*
14 2012;28:13570-6.
- 15 [40] Wang P, Zhu T, Hou X, Zhao Y, Zhang X, Wang T, et al. Responsive wormlike micelle
16 with pH-induced transition of hydrotrope based on dynamic covalent bond. *J Mol Liq*
17 2019;286:110935.
- 18 [41] Minkenberg CB, Li F, van Rijn P, Florusse L, Boekhoven J, Stuart MCA, et al. Responsive
19 vesicles from dynamic covalent surfactants. *Angew Chem Int Ed* 2011;50:3421-4.
- 20 [42] Nguyen R, Allouche L, Buhler E, Giuseppone N. Dynamic combinatorial evolution within
21 self-replicating supramolecular assemblies. *Angew Chem Int Ed* 2009;48:1093-6.

- 1 [43] Wu X, Chen X-X, Zhang M, Li Z, Gale PA, Jiang Y-B. Self-assembly of a “double dynamic
2 covalent” amphiphile featuring a glucose-responsive imine bond. *Chem Commun*
3 2016;52:6981-4.
- 4 [44] Kang X, Kang W, Yang H, Hou X, Zhu T, Wang P, et al. pH-responsive aggregates
5 transition from spherical micelles to WLMs induced by hydrotropes based on the dynamic
6 imine bond. *Soft Matter* 2020;16:9705-11.
- 7 [45] Wang J, Chen X, Cui W, Yi S. pH-responsive vesicles from supra-amphiphiles based on
8 dynamic imine bond. *Colloids Surf A* 2015;484:28-36.
- 9 [46] Lu P, He S, Zhou Y, Zhang Y. Oxidation-induced breakage of the imine bond and aggregate
10 transition in a Se-containing dynamic covalent surfactant. *Langmuir* 2021;37:2833-42.
- 11 [47] Wang P, Zhu T, Hou X, Zhao Y, Zhang X, Yang H, et al. Responsive morphology transition
12 from micelles to vesicles based on dynamic covalent surfactants. *Soft Matter* 2019;15:2703-
13 10.
- 14 [48] Wang Y, Xing P, Li S, Ma M, Yang M, Zhang Y, et al. Facile stimuli-responsive
15 transformation of vesicle to nanofiber to supramolecular gel via ω -amino acid-based
16 dynamic covalent chemistry. *Langmuir* 2016;32:10705-11.
- 17 [49] Li S, Hao A, Shen J, Shang N, Wang C. UV and pH-responsive supra-amphiphiles driven
18 by combined interactions for controlled self-assembly behaviors. *Soft Matter* 2018;14:2112-
19 7.
- 20 [50] Li Z, Shi Y, Zhu A, Zhao Y, Wang H, Binks BP, et al. Light-responsive, reversible
21 emulsification and demulsification of oil-in-water Pickering emulsions for catalysis. *Angew*
22 *Chem Int Ed* 2021;60:3928-33.

- 1 [51] Rajbanshi A, da Silva MA, Murnane D, Porcar L, Dreiss CA, Cook MT. Polymer
2 architecture dictates thermoreversible gelation in engineered emulsions stabilised with
3 branched copolymer surfactants. *Polym Chem* 2022;13:5730-44.
- 4 [52] Wu H, Chen X, Tan R, Luo Y, Hu Y, Li Y, et al. Controllable regulation of emulsion
5 stability by a pH-responsive zwitterionic/anionic surfactant system. *Fuel* 2022;312:122921.
- 6 [53] Zhang H, Ge L, Ding C, Guo R. Magnetic response Janus emulsions stabilized by Mangeto-
7 surfactant. *J Mol Liq* 2022;349:118416.
- 8 [54] Zhu P, Liu D, Dai S, Wang B, Lu H, Huang Z. Redox and pH dual-responsive emulsion
9 using ferrocenecarboxylic acid and N,N-dimethyldodecylamine. *Langmuir* 2020;36:2368-
10 74.
- 11 [55] Ren G, Wang L, Chen Q, Xu Z, Xu J, Sun D. pH switchable emulsions based on dynamic
12 covalent surfactants. *Langmuir* 2017;33:3040-6.
- 13 [56] Ren G, Li B, Ren L, Lu D, Zhang P, Tian L, et al. pH-responsive nanoemulsions based on a
14 dynamic covalent surfactant. *Nanomaterials* 2021;11:1390.
- 15 [57] Pickering SU. CXCVI.—Emulsions. *J Chem Soc Trans* 1907;91:2001-21.
- 16 [58] Binks BP, Rodrigues JA, Frith WJ. Synergistic interaction in emulsions stabilized by a
17 mixture of silica nanoparticles and cationic surfactant. *Langmuir* 2007;23:3626-36.
- 18 [59] Frelichowska J, Bolzinger M-A, Chevalier Y. Effects of solid particle content on properties
19 of o/w Pickering emulsions. *J Colloid Interface Sci* 2010;351:348-56.
- 20 [60] Liu P, Wu J, Pei X, Cui Z, Jiang J, Song B, et al. Recyclable surfactant containing a
21 dynamic covalent bond and relevant smart emulsions. *Green Chem* 2022;24:7612-21.
- 22 [61] Zhang Y, Lu H, Wang B, Wang N, Liu D. pH-responsive non-Pickering emulsion stabilized
23 by dynamic covalent bond surfactants and nano-SiO₂ particles. *Langmuir* 2020;36:15230-9.

