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ARTICLE

Shaping Interfaces with Light: Evolution and Application of Azobenzene containing Photoresponsive Surfactants

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Surfactants are ubiquitous, having critical roles in biological processes, such as with lung surfactants, as well as in many consumer and industrial applications. This versatility is significantly expanded and demonstrated by stimuli-responsive surfactants, among which photoresponsive systems have garnered considerable research interest, especially in recent years. A thorough analysis of the subject is required because there aren't many review papers on photoresponsive surfactants, which limits our knowledge of this area. This review describes the historical emergence and evolution of photoresponsive surfactants. It provides a detailed analysis of the various photoresponsive moieties (e.g., azobenzene, spiropyran) that are covalently integrated into surfactant architectures, focusing on their distinct types, operational limitations, and applications. A comparative analysis of conventional versus gemini photoresponsive surfactants is presented, highlighting key differences in their physicochemical properties. This review elucidates the mechanisms of photoisomerization in azobenzene and its direct impact on molecular-level properties (e.g., polarity, geometry) and their macroscopic physical outcomes (e.g., surface tension, viscosity) in both azo-based and non-azo surfactants. The review comprehensively surveys the diverse applications for these materials, including enhanced oil recovery, environmental remediation, motion manipulation, catalysis, smart materials, and controlled drug delivery.

1. Introduction

Surfactants or Surface-Active Agents, are a class of chemical compounds which act on interfaces, primarily to lower the surface tension of liquids, which make it easier for them to spread or mix with other substances and to facilitate the mixing of otherwise immiscible substances which gave rise to various applications such as stabilizing agents for emulsions[1] or the relatively newer area, stabilizing microemulsions for nanomaterial synthesis.[2] The applications are numerous and span a wide area, which have been discussed in the application section. A surfactant molecule has both hydrophilic (water-attracting) and hydrophobic (water-repelling) regions, allowing them to interact with different phases simultaneously, giving rise to their stabilization properties. Generally, the head of the molecule is the hydrophilic part, and the tail, which is usually a carbon chain, is the hydrophobic part, the two differently natured parts acting as “connecting points” and the rest of the molecule as the “bridge” between the two different phases.[3]

There can be different types of surfactants based on the number of head and tail groups. surfactants with only one head group and one long tail per molecule are called monomeric or conventional surfactants and ones with two head groups and tails are called dimeric or Gemini surfactants.[4] They can also be thought of being different based on the charges on the head group. There can thus be non-ionic, cationic, anionic, and zwitterionic surfactants. Surfactants are present all around us in different capacities; be it the human body[5], petroleum industry[6], food industry[7], water purification[8], pharmaceuticals[9,10] , controlled drug release[11], soil and water purification[12], nanoparticle synthesis[2], or metal detection as sensors[13].

At low concentrations, surfactants dissolved in water are either adsorbed at the interface or distributed in a monomolecular state. The lowest concentration at which micelles form in solution is known as the Critical Micelle Concentration (CMC)[14]. Switchable surfactants, or stimuli-responsive surfactants, are a special class of surfactants, namely which alter their rheological properties based on one or more external stimuli. In addition to the benefits of conventional surfactants, switchable surfactants also solve the technical issue of surfactant separation from aqueous solution, resulting in significant cost savings. Recently, a wide range of stimuli-responsive surfactants have been discovered which respond to a variety of stimuli, like pH responsive[15,16], redox responsive [17,18], CO_2 exposure[19,20], magnetic field responsive[21,22], light responsive (photo responsive)[11], temperature responsive[23]. The changes or transitions in interfacial properties due to surface active molecules can be attributed to the deviation of the interface from an equilibrium state to a non-equilibrium state based on the external stimuli provided. This has broad implications in terms of the stimulus. As observed in the case of pH or temperature responsive surfactants, the time scale of the equilibrium deviation is comparable to the time scale of surfactant diffusion time, complicating their use and applications[24].

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One stimulus which can reach most of the bulk at an apparently instantaneous rate depending on the bulk characteristics is light. This gives rise to photochromism as a very tempting phenomenon to exploit. Photochromism is the phenomenon in which a molecule reversibly transfers between two different forms with different absorption spectra upon exposure to light. In addition to absorption spectra, many other physiochemical properties like isomeric structure, polarity, magnetic strength, refractive index, quantum yield, reduction/oxidation potentials can also change.[25,26,27] Exploring photochromism in context to surfactants give rise to light responsive surfactants, which are immensely popular currently because of their rapid and tunable isomerization, green stimulant, and cyclability.[28] They find applications in many fields like liquid crystals[29], molecular switches[30], micellar catalyst[31], photo foam[32], and polymers.[33]

Many functional groups or structural modifications can be introduced in a molecule to induce Photoresponsive behavior. Some of these include azobenzene, hemiindigo (and other hemiindigoids) stilbene, diarylethene and spiropyran and hemiindigo (fig. 1). In these, azobenzene and stilbene undergo photoisomerization upon irradiation and diarylethene and spiropyran undergo structural isomerization by open-close ring transition.[24,34,35] Stilbene derivatives find relatively less applications because of their low solubility in aqueous media.

Azo group containing molecules have been very attractive to researchers recently and some work has been done on them including static properties like equilibrium surface tension, Critical Micellar Concentration (CMC), photo switching between equilibrium assemblies, formation of complexes, contact angle etc.[24] and dynamic properties as by Diguet *et al.*,[36] who studied the manipulation of oil droplets at water-air interface in the presence of a cationic azo surfactant and by Liang *et al.*,[37] who studied dynamic manipulation of droplets on liquid-infused surfaces using a spiropyran based photoresponsive surfactant. Kunitake *et al.*,[38] in 1981, was the earliest reference we could find who talked about azobenzene containing amphiphile structures and the effect of those structures on their aggregate morphologies. Shinkai *et al.*,[31] showed that the trans-cis isomerization of azobenzene head groups in a surfactant affected their aggregation mode. They were the first to demonstrate light based control of micellar catalysis. The azobenzene group can be present in any part of the surfactant to give it photoresponsive nature with differing effects, be it the head group, tail group, or the spacer part in geminal surfactants.[32] The number of azobenzene group can also be modified and their effects studied. Gemini surfactants with an azobenzene group per tail have been synthesized and studied.[39]

This article aims to study the importance and evolution of responsive surfactants. The surfactant can be responsive with respect to pH, temperature, CO_2/N_2, and light. Among all the responsive surfactants, photoresponsive surfactants are being talked about in this article due to its versatility on irradiation with UV-Vis light. This includes the effects of molecular substitutions, functional group, number of head groups, and the position of azobenzene moiety on the rheological properties of the surfactants. We have also studied the uses of azobenzene based Gemini surfactants in conjugation with conventional surfactants in various applications. We also wish to compile a comprehensive list of the applications of Photoresponsive surfactants and to study the effects of surfactant structure making them suitable for an application with an emphasis on their future scope in various industries.

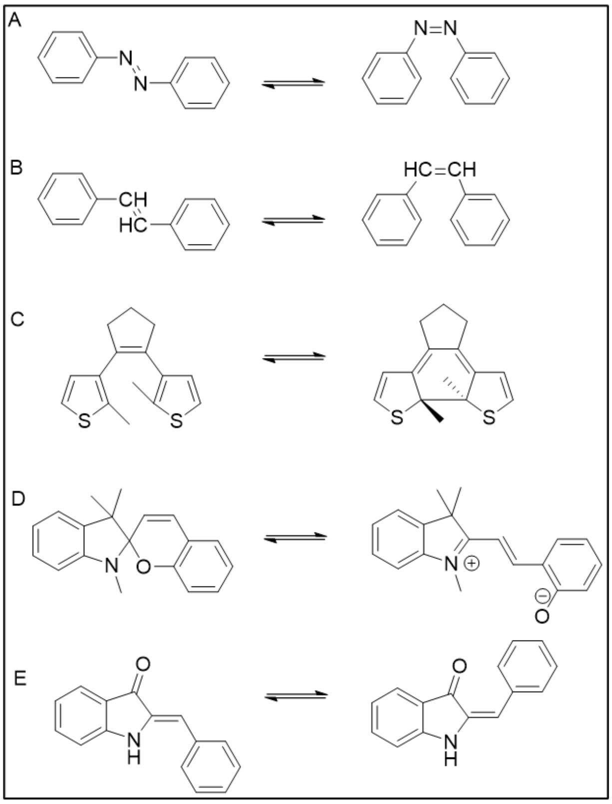

Figure 1. Photoisomerization in (A) Azobenzene, (B) Stilbene, (C) Diarylethene, (D) Spiropyran, (E) Hemiindigo.