- 1 [62] Zentner CA, Anson F, Thayumanavan S, Swager TM. Dynamic imine chemistry at complex
2 double emulsion interfaces. *J Am Chem Soc* 2019;141:18048-55.
- 3 [63] Tchakalova V, Lutz E, Lambolely S, Moulin E, Benczédi D, Giuseppone N, et al. Design of
4 stimuli-responsive dynamic covalent delivery systems for volatile compounds (part 2):
5 fragrance-releasing cleavable surfactants in functional perfumery applications. *Chem Eur J*
6 2021;27:13468-76.
- 7 [64] Lamberth C, Jeanmart S, Luksch T, Plant A. Current challenges and trends in the discovery
8 of agrochemicals. *Science* 2013;341:742-6.
- 9 [65] Liu B, Fan Y, Li H, Zhao W, Luo S, Wang H, et al. Control the entire journey of pesticide
10 application on superhydrophobic plant surface by dynamic covalent trimeric surfactant
11 coacervation. *Adv Funct Mater* 2021;31:2006606.
- 12 [66] Jeon I, Peeks MD, Savagatrup S, Zeininger L, Chang S, Thomas G, et al. Janus graphene:
13 scalable self-assembly and solution-phase orthogonal functionalization. *Adv Mater*
14 2019;31:1900438.

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17 **Fig. 1.** Model and examples of surfactants: sodium undecyl (anionic surfactants),
18 sulfatehexadecyltrimethylammonium bromide (cationic surfactants), *N*-Dodecyl-*N,N*-dimethyl-
19 3-ammonio-1-propanesulfonate (amphoteric surfactants), D-Glucitol (non-ionic surfactants) (a).
20 Relationship between the packing parameter p and the morphology of surfactant aggregates (b).
21 Free energy profiles illustrating kinetically (left) and thermodynamically (right) controlled
22 reactions (c). Schematic illustration of dynamic covalent chemistry (DCC) and a typical type of
23 DCC based on dynamic imine bonds (d). Fig. 1b is reprinted with permission from ref 1.

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2 2002 WILEY-VCH Verlag GmbH, Weinheim, Fed. Rep. of Germany.

3 **Fig. 2.** Reversible spherical micelles formed by a dynamic imine surfactant. Dynamic formation
4 of imine surfactants and spherical micelles based on water-soluble nonamphiphilic precursors of
5 short-chain alkylamines and an aromatic aldehyde bearing a cationic ammonium bromide group
6 (a). The dependency of Nile Red maximum emission wavelength on pH (b). pH-reversible Nile
7 Red encapsulation (c). Fig. 2b and 2c are reproduced with permission from ref. 28. Copyright ©
8 2009 American Chemical Society.

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

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

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

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2 reproduced with permission from ref. 39. Copyright © 2009 WILEY-VCH Verlag GmbH & Co.
3 KGaA, Weinheim.

4 **Fig. 6.** The proposed mechanism suggests aggregation of amphiphiles synthesized in-situ
5 triggered by glucose, involving the formation of 2 orthogonal dynamic covalent bonds. Reprinted
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7 **Fig. 7.** Diagram illustrating the responsive properties of the Se-containing dynamic covalent
8 surfactant (a) and its assemblies in response to redox and pH stimuli (b). Fig. 7b is reproduced
9 with permission from ref. 43. Copyright © 2021 American Chemical Society.

10 **Fig. 8.** Dynamic covalent surfactants formed by benzaldehyde (BA) or 1-naphthaledhyde (NA)
11 with 11-aminoundecanoic acid (AUA) and the morphological transformation from vesicles to
12 nanofibers controlled by pH (a). Schematic illustration of the chemical structures of the
13 components and the formation of the supramolecular amphiphile PPBI (b). TEM images and
14 schematic representation of the assembly behaviours of the α -CD/PPBI samples subject to pH
15 variation and UV irradiation (c). Fig. 8a is reprinted with permission from ref. 45. Copyright ©
16 2016 American Chemical Society. Fig. 8b and 8c are reproduced and adapted with permission
17 from ref. 46. Copyright © The Royal Society of Chemistry 2018.

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

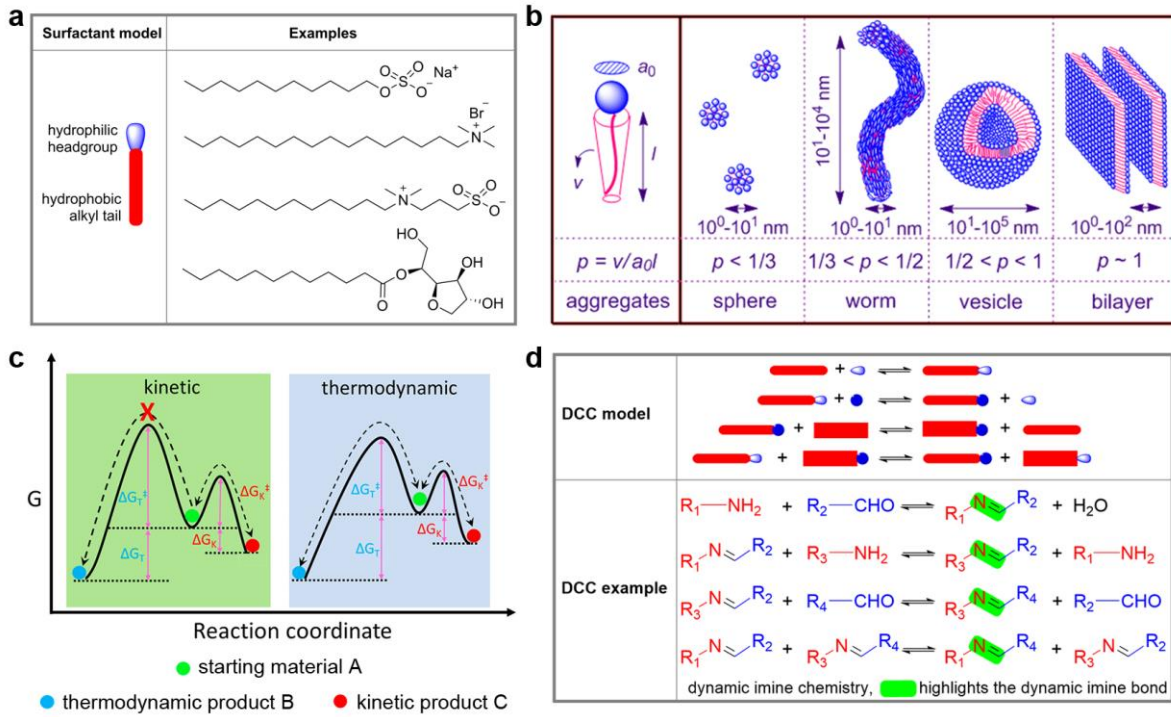
1 droplets (d right). Reproduced with permission from ref. 59. Copyright © 2019 American
2 Chemical Society. Adapted with permission from ref. 46. Copyright © The Royal Society of
3 Chemistry 2018.