2. Classification of surfactants

The surfactants are classified as conventional and Gemini surfactants based on the number of head and tail groups attached.

2.1 Conventional Surfactants

The primary class of surfactants is the conventional surfactants. These types of molecules have the unique quality of having a singular head and tail group to act as the hydrophilic and hydrophobic part, respectively. When the studies on surfactants began, these were the fine kind of surfactants made in laboratories owing to their simple design. Naturally, the first kind of synthetic photoresponsive surfactants were also conventional surfactants.[31] A plethora of experiments were done to induce light-responsive character in the molecules. Some methods included introduction of moiety that undergoes photoisomerization on the tail end[26,32] near the head group[34] or even somewhere in the middle.[24] As with most of these compounds, azobenzene was the preferred moiety because of its reversible photoisomerization characteristics.

Some efforts have been made to study the effect of the position of the azobenzene groups on the properties of the surfactant.[40] Peng *et al.*,[40] synthesize two kinds of surfactants, one where azobenzene was placed in the center of the hydrophobic tail and one in which azobenzene was placed directly between the hydrophilic head and hydrophobic tail. The first kind formed multiple lyotropic liquid crystal (LLC) phases (such as hexagonal and lamellar) depending on the water content, and showed significant photoinduced changes in its self-assembled structure and bulk physical properties. Whereas the second kind was less responsive to light stimuli overall. They concluded that if the azobenzene is too close to the hydrophilic/hydrophobic boundary (interface) in a surfactant structure, the steric constraints and packing requirements prevent the molecule from rearranging after it switches shape. Conventional surfactants can then further be classified based on the charge present on the head group, these being conventional nonionic surfactants[32,34] conventional cationic surfactants[24,26,34] and conventional anionic surfactants.[41] Nonionic surfactants do not have any charge on their head groups, while cationic surfactants have a positively charged head, and anionic surfactants have a head with a negative charge present.

Many synthetic procedures have been devised to synthesize conventional photo responsive surfactants. The simplest way includes attaching the photo responsive unit towards the end of the tail with a quaternary ammonium salt as the head group. This method must be the simplest and easiest way to introduce photo responsive behavior in conventional surfactants. More methods which include introducing the photo responsive moiety near the head group or even in between the carbon chain have also been devised as seen previously and their synthetic procedures are also very well known. The structure has been mentioned in (Table 2).

From a performance standpoint, conventional photoresponsive surfactants generally exhibit critical micelle concentration (CMC) values in the range of 10^{-3}-10^{-4} M, requiring relatively higher concentrations to achieve micellization. Correspondingly, their equilibrium surface tension values are typically reduced to 35-45 mM m^{-1}, depending on molecular structure and experimental conditions[39]. while these systems are effective, their higher CMC can lead to increased material usage, which may have economic and environmental implications at larger scales.

Despite these limitations, conventional surfactants offer important advantages, including synthetic simplicity, cost-effectiveness, and well-established scalability, which continue to make them relevant for practical applications.

2.2 Gemini Surfactants

Gemini surfactants represent an advanced class of surfactants characterized by the presence of two hydrophilic head groups and two hydrophobic tails, typically linked by a spacer unit. This unique architecture leads to markedly different interfacial and aggregation behavior compared to conventional surfactants.[4] As a result, gemini surfactants exhibit significantly lower CMC values (~10^{-5}-10^{-6} M), corresponding to reductions of approximately 1-3 orders of magnitude compared to conventional surfactants. In addition, they often achieve greater reductions in surface tension, which typical values reaching ~25-30 mM m^{-1}, indicating enhanced surface activity and adsorption efficiency[39]. These properties make gemini surfactants particularly attractive for applications requiring high efficiency at low concentrations, such as controlled drug delivery, nanostructure templating, and responsive interfacial systems. Furthermore, their lower operational concentrations can reduce the overall chemical load in a system, offering potential environmental benefits. However, it is important to note that gemini surfactants are not universally superior. Their synthesis is often more complex, and factors such as spacer length, flexibility, and molecular symmetry can significantly influence their behavior. Additionally, higher production costs and challenges in large-scale synthesis may limit their widespread industrial adoption. Therefore, gemini surfactants demonstrates enhanced interfacial efficiency in terms of lower CMC and improved surface activity, conventional and gemini surfactants offer complementary advantages, and the choice between them should be guided by the specific requirements of the intended application.[42] Table 1 represents two examples where comparative structures of conventional and gemini surfactants along with their CMC values and surface tension.

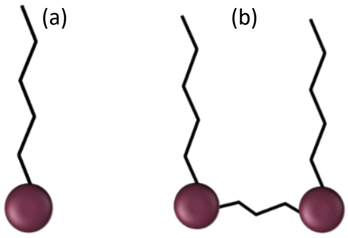

Figure 2. Structural of (a) Conventional (b) Gemini Surfactants.

3. Evolution of photoresponsive surfactants

The first mention of a surfactant changing the morphology of its micellar structures comes from Kunitake *et al*, in 1981.[38] Their work focused on the formation of stable bilayer assemblies in water from single-chain amphiphiles and the relationship between the amphiphile structure and the aggregate morphology. They had used as ‘spacer’, a rigid part, in the amphiphile structures. They talked about azobenzene in the context of introducing ‘dynamic’ control of the amphiphile aggregate morphology. In their work, it was seen that the trans-azobenzene spacer unit took the extended geometry, and the globular aggregates were formed. It was also seen that the cis-azobenzene unit possessed a bent geometry and should act as a bent rigid segment. However, the photochemical properties of the aggregates were not thoroughly studied.

Many groups tried manipulating the basic structure of the surfactant with different number of head groups or tail groups, changing the length of the alkyl chain, introducing different functionalities in the head group or the tail group including but not limited to ether linkages[40,13] carbonyl groups in the form of both esters[43] and carboxylic acids.[44] Different lengths of the spacer group were studied by different groups in the case of Gemini surfactants[45,46,47,48] the effects of which have been briefly discussed in the following sections. There were attempts with different photo responsive moieties including azobenzene, stilbene, merocyanine, diarylethene, spiropyran, etc. In most applications, the azobenzene group has proved to be the most synthetically viable and experimentally functional and usable group due to its properties like quick and tunable photo responsive behavior, higher levels of cyclability, excellent quantum yield, etc.[49,50]

Many photo-mechanisms have been considered for introducing photoresponsive behavior. The most common is, of course, cis-trans photoisomerization as seen in the case for azobenzene and stilbene type moieties. Spiropyran, follows ring opening/closing mechanism. An interesting effort was made by Ahmadi *et al*. who employed photodimerization property of coumarin to synthesize photoresponsive polymeric micelles.[51] This was also a meticulous effort to make polymeric surfactants which were not only light responsive but pH and temperature responsive as well. The surfactant also went from its initial investigations as a proof of concept to more real-life applications. As we saw in the beginning, there were major solubility issues with azobenzene containing surfactants which were later resolved with introductions like a charged head and now, after decades of work, the stimuli responsive surfactant industry is an emerging field both in science and in industry.

4. Mechanism and kinetics of cis-trans isomerization of azobenzene

Based on the wavelength of the irradiated light, the azobenzene molecule undergoes isomerization, changing its chemical structure and subsequently, its properties. The most common type of this isomerization is the cis-trans isomerization, shown by moieties like azobenzene and stilbene. The cis-trans isomerization of azobenzene has been thoroughly studied with studies starting as soon as in 1954.[52]

In case of azobenzene based surfactants, the trans isomer absorbs at about $\lambda = 360$ nm and changes into the cis form. When the cis state is illuminated, it absorbs at around $\lambda = 460$ nm and relaxes back to trans. This cis to trans isomerization also happens thermally. Obviously, these numbers change based on other functional groups present in the molecule. In most cases, full conversion to the cis or trans isomer is generally not possible.[53] Rather, these systems usually achieve photostationary states that are made up of a mixed population of trans and cis isomers, the makeup of which depends on the chromophore's chemical substituents and the incident wavelength of light used to illuminate the system.[54] Mechanistic insight for light induced interfacial processes has also been studied.[55] For the azobenzene molecule, two major mechanisms for the photoisomerization process have been proposed, namely rotational mechanism and inversion mechanism.[56] Additionally, cases where the two mechanisms act in cohort have also been theorized.[57] Some groups have come to call them as inversion assisted rotation[58] and concerted inversion[59] (figure 3).

The rotational mechanism draws its basis from the evolution of the N=N double bond to have greater single bond characteristics, allowing for bond rotation and easing on the requirements for coplanarity. This causes one of the phenyl rings to move out of the molecular plane and the dihedral angle of C-N-N-C to change from 180° to 0°.[60] The N=N-C bond angle stays 120°. Inversion process involves the change of the N=N-C bond angle from 120° to 240° by rotation of a phenyl ring through the N-C single bond.[61] During inversion, the dihedral angle remains unchanged. During inversion-assisted rotational pathway, the C-N=N-C dihedral angle decreases and the N=N-C bond angle also decreases. During concerted inversion, something unusual happens and we see a linear transition state due to the increase of both N=N-C bond angles to 180°.[62]

Rotation, inversion, co-inversion, and inverse-assisted rotation vary in the structural motion around the N=N-azo link and the accompanying energy barriers. Torsion around the N=N double bond causes isomerization in the rotation mechanism (A), which involves a 180° rotation that momentarily breaks π-conjugation and passes through a high-energy twisted transition state where the dihedral angle (C-N=N-C) approaches 90°. The inversion process (B), on the other hand, does not involve bond rotation; instead, one of the nitrogen atoms rehybridizes from sp^2 to a quasi-linear sp configuration, which causes a bending motion (change in CNN angle) while preserving the π-bond formation. A coordinated geometric rearrangement that avoids complete bond rotation but necessitates a greater cooperative distortion energy is produced by the co-inversion pathways (C), which entails simulations or sequential inversion at both nitrogen atoms. The inverse-assisted rotation mechanism (D) is a hybrid pathway that facilitates rotation about the N=N bond by lowering the rotational barrier through partial inversion at one nitrogen. This pathway is frequently thought to be energetically advantageous under specific excited-state conditions. Depending on the electronic state (n to π^* or π to π^* excitation), solvent environment, and substitution pattern, these mechanisms can be selectively favored; rotation usually predominates in the excited state, whereas inversion contributes more heavily in the ground state thermal isomerization.

Depending on the direction of the isomerization, conditions, and the substituents involved, azobenzene containing molecules undergo isomerization by one of the paths. For azo compound with a strong dipole moment, the rotational pathway has been seen to occur, especially in polar solvents.[63] Due to the higher single bond characteristics in the N=N bond, it is feasible to consider it as partially broken, which gives rise to the feasibility to the formation of the NH-N= hydrazone group. This is called the azo-hydrazone tautomerism. The formation of the hydrazone group dramatically increases the rate of the cis-trans isomerization by significantly increasing the N-N bond rotation potential. This process is especially seen in polar solvents like ethanol.[57,64] The kinetics of surfactant isomerization differ significantly below and above the critical micelle concentration (CMC) of the trans isomer, primarily due to steric constraints within tightly packed micelles. However, this behavior remains largely unaffected by variations in spacer length.[65]

There have been studies to investigate the effect of different substituents on the isomerization process. One such work was by Konieczkowska *et al.*,[66] who worked on 4-hydroxyl and 6-hydroxy-4-hexyloyl derivatives of azobenzene. They concluded that if a hydroxyl group is attached directly with the azo molecule, it increases the rate of thermal cis-trans isomerization as compared to the hydroxyalkoxyl group. They also concluded a strong influence of intermolecular interactions on cis-trans isomerization. The push-pull effect is also famous for affecting the cis-trans back reaction kinetics, particularly increasing the rate. There have even been reports of compounds reverting to their trans state within microsecond or faster after conversion to the cis state by photoirradiation.[67,63,68] This makes it a suitable candidate where fast-switching molecules are needed.[69,70,71,72] Bichot *et al.*,[73] synthesized 4,4'-disubstituted azobenzene compounds with three model compounds having a $t_{1/2}$ of 57 h, 5 min, and 9 ms, signifying the effect of substituents. Here, $t_{1/2}$ corresponds to the *half-time* reappearance time of the trans isomer after irradiation.

5. Effect of cis-trans isomerization on surfactant properties

Photoresponsive surfactants are important because of their isomerization properties in the presence of light. Hence, it is imperative that we understand the effects of said isomerization. Miyata *et al.*,[74] talked about CMC and electrical conductivity differences of the cis and trans forms. According to them, there is a difference in the hydrophilic-lipophilic balance (HLB) between the trans and cis forms hence, due to this difference in HLB, there

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emerges a significant difference in the CMC values and electrical conductivities of the surfactant upon cis/trans isomerization. They found that for surfactants having moderate alkyl chain lengths like ethyl and butyl corresponded to a larger change in CMC values of upto 5.9 mmol/L upon cis/trans isomerization. The photoresponsive function was similarly impacted by the substitution of the tail chain species. This included both the length and the type of the tail chain. When compared to a structurally similar surfactant with an ethyl unit as its tail group, the surfactant with the p-ethoxy group as the tail chain was found to form a stable micelle aggregation. Additionally, it showed a significant shift in CMC (5.3 mmol/L) when exposed to UV light.

The introduction of an azobenzene group in the tail has been a particular point of interest for both application and proof of concept points of view. In the case of charged surfactants, as are a wide portion of the surfactants synthesized and commercially available, the charged head has a relatively high effective cross-sectional area, this translates to the effect of tail groups on the surface tension properties to be minimized as the effect of the conformation taken by the tails upon cis/trans isomerization on the packing of the surfactant is minimized[75]

A very important change that occurs upon photoisomerization is the change in surface tension of the solution which can be seen as a change in the contact angle of a drop of the solution upon a hydrophobic surface. The contact angle can be measured by Young's equation (1).

$$\gamma cos\theta = \gamma_{SV} - \gamma_{SL} \qquad (1)$$

where, θ is the contact angle and γ_{SV} is the surface energy at the solid-vapour interface and γ_{SL} is the surface energy at the solid-liquid interface.

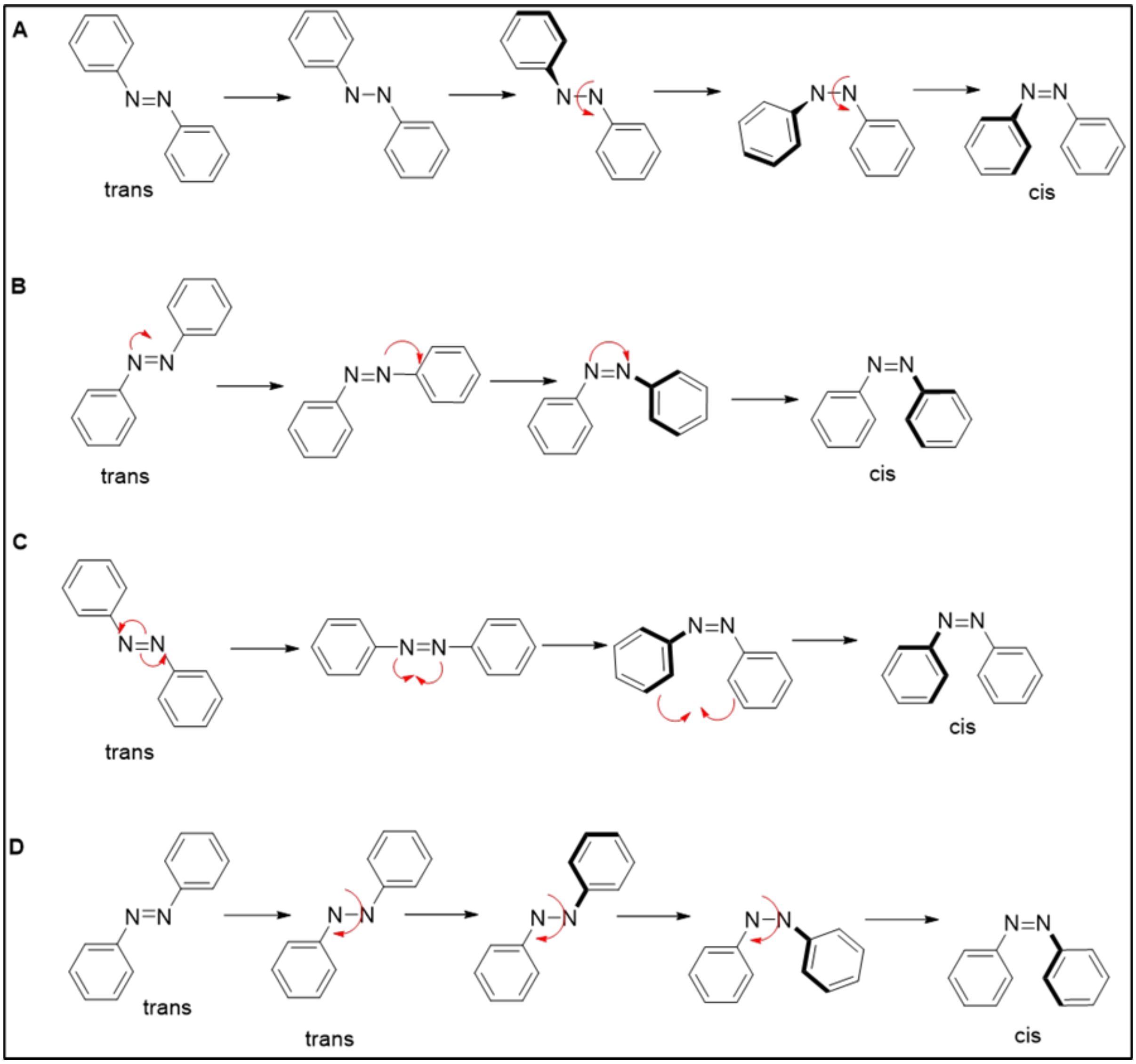

Figure 3. Mechanism of cis-trans isomerization of azobenzene by (A) Rotation, (B) Inversion, (C) Concerted inversion, and (D) Inversion assisted rotation.