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

8 **Fig. 11.** Diagram outlining the process for preparing FG-H, FG-F, JG-1, JG-2, and JG-3 (a). JG-
9 1 ascends from the water-hexane interface to the air-glass interface along the glass vial surface,
10 propelled by hexane-induced Marangoni flow (b, left). The interfacial jamming of the JG-1
11 surfactants (b, right). Water droplets slide on the hydrophobic surface of the 2D JG-1 assembly
12 (c). Injection of 2D JG-1 into the microfluidic system designed to mimic oil in a carbonate
13 mineral formation. (d). Left: Following flooding with green-dyed water, $39 \pm 2\%$ of crude oil
14 (red) remained. Right: After flooding with a JG-1 water solution, $25 \pm 1\%$ of crude oil remained.
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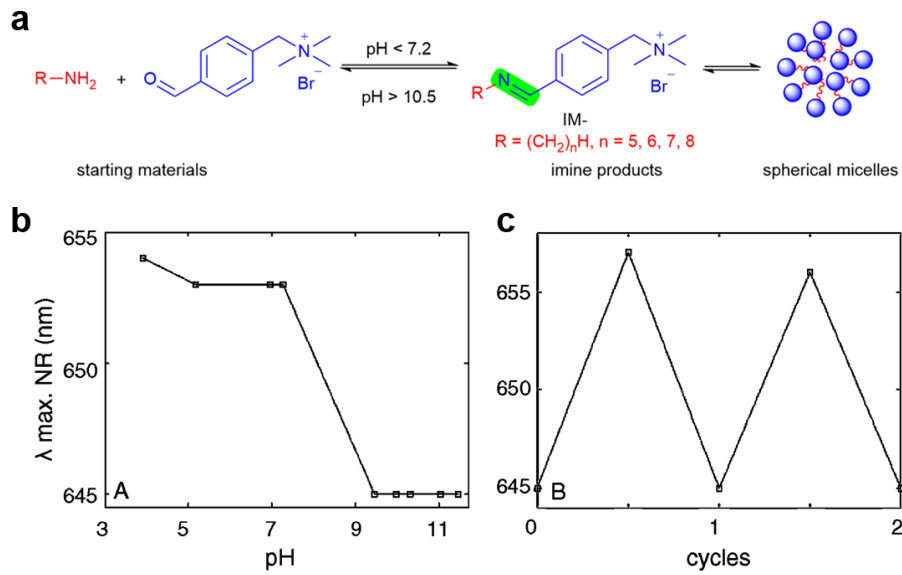
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1 Fig. 1.



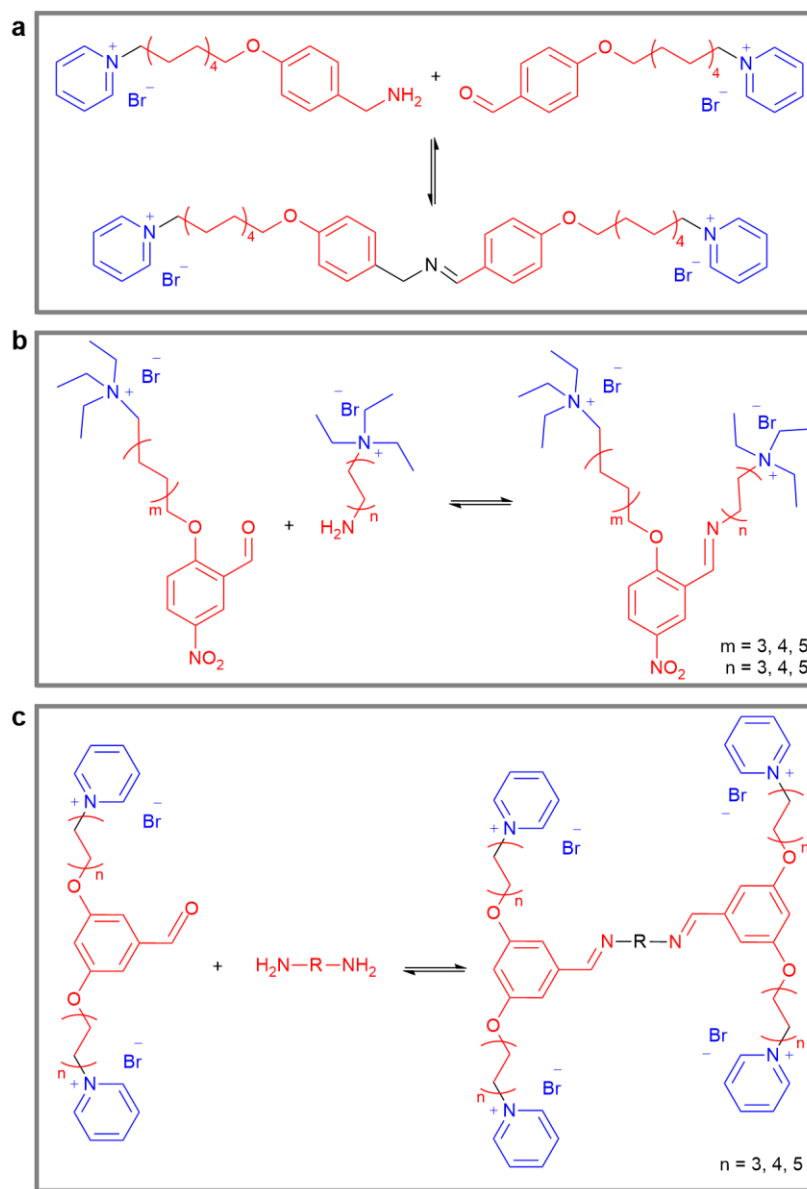
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3 Fig. 2.



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1 **Fig. 3.**



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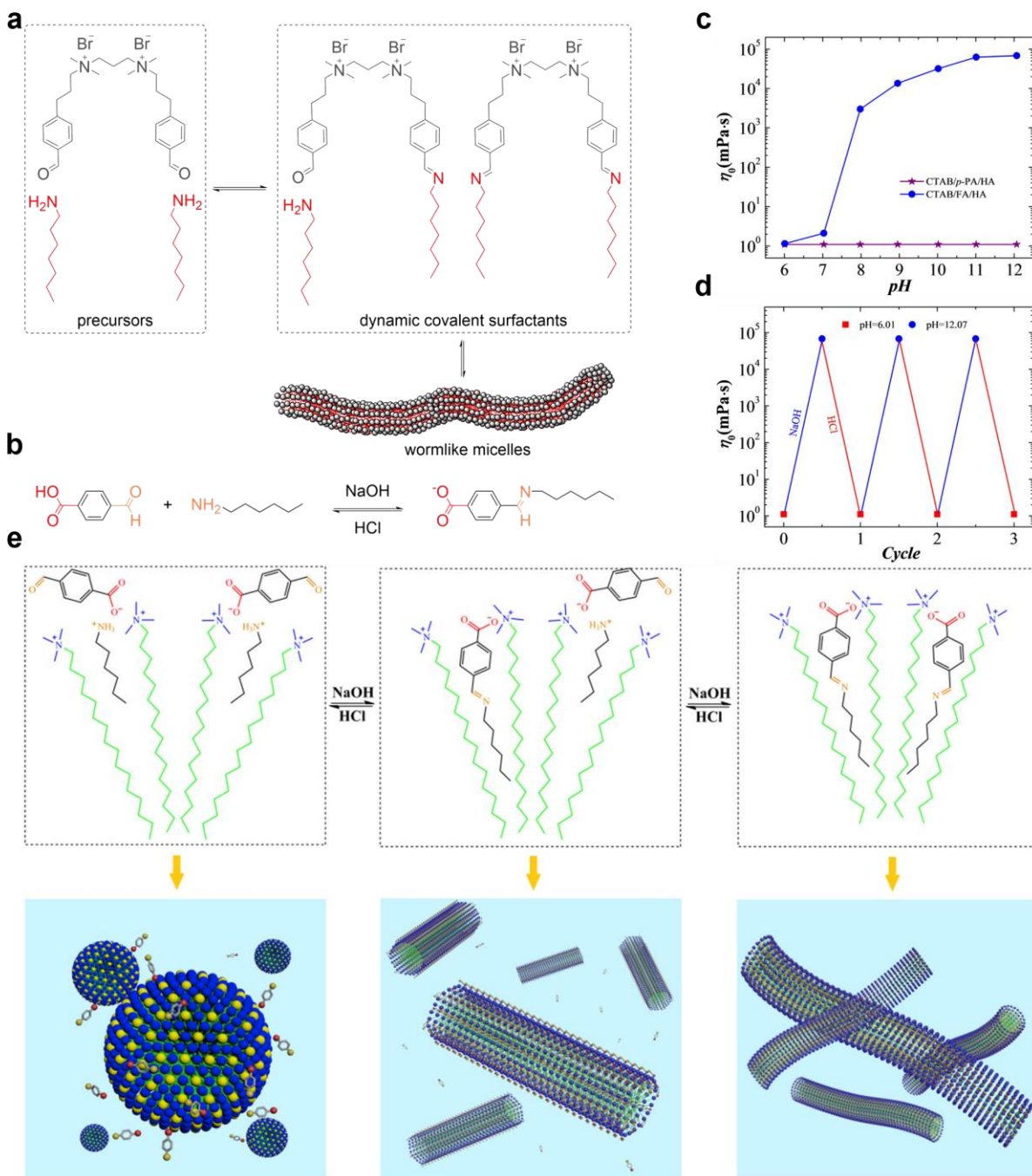
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1 **Fig. 4.**