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Another important change in relation to a surfactant upon light irradiation is a change in CMC. As shown by Shang *et al.*, [75] for nonionic surfactants, the trans confirmations show remarkably lesser CMC than their corresponding cis confirmations. This can be attributed to a greater packing efficiency of the trans form, which allows for easier micellar formation even at lower concentrations while their cis counterparts are not as well packed and need a higher concentration to come close enough to form micelles. In some cases, the difference was even as much as 15-fold from the trans to cis forms. A similar result was shown by Hayashita *et al.*,[74] with ionic photoresponsive surfactants. Both Shang *et al.*, and Hayashita *et al.*, interestingly reported that for a given surfactant with varying spacer or tail chain lengths, the maximum difference between the CMCs of the cis and trans forms was observed in the case of moderate alkyl spacer or tail chain length. In case of azobenzene based surfactants, it was also reported that the adsorption coefficient, *k*, was lower for the cis counterparts. This was attributed to the more polar nature of the azobenzene group.

Shang *et al.,* also showed another interesting phenomenon. The quantum efficiencies of cis to trans isomerization and trans to cis isomerization were different. They did the experimental procedure for $C_4AzoOC_6E_2$ and found that for the trans-to-cis conversion, the quantum efficiency was close to unity, that is, $\phi \cong 1$. For cis-to-trans conversion, however, the quantum efficiency was found to be around 0.69. The explanation they provided was based on the geometrical differences in both the excited and ground states, due to which the differing quantum efficiencies shown might represent distinct reaction mechanisms in these two photoisomerization processes. This correlates to the proposed differing mechanisms, which have the trans azobenzene converting to the cis form through a rotation mechanism and the cis form converting to the trans form through a slower inversion mechanism.[76]

The ground state absorption spectra of azobenzene have two bands in the UV-Vis region. The symmetry-forbidden S_1 (nπ*)$\leftarrow S_0$ transition appears as a weak band at about 450 nm, and the symmetry-allowed S_2 (ππ*) $\leftarrow S_0$ absorbs at around 320 nm.[59] Upon excitation, both S_1 and S_2 states lead to the trans to cis isomerization, but S_1 relaxes with a higher quantum yield of isomerization.[77] It was shown by femtosecond time-resolved spectroscopic studies that $S_1 \leftarrow S_2$ occurs with a quantum yield of about one, indicating that $S_1 \leftarrow S_2$ occurs before S_2 can relax to the ground state.[78] Azobenzene with steric constraints blocking N-N bond rotation also has quantum yields independent of the excitation wavelength, suggesting photoisomerization dominates from S_1 irrespective of the initial excited state.[79,80]

The lifetime of the S_1 state generated by $S_1 \leftarrow S_0$ excitation has a lifetime of 2.6 ps,[81] while that of the S_1 state generated by $S_1 \leftarrow S_2$ is 500 fs.[78] The $S_1 \leftarrow S_2$ process creates a vibrationally excited S_1 state, leading to its shorter lifetime, and it relaxes rotationally to the trans form, resulting in a lower quantum yield of isomerisation. While experimental and theoretical data agree that isomerization proceeds mainly from the S_1 state, when the S_2 state relaxes to the S_1 state, other isomerization pathways become possible. Theoretical studies suggest this alternative pathway is a concerted inversion mechanism, defined by the simultaneous change of both C−N═N and N═N−C angles.[82,83]

Shang *et al.*,[75] synthesized a new class of photoresponsive surfactants called $C_4AzoOC_nE_2$ (n=2,4,6,8). They performed a variety of studies on them including variations in the surfactant solution properties with changing spacer length. They used the Frumkin isotherm to relate the surface excess concentration to the true bulk concentration, with the following equation (2).

$$kC_b = \frac{\Gamma}{\Gamma_\infty - \Gamma}\, exp\left[-2\left(\frac{h}{RT}\right)\frac{\Gamma}{\Gamma_\infty}\right] \qquad (2)$$

Where, k is the limiting adsorption coefficient for the surfactant between the interface and the bulk solution at low surface pressure, C_b is the Frumkin adsorption isotherm, h is the infinite dilution surface partial molar heat of mixing of the surfactant at the interface, R is the gas constant, T is the absolute temperature, Γ_∞ is the saturation surface excess concentration and Γ is the surface excess concentration.

Further, the Gibbs adsorption isotherm was employed to relate the surface excess concentration to the slope of the surface tension curve in relation to the true bulk concentration, employing the following equation (3).

$$\Gamma = -\frac{1}{RT}\frac{d\gamma}{dlnc} \qquad (3)$$

To get the surface tension as a function of the surface excess concentration, the above equation was integrated and Frumkin isotherm was further used to eliminate the true bulk concentration to get the following equation (4).

$$\gamma = \gamma_o + \Gamma_\infty RT\left[ln\left(1-\frac{\Gamma}{\Gamma_\infty}\right)+\frac{h}{RT}\left(\frac{\Gamma}{\Gamma_\infty}\right)^2\right] \qquad (4)$$

Where, γ_o is the surface tension of pure water

The area occupied per molecule at the surface is calculated by the following equation (5)

$$A_s = \frac{1}{\Gamma N_A} \qquad (5)$$

where, N_A is Avogadro's number

They found the following trends with their new class of surfactants with the help of the above equations and other experimental procedures. Figure 4 shows the effect of spacer on photoresponsive surfactant properties.

6. Applications of Photoresponsive Surfactants

Surfactants themselves permeate our everyday lives, as discussed before. Adding a stimuli sensitivity to light makes them a niche class of compounds with applications in a diverse range of fields from foams to drug delivery and metal detection to molecular machines.

6.1. Industrial Applications

A huge number of surfactants have been synthesized for stabilizing foams and emulsions. Obviously, emulsion stabilization is

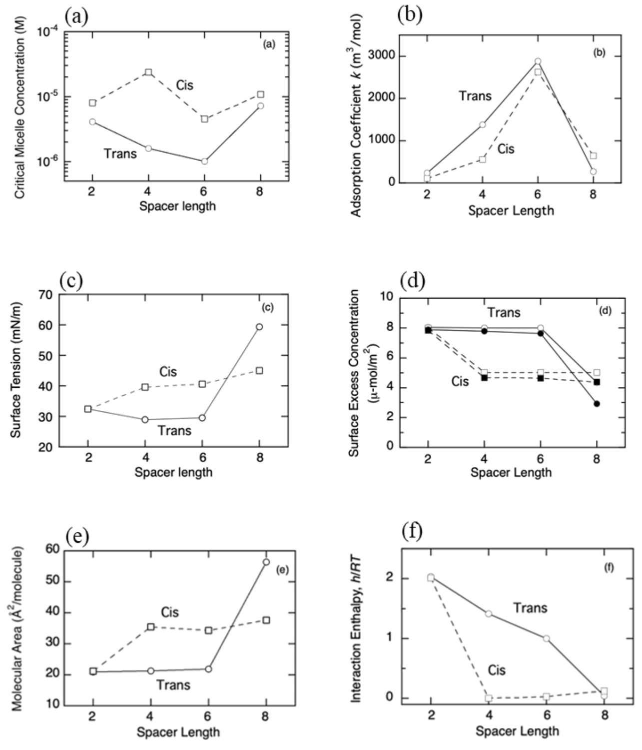

Figure 4. The variation of photoresponsive surfactant solution properties with spacer length. Circles represent properties under visible illumination (trans isomer); squares represent cis isomer properties, under UV irradiation. (a) Critical micelle concentrations; (b) adsorption coefficients, k; (c) surface tensions, γ; (d) surface excess concentrations, Γ_{cmc} (solid symbols) and $\Gamma\infty$ (open symbols); (e) molecular areas at the cmc's, $A_{s,cmc}$; (f) interaction enthalpies, h/RT. (Reused with permission).

an inherent property of surfactants and comes with the amphiphilic nature which is again an inherent part of surfactants. Introducing a photoswitch gives us the ability to stabilize and destabilize the emulsion, giving us a "switch" to turn the form "on or off." Many examples of such surfactants are available.[84,85,86,] Wang *et al.,*[32] synthesized 4-hydroxy-4'-oxoalkyl azobenzene (HC_nAzo, n = 4, 8, and 12), a class of compounds specifically to act as photofoam switch. They concluded that both photoresponsive qualities and the controllability of foam stability were impacted by the hydrophobic chain length. They reported a higher foam stability for the trans form as compared to the cis form. This dynamic behavior offers significant advantages in industrial applications where external, non-invasive triggers are essential, such as in controlled drug delivery,[87] oil recovery, smart coatings,[88] and responsive formulations in cosmetics and cleaning agents. Recent advances in the design of photoresponsive surfactants have focused on optimizing structural features to enhance their switching behavior and interfacial performance under light, providing new tools for precisely controlling multiphase systems.