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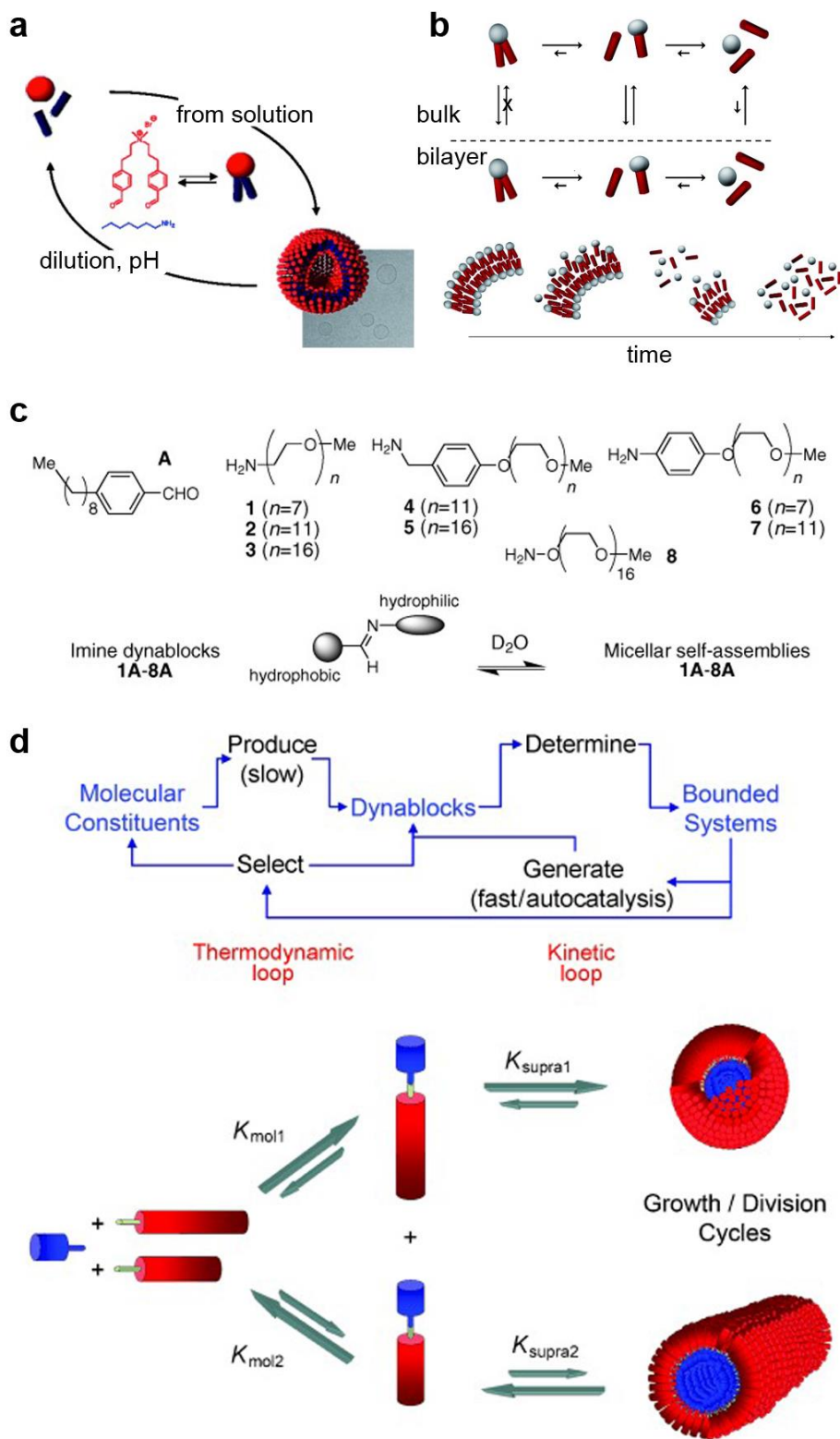
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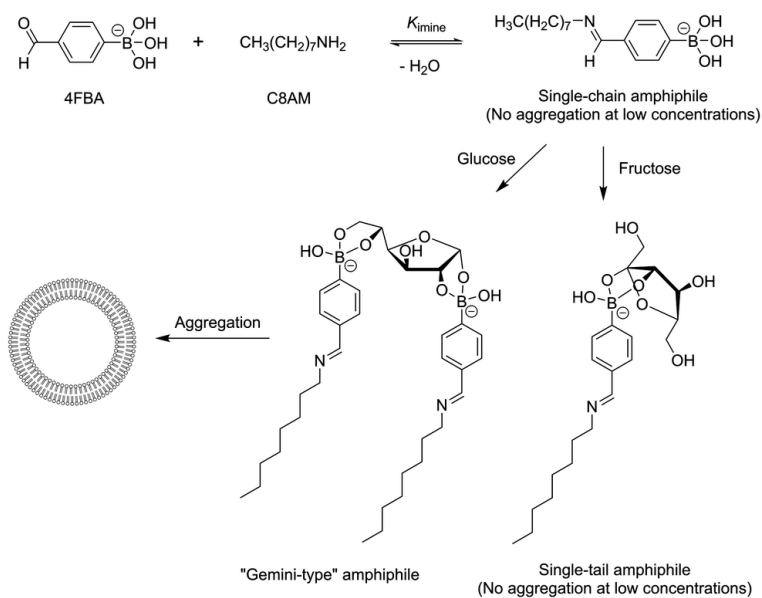
1 Fig. 5.



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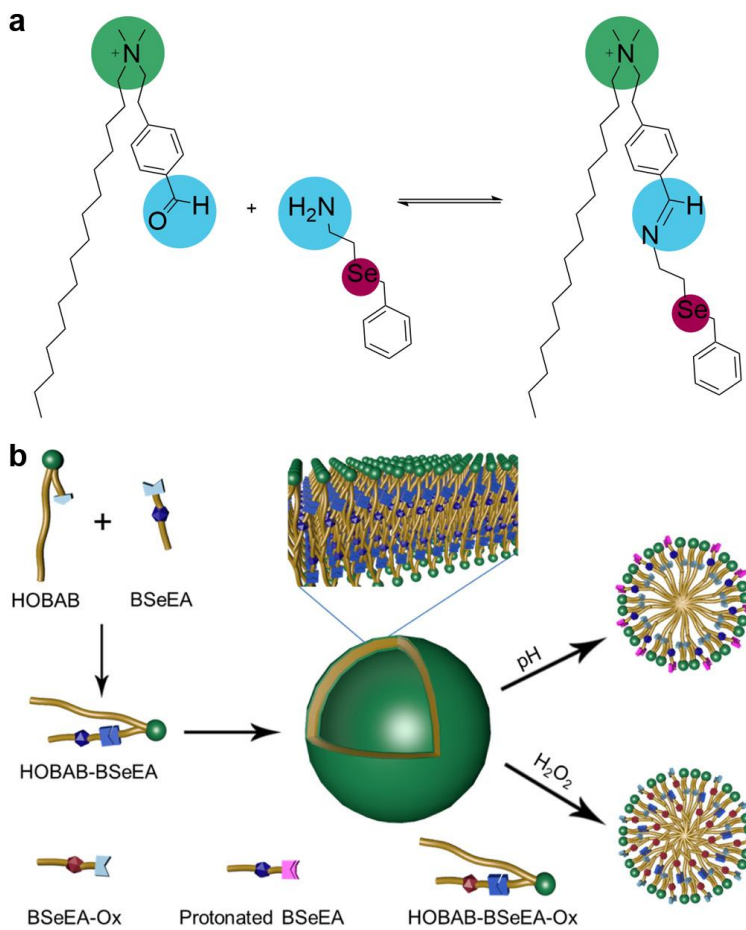
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1 **Fig. 6.**