Kang *et al.,*[4] synthesized new surfactants with two azobenzene groups in the structure and studied their foam and emulsion stabilizing abilities. The two surfactants synthesized were qDAZDA-0 and qDAZDA-1. For 0.1% solutions of the trans forms of qDAZDA-0 and qDAZDA-1, after 5 minutes the foam volumes were 30 and 68 ml respectively and 29 and 65 ml respectively. However, for the cis forms in the same order, it was 28 and 48 ml originally and 27 and 45 ml after they were left standing for 5 minutes respectively. They also reported a higher foam stability for the trans form as compared to the cis form. Similarly recent articles also show the foaming ability of the azobenzene as a core moiety for the surfactant.[89,90]

Kondo *et al.,*[91] reported a "hybrid" surfactant, where one hydrophobic chain was a hydrocarbon alkyl chain and the other hydrophobic chain was a fluorocarbon chain where all hydrogens of a normal alkyl chain were replaced by fluorine atoms. They reported a tunable superhydrophobic nature due to the fluorocarbon chain and a central azobenzene group. One interesting takeaway from their work was the effect of photoisomerization on surface tension, which was measured as surface tension variation ($\Delta\gamma$). They reported a surface tension variation of up to 30 mN/m for their surfactant containing the octyl-fluorocarbon chain.

Jia *et al.*,[92] did a study to explore the design and control of photoresponsive complex emulsions comprising hexane and perfluorooctane, stabilized in water by a binary surfactant system of fluorosurfactant (Zonyl FS-300) and a synthesized azobenzene-based surfactant (C_4AZOC_2TAB). The emulsion morphology, including double and Janus emulsions, was reversibly modulated by varying the surfactant ratios and applying UV or blue light. The Marangoni effect explains how light-induced changes in interfacial tension brought on by surfactant photoisomerization caused these transitions. The system provided a remote way to modulate multiphase processes by acting as a light-controlled switch to control hexane evaporation. This method offered a straightforward, expandable framework for producing stimuli-responsive emulsions that may find use in chemical processing, drug delivery, and sensing.

An important application of photoresponsive surfactants is as Phase Change Materials (PCMs) called Photoresponsive Phase Change Materials (PPCMs). Phase change materials are substances which change their phase when subjected to stimuli, the most used stimulus being heat. However, heat cannot be used as a reliable stimulus in all applications especially where heat can alter the properties of the surrounding system as well. Azo-based compounds are highly useful in these applications due to the high viability of trans-solid to cis-liquid interconversion based on light irradiation.[93]

6.2. Medical Applications

Due to light being a non-invasive stimulus, photoresponsive surfactants are gaining significant interest in medical applications, especially as drug carriers and in drug release.[94] The materials exhibit a pronounced capacity to modulate their structural configuration, optical characteristics (including color and transparency), and physical properties in response to irradiation with light of a specific wavelength. Notably, these photoinduced transformations can be either reversible or irreversible, depending on the system's molecular design and the irradiation parameters. This photoresponsive functionality enables highly controlled, site-specific, and temporarily regulated drug delivery, thereby mitigating off-target effects and enhancing therapeutic efficacy.[95,96,97]

Recently, Wang & Chen *et al.,*[11] demonstrated the viability of surfactants as drug carrier agents. They used a novel azobenzene containing cationic surfactant which formed self-assemblies with the

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drug to be carried. The drugs used for the studies were beta cyclodextrin and an antitumor drug called doxorubicin hydrochloride (DOX). They reported based on the photo stimulated behavior of the surfactant; it can act as a viable drug delivery agent as it showed a quick photo responsive drug release.

The use of photoresponsive nanocarriers (NCs) for targeted drug delivery, via either passive or active mechanisms, represents a promising approach in precision medicine.[98,99] A key concept in nanomedicine is the Enhanced Permeability and Retention (EPR) effect, which takes advantage of the distinctive features of tumor physiology, such as leaky blood vessels. These structural abnormalities facilitate the preferential passage of larger entities like NCs into tumor tissue. Additionally, tumors often have compromised lymphatic drainage, resulting in the retention and buildup of macromolecules and NCs within the tumor microenvironment. The EPR effect plays a pivotal role in the rational design and effective application of self-assembling NCs for cancer treatment. A micellar system can be designed in a way that an anti-tumor drug is encapsulated inside the micelle and which can be released upon light irradiation (figure 6).

Azobenzene and its derivatives are among the most extensively explored light-responsive chromophores, owing to their reversible photoisomerization behavior. Upon exposure to UV light, these molecules undergo a trans-to-cis isomerization around the nitrogen double bond, a process that can be reversed back to the trans form using visible light. In contrast, other chromophores such as 2-diazo-1,2-naphthoquinone (DNQ) exhibit irreversible photoreactivity, where light exposure leads to bond cleavage, transforming hydrophobic compounds into hydrophilic ones.[100] Based on these mechanisms, light-responsive polymeric micelles (PMs) are typically classified into two categories: those that undergo reversible conformational changes and those that rely on irreversible photocleavage for structural destabilization.

Poelma *et al.*,[101] introduced polymeric micelles (PMs) that respond to one-photon visible light using a reversible structural transformation approach for controlled, on-demand delivery of small molecules. They employed donor–acceptor Stenhouse adducts (DASAs), a class of photochromic compounds capable of undergoing a light-induced polarity shift from hydrophobic to hydrophilic when exposed to visible light in the 530–570 nm range. Compared to two-photon systems, one-photon responsive materials offer advantages such as more suitable activation wavelengths and higher efficiency, with DASA-based isomerization occurring at low light intensities (~1 mW cm^{-2}). In their work, DASA units were incorporated into PM structures, enabling visible light-triggered micellar disassembly and subsequent release of encapsulated small molecules into the cells.

Beyond reversible photoisomerization, light-triggered bond cleavage is another widely applied strategy in designing light-responsive polymeric micelles (PMs).[102] Saravanakumar et al.,[103] developed a biocompatible amphiphilic block copolymer, $^{1}O_2$-PEG-b-PCL, which self-assembles into PMs featuring a singlet oxygen ($^{1}O_2$)-sensitive vinyldithioether linker at the core–shell interface. Upon exposure to visible light, this linker undergoes $^{1}O_2$-mediated photocleavage, enabling the controlled release of both singlet oxygen and anticancer agents, thereby enhancing the effectiveness of photodynamic therapy. The mechanism involves the double bond of the vinyldithioether moiety reacting with $^{1}O_2$ to form an unstable dioxetane intermediate, which rapidly breaks down. Unlike traditional photoresponsive micelles that require direct UV activation, these PMs rely on $^{1}O_2$ generated under visible light during photodynamic therapy to trigger disassembly and release therapeutic cargo within tumor cells (Figure 5).

Unksov & Kasyanenko[104] did a study to explore the conformational changes in DNA upon interaction with a light-responsive cationic surfactant, azobenzene trimethylammonium bromide (AzoTAB), which undergoes reversible trans–cis isomerization under UV irradiation. Binding of AzoTAB to DNA induced compaction of the DNA strands, with the extent of this compaction strongly influenced by both the isomeric state of the surfactant and the ionic strength of the surrounding medium. At lower NaCl concentrations (0.003 M and 0.005 M), the trans-isomer promoted more pronounced DNA compaction and significant reductions in macromolecular volume and solution viscosity. In contrast, the cis-isomer also led to DNA condensation but required higher surfactant concentrations to induce comparable phase separation, and the associated changes in volume and viscosity were comparatively less marked. The photoisomerization of AzoTAB enabled reversible modulation of DNA conformation, as UV light facilitated the transition between trans and cis forms, thereby offering a dynamic and controllable method of influencing DNA structure. These findings provide key insights into the manipulation of DNA–surfactant complexes, with potential applications in gene therapy, nanobiotechnology, and the development of light-controlled biomolecular systems.