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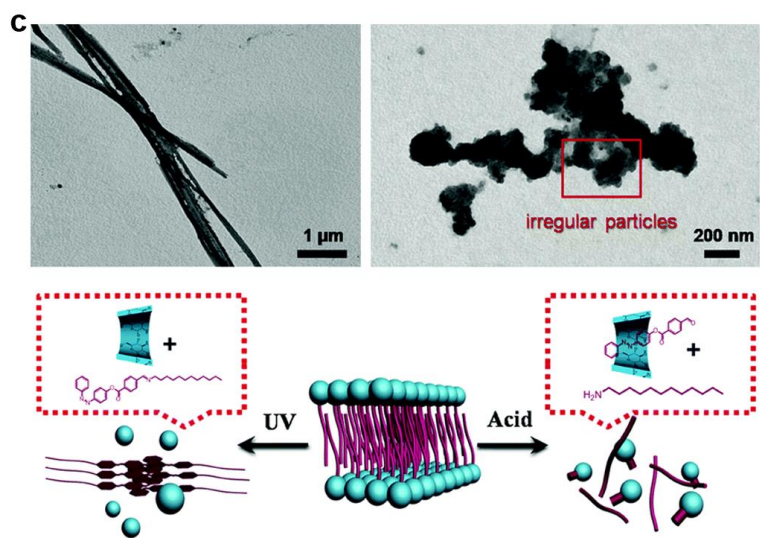
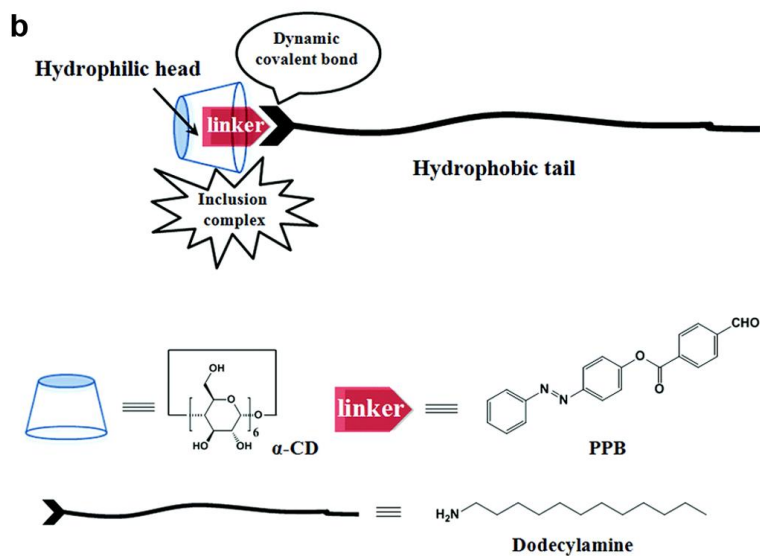
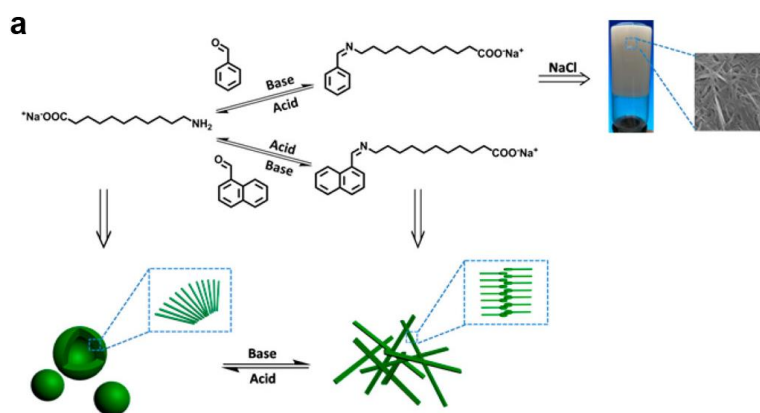
3 **Fig. 7.**



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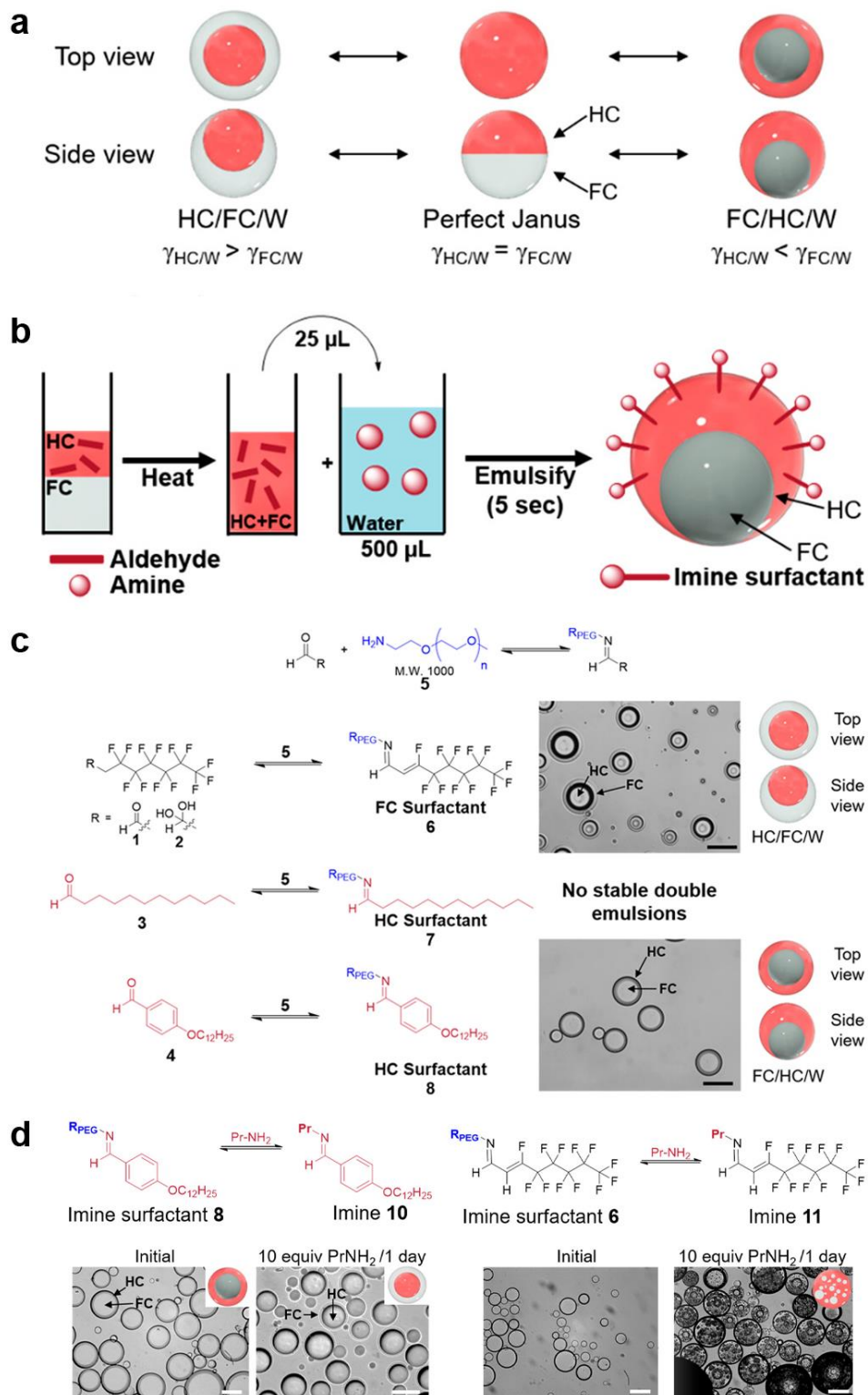
1 Fig. 8.



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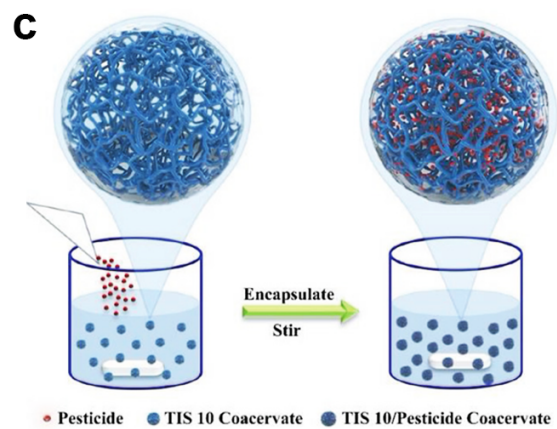
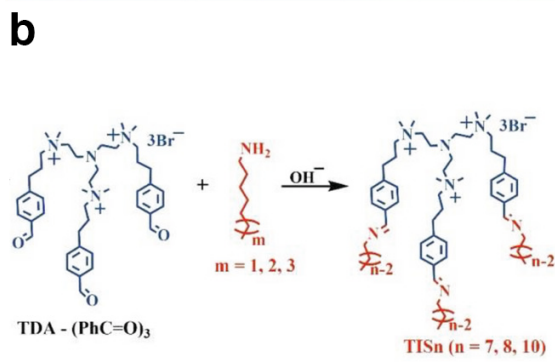
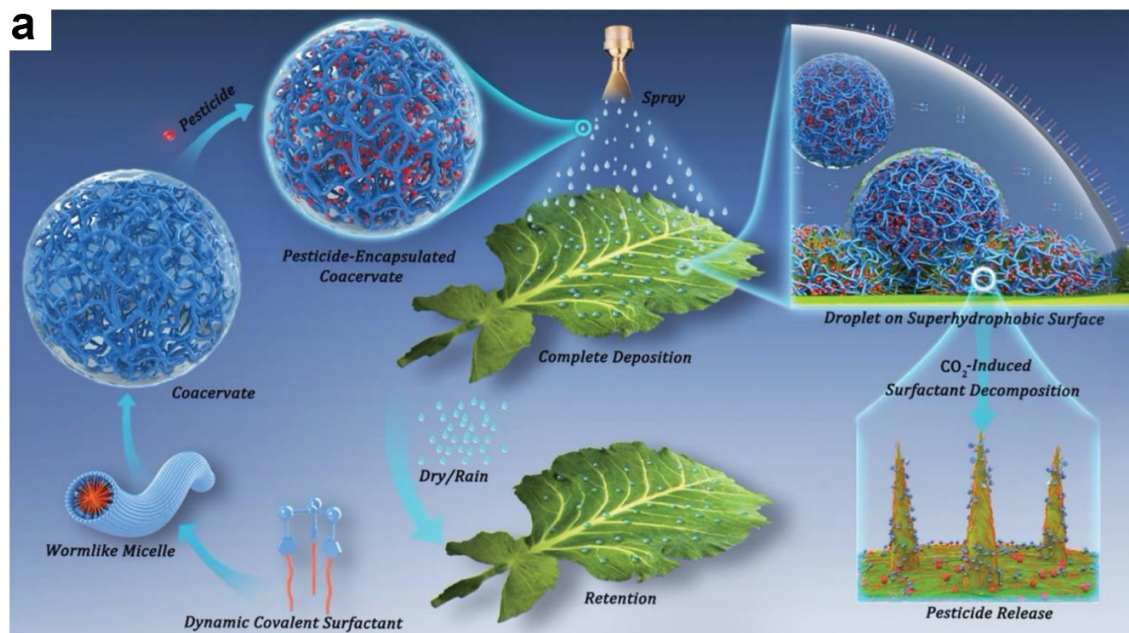
1 Fig. 9.