Photosensitive surfactants have also been used to increase the efficiency of enzyme action. Seidel *et al.*,[105] investigated the use of AzoTAB to enhance the activity of β-glucosidase from *Aspergillus niger*, an enzyme crucial in converting cellulose to glucose for bioethanol production. AzoTAB shifts the enzyme from dimers to monomers, increasing activity by 60%, unlike traditional surfactants, which deactivate it. Small Angle Neutron Scattering (SANS) data revealed selective unfolding of the dimer interface, reducing substrate inhibition and improving catalytic efficiency. This approach highlights a novel method for creating glucose-tolerant β-glucosidases to boost biomass conversion.

In his recent work, Wang et al.,[106] introduced azobenzene-bridged ionizable amphiphilic Janus glycosides (IAJGs). These conjugates have charged amine heads and long alkyl chains attached to the glucose rings, imparting the amphiphilic nature. These were shown to form stable nanocomplexes with plasmid DNA independently. The photoisomerization can be used to spatiotemporally control the size, surface charge, and internal order of the nanocomplex. This allowed them to achieve distinct cellular transfection results, characterized by programmable, organ-modulable pDNA delivery. This work paves the way for precision gene therapy and targeted nucleic acid delivery.

6.3. Environmental pollution detection and remediation

Environmental contamination poses significant challenges that threaten both ecosystems and human health. Addressing these challenges has led researchers to explore innovative approaches, such as using photoresponsive surfactants for environmental remediation and pollutant detection. Photoresponsive surfactants are unique amphiphilic molecules featuring a hydrophilic head and a hydrophobic tail that self-assemble into micelles. These micelles can encapsulate various hydrophobic pollutants, and upon exposure to specific wavelengths of light, the surfactants' photochromic groups undergo structural changes. This transformation can trigger the disassembly of the micelles and the subsequent release or activation of the encapsulated agents, making them potent tools for both remediation and detection.

In environmental remediation, one promising application involves the degradation of persistent organic pollutants like polycyclic aromatic hydrocarbons (PAHs) in contaminated groundwater. For instance, in 2023, Dai & Li *et al.*,[8] developed a system that combines a photoresponsive surfactant with peroxymonosulfate (PMS) to remediate PAHs. In their research, the application of a directed light beam activated the surfactant, which in turn accelerated the generation of reactive species that broke down PAHs efficiently. This approach not only enhanced degradation efficiency but also minimized adverse effects on the surrounding

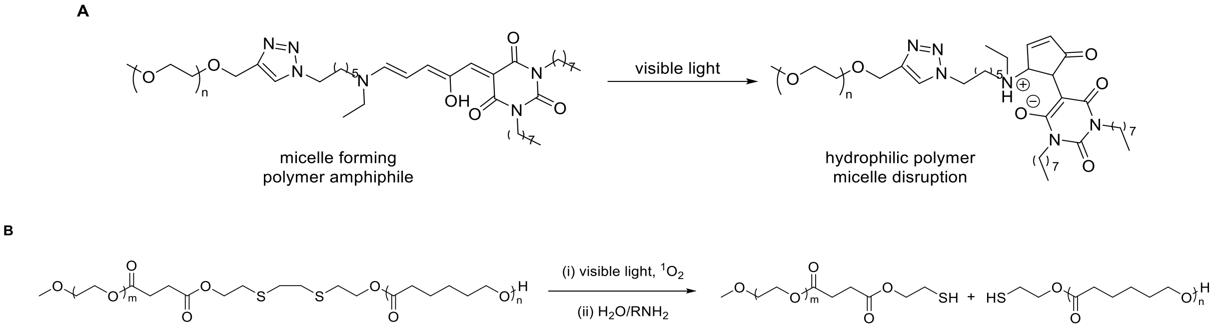

Figure 5. (A) Photoswitching of micelle-forming polymer amphiphile. (B) Light-triggered bond cleavage of $^1O_2$-PEG-b-PCL.

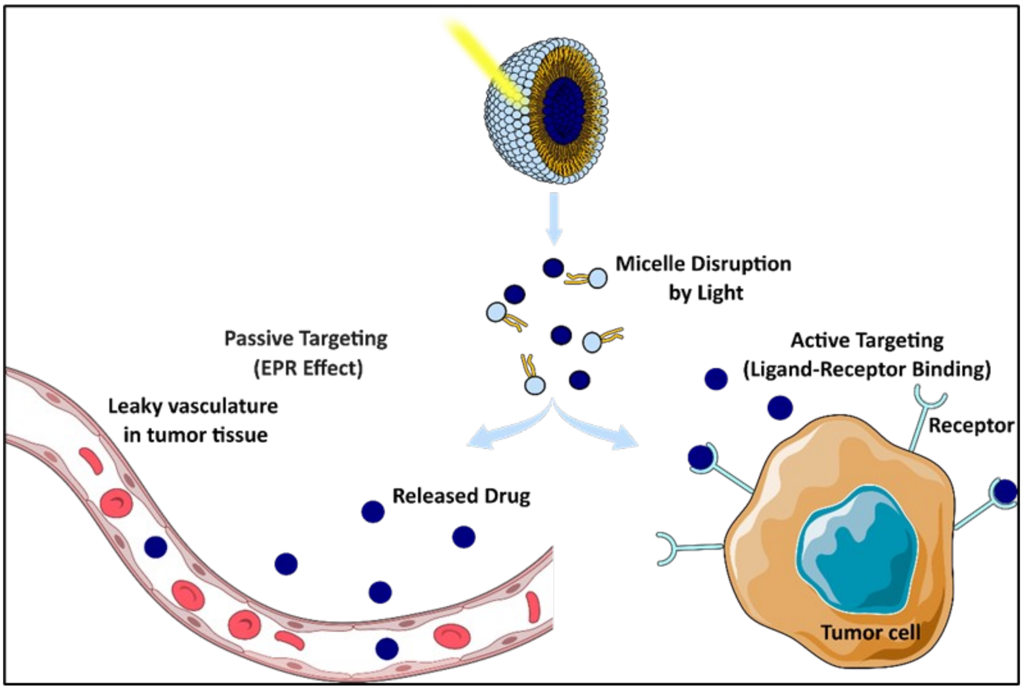

Figure 6. Photoresponsive nanocarriers enable controlled drug release through passive and active targeting mechanisms.

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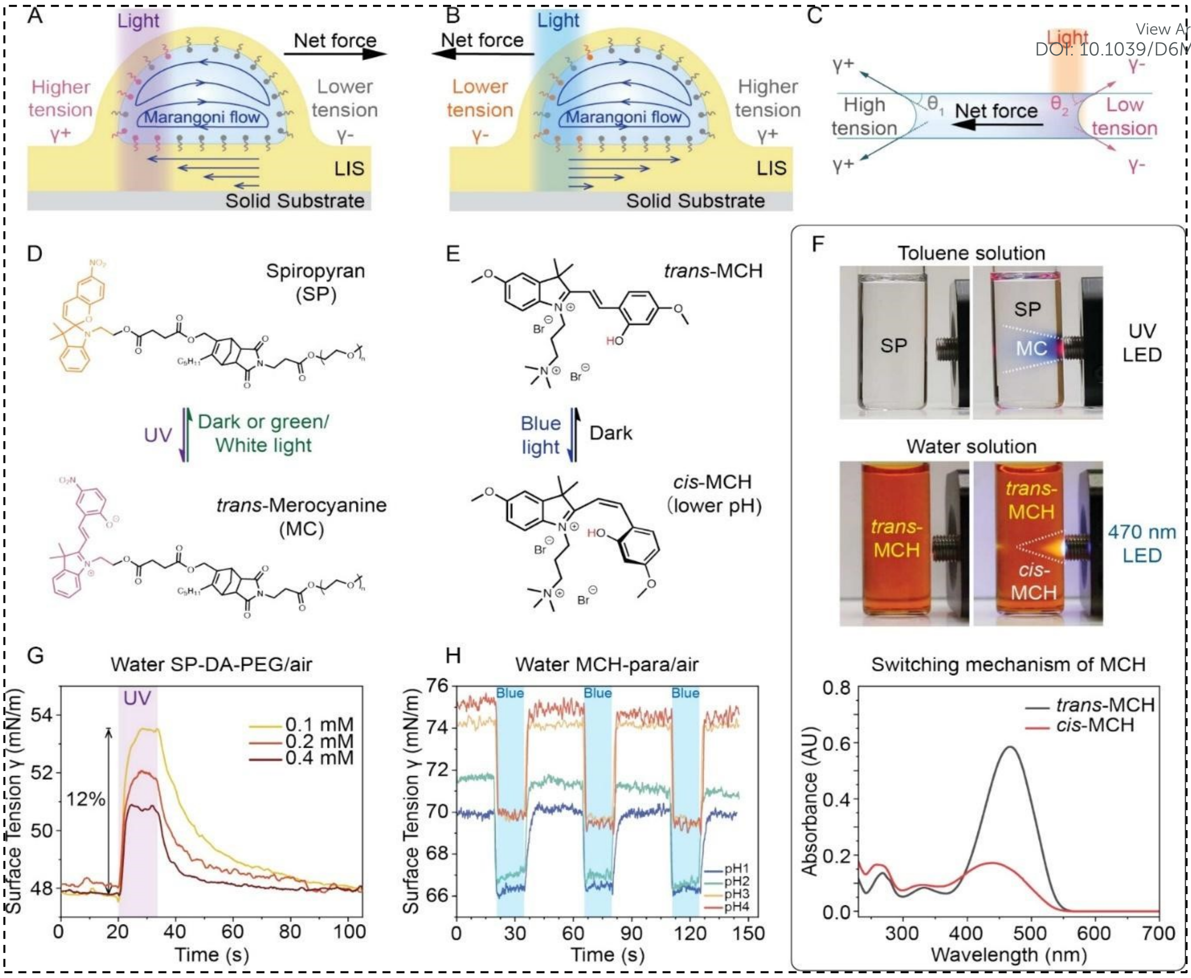

Figure 7. Mechanisms of liquid movement driven by photoresponsive surfactants, molecular structures of the photoresponsive surfactants, and surface tension response. (A) Schematic of a lubricant-cloaked droplet on a liquid-infused surface (LIS). The interfacial tension increases under illumination, causing a Marangoni flow from the unilluminated region to the illuminated region, and a net shear force away from the light. (B) Schematic of a lubricant-cloaked droplet on LIS. The interfacial tension decreases under illumination, causing a Marangoni flow from the illuminated region to the unilluminated region, and a net shear force toward the light. (C) Schematic of liquid in a microchannel or capillary tube. The surface tension changes under illumination, which results in an unbalanced total surface tension force on the liquid column and the subsequent liquid movement. Molecular structures and photoswitching of (D) SP-DA-PEG and (E) MCH-para. (F) The change of color of SP-DA-PEG in toluene under UV illumination and MCH-para in aqueous solution (phosphate buffer, pH 3) under 470 nm illumination. UV–vis spectrum demonstrating the switching mechanism of MCH-para in aqueous solution (pH 1).(G) Surface tension response of SP-DA-PEG in water under UV (365 nm) illumination with an optical intensity of 37.1 mW/cm^2 . (H) Surface tension response of MCH-para in water at various pH levels under blue light (470 nm) illumination with an optical intensity of 31.8 mW/cm^2.[37]

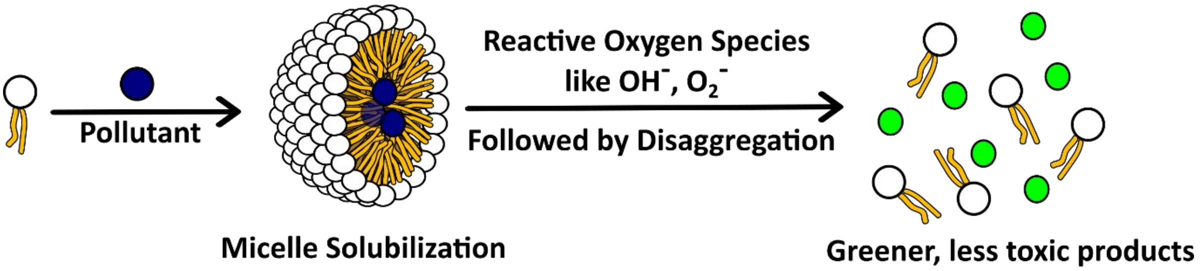

Figure 8. Mechanism of pollutant conversion into green products through ROS generation by photoresponsive surfactants

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ecological systems by leveraging a controlled light-triggered activation mechanism. Beyond remediation, photoresponsive surfactants also offer significant promise in pollutant detection. When integrated into sensor platforms, these surfactants can provide real-time detection signals through changes in optical properties such as shifts in fluorescence or absorbance triggered by micellar assembly or disassembly. The dynamic behavior of the micelles allows for the encapsulation of pollutants followed by a light-induced release, which can serve as a measurable signal for pollutant presence. This dual function, capturing and then signaling, improves the sensitivity and accuracy of environmental monitoring systems. Such capabilities were further emphasized in a comprehensive review by Saxena *et al*.,[107] which discussed the versatility of surfactant-based approaches in removing contaminants ranging from heavy metals and dyes to pesticides through enhanced photo-induced micellar solubilization.

However, while the benefits are clear, the potential toxicity and environmental impact of surfactants must also be addressed. Badmus *et al*.,[108] highlighted the importance of evaluating the fate of both surfactants and their degradation products to avoid secondary contamination. Their analysis underscores the need for developing biodegradable and eco-friendly surfactants that maintain high remediation efficiency without adverse environmental footprints (Figure 8).

The unique structures and different chemical moieties in these molecules give them a few very intriguing properties in terms of binding with other molecules via non-covalent interactions. Dai & Duan *et al.,*[38] synthesized a conventional surfactant, 4-[4-[(4-butylphenyl)azo]phenoxy]butyldimethylethylammoniumbromide (AzoPB) and a gemini photoresponsive surfactant N^1,N^2-bis[4-[4-[(4-butylphenyl)azo]phenoxy]butyl]-N^1,N^2-tetramethyl ethane-1,2-diammoniumbromide (AzoPBT). These two surfactants were studied in relation to phenanthrene and acenaphthylene, two common polyaromatic hydrocarbons which pollute groundwater. The surfactants were studied in relation to their properties of solubilizing these hydrocarbons via self-assembly modes and being able to dissipate these hydrocarbons on the subsequent destruction of those self-assemblies which would be facilitated by the photo responsive azobenzene group. They found out that the Gemini surfactant was significantly better than the conventional surfactant in terms of surface activity, recyclability, reducing the hydrophobicity of the hydrocarbons and subsequently solubilizing them, the ability to release the solubilized hydrocarbons, and hence they concluded the Gemini surfactant was superior in relation to the conventional surfactant in this area of applications.

Surfactants are also known for their metal detection activities as shown by Xie & Wu *et al*.,[13] They synthesized a surfactant which was able to selectively detect Hg(II) ion which is detectable by UV spectroscopy studies in the form of a characteristic UV-Vis signal change in the band around 240 nm and this change was visible over a wide range of pH. Additionally, the surfactant was water soluble owing to its cationic head, making it an attractive option for mercury detection in water. Photoresponsive surfactants merge the capabilities of advanced pollutant detection and targeted remediation, paving the way for next-generation environmental cleanup technologies.

6.4. Motion Manipulation

The precise manipulation of colloidal particles within microfluidic environments is a central challenge in soft matter and biomedical applications. Recent advances have demonstrated the integration of optically tunable flow mechanisms using photo-responsive surfactants to achieve fine control over fluid motion. One such approach utilizes a gold surface in aqueous media, coated with a photosensitive surfactant and irradiated by a focused UV laser. This setup induces two distinct interfacial flow regimes arising from diffusion-osmosis and thermo-osmosis.

At lower laser intensities, diffusio-osmotic flow dominates due to localized photoisomerization of the surfactant molecules, driving this optofluidic strategy offers a highly controllable platform for the dynamic regulation of microscale flow fields, presenting significant potential for targeted particle transport, on-demand assembly, and programmable microfluidic operations in next-generation lab-on-a-chip technologies.[109]

Recent advances demonstrate versatile light-controlled manipulation of microscopic droplets—including wetting, splitting, merging, and transport—using photoswitchable azobenzene-based surfactant films. These adaptive surfaces, formed by ionic assembly of azobenzene surfactants with oppositely charged polymers, undergo reversible trans–cis isomerization under light irradiation. This induces dynamic changes in surface energy, orientation of surfactant tails, and local temperature, enabling precise, reversible control over droplet behavior. Notable outcomes include a fivefold increase in droplet basal area, directional wetting, and controlled droplet locomotion at velocities up to $150\ \mu m \cdot s^{-1}$. This approach presents a promising platform for programmable, contactless microfluidic operations.[110]

A very interesting work was recently published in 2024 by Luzzatto-Fegiz, Alaniz & Zhu *et al.,*[37] which talked about the dynamic manipulation of a water droplet on surfaces. The group used photo responsive surfactants for their surface acting properties and photo switchability to show 2D motion of water droplets on a liquid infused surface as well as rectilinear motion in capillary tubes. The surfactants they designed were based on spiropyran and merocyanine in which were interestingly capable of surface tension changes of up to 5.5 mN/m on very short time scales of about 1.7 seconds. They were able to move a millimeter sized droplet with a speed of up to 5.5 mm/s on liquid and 0.25 mm/s on a liquid infused surface (Figure 7).