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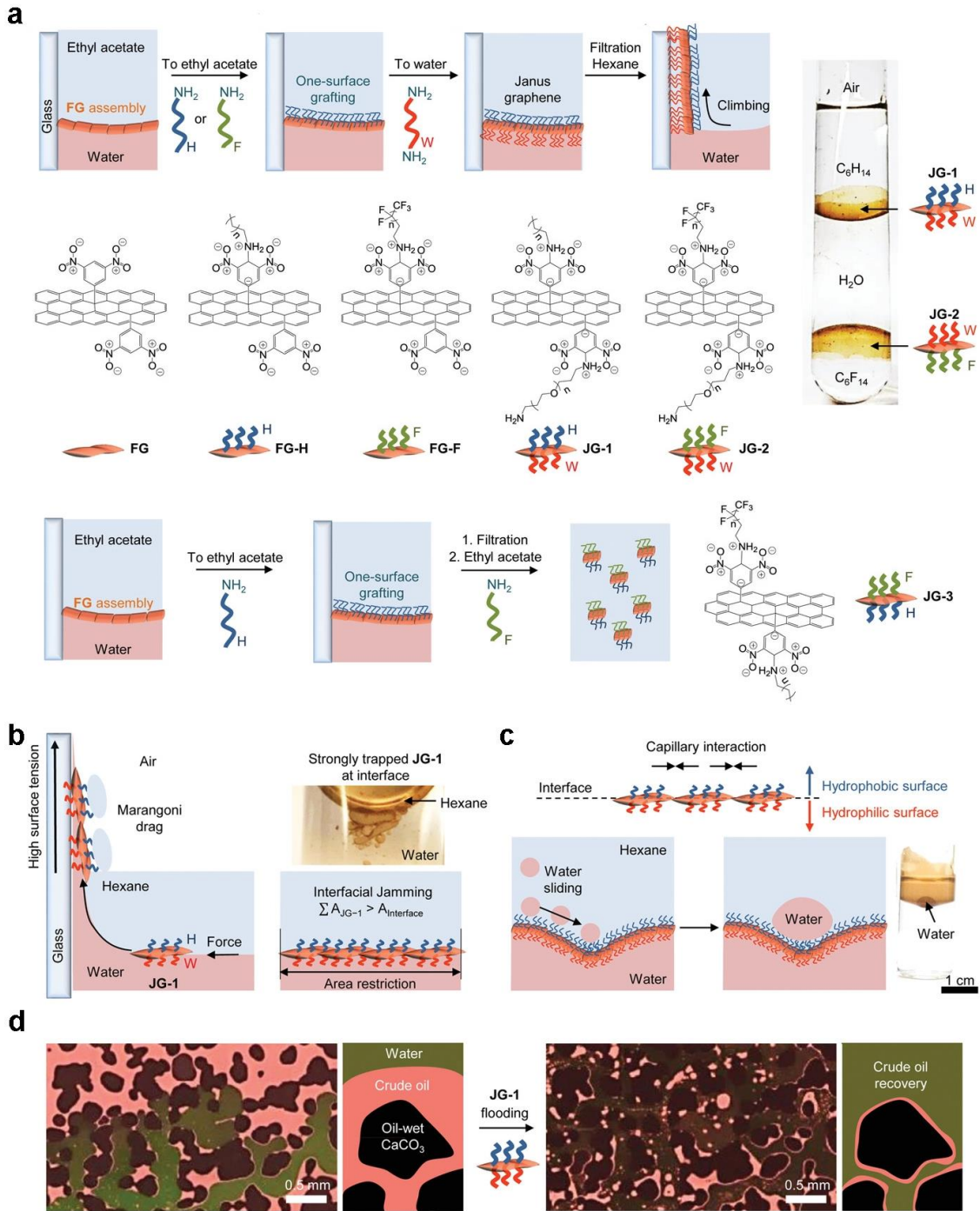
1 Fig. 10.



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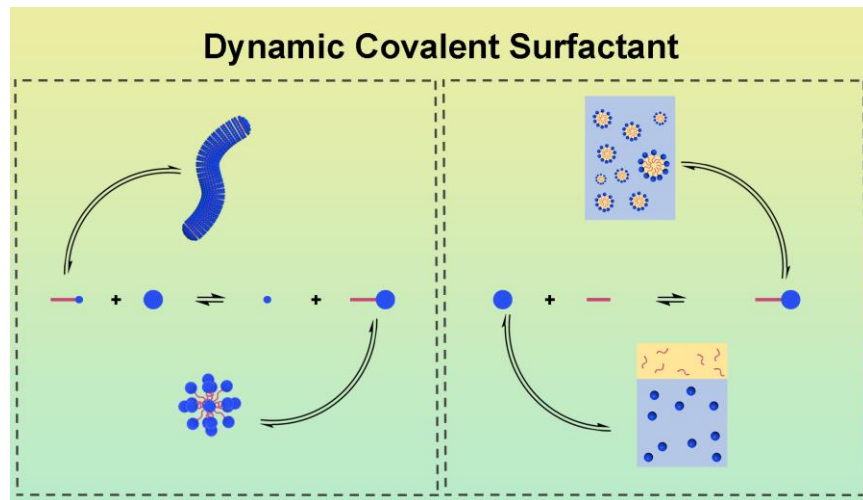
1 Fig. 11.



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



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