While the manipulation of colloidal droplets or synthetic microbeads is certainly impressive, Umlandt et al.,[111] took it to the next level by demonstrating the manipulation of living microorganisms using a simple azo-based surfactant. It proves that the technique is non-invasive and gentle enough to sustain biological entities. They used light to trigger the characteristic isomerization of azobenzene, which created an osmotic pressure gradient that pulled the liquid and the bacteria within it toward the light, demonstrating light-driven diffusioosmotic (LDDO) flow. This, of course, has implications for programmable micro-bioreactors or light-controlled environmental remediation, where blooms of cyanobacteria can be removed from water samples using light and smart surfactants.

6.5. Catalysis

Owing to their stabilization properties and micelle formation, surfactants are seeing an increased level of application in catalysis. Many of these properties arise from their mode of action being like

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that of phase transfer catalysts due to the stabilization of a mixture of phases by surfactants and the tunable stabilization-destabilization by photoresponsive surfactants without using any chemical additives. Micelles function as heterogeneous nanoreactors, with a hydrophobic interior and a hydrophilic exterior, all suspended in a seemingly uniform aqueous environment.[112] Their structure enables the solubilization of both organic reactants and catalysts, primarily through interactions like hydrophobic forces[113] and ion pairing.[114]

Blayo *et al.*,[115] studied the effect of micellar size and shape on micellar catalysis of a model Claisen–Schmidt aldol condensationreaction by cationic azobenzene trimethylammonium bromide (AzoTAB) in water. They concluded that the reaction efficiency depended on the ratio of micelle volume to the micelle–water interfacial area (the Stern layer), with compact, spherical micelles, shown by cis-AzoTABs, showing enhanced reaction yields. Trans- AzoTAB forms ellipsoidal micelles which showed lower reaction yields. They also concluded that the reaction occurred at much lower temperatures of 35 °C and milder conditions than conventional setups (Figure 9).

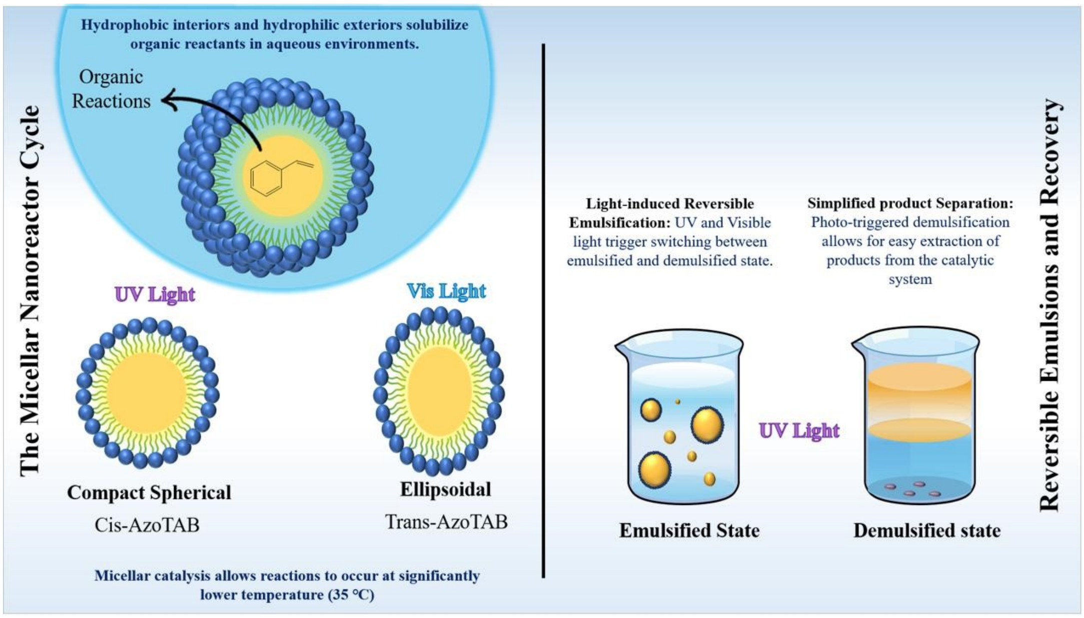

Figure 9. Light controlled micellar nanoreactors enable reversible emulsification and efficient catalytic reactions with easy product recovery.

Li *et al.*,[116] developed oil-in-water Pickering emulsions for catalysis. A light-responsive Pickering emulsion was developed using Pd-loaded silica nanoparticles, an azobenzene-based ionic liquid surfactant, *n*-octane, and water. UV and visible light caused this emulsion to undergo reversible emulsification and demulsification, which was attributed to the azobenzene surfactant. The system enabled catalytic hydrogenation at ambient conditions, while also allowing for product separation and reuse of both emulsifier and catalyst. Catalysis using photoresponsive surfactants is still a very new field of work and consistent efforts are being made by many groups to find new information every day.

Similarly, many other photo responsive surfactants have been widely used in a variety of different fields, the mention of all of which is not very feasible due to a wide array of fields and applications covered. But anywhere from engines to drugs, from biological systems to water purification, from lithography to sensors, surfactants and more specifically photo responsive surfactants are present and have started to be employed actively in the industry.

6.6 Harnessing Solar Energy

Krishna et al.,[117] introduced the first class of visible-light responsive solar thermal fuels (STFs) based on liquid crystals, utilizing a series of azobenzene and cholesterol-based surfactants that exhibit enantiotropic chiral nematic mesophases. This LC-based approach helped them overcome the drawbacks of solid-state STFs, like light scattering and nonuniform heat release, by introducing self-organized and self-healing thin films. They achieved a maximum solar charging efficiency of 70% and a record thermal half-life of 110 days for ortho-fluoro substituted derivatives. Additionally, the transition through multiple phase states during discharging yielded a macroscopic heat release of 5.4 °C, a significantly larger amount than previous attempts.

In a recent study, Jones et al.,[118] were the first to use lyotropic liquid crystals (LLCs) for Molecular Solar Thermal (MOST) energy storage. The authors drove the self-assembly of azobenzene photo-surfactants into highly ordered liquid crystalline phases through a sparing addition of solvent. This helped reduce the steric hindrance that usually stops photoisomerization in rigid solid-state systems. They used small-angle X-ray scattering (SAXS) and in situ differential scanning calorimetry (DSC) to show that these light-responsive LLCs allowed isomerization without considerable hindrances. This work demonstrated a record energy storage density of 123 J/g. This hybrid method works well because it combines the high isomerization efficiency of liquids with the structural benefits of solids. This makes it a very interesting framework for the next generation of solar fuels.

Chen et al.,[119] recently addressed the environmental concerns of lipophilic STFs, which use toxic organic solvents to function, by developing a family of water-soluble azobenzene derivatives (WASTFs) through a one-step quaternization strategy. These use the intra- and intermolecular cation-π interactions to stabilize the cis isomer. This resulted in a thermal half-life of more than 30 days and a maximum energy density of 143.6 J/g. The authors showed a 2.5-fold increase in storage enthalpy compared to neutral analogues.

7. Future Outlook

The field of photo-responsive surfactants has grown from a niche academic curiosity into a rapidly expanding area of material science with significant potential. While substantial progress has been achieved, the next phase of development must address several unresolved scientific and technological challenges to enable the translation of laboratory-scale concepts into functional, real-world applications. Despite the wide range of demonstrated applications, critical gaps remain in mechanistic understanding, molecular design, and system-level integration, which must be systematically addressed to fully realize their practical potential.

An obvious path forward is the diversification of the photo-responsive core. Although azobenzene continues to dominate due to its synthetic accessibility and reliable switching behavior, its applicability, particularly in biological contexts remains limited. A key unresolved issue is the incomplete understanding of how cis-trans isomerization pathways are influenced by complex environments, such as micellar assemblies, interfaces, and biological media, where deviations from idealized behavior are frequently observed. Furthermore, systematic comparative studies between azobenzene and alternative photoswitches remain scarce, hindering the establishment of universal design principles. In response, increasing attention is being directed towards red-shifted photoswitches such as spiropyran, diarylethene, and hemithioindigo, which enable activation using visible or near-infrared light. While these systems offer clear advantages, challenges related to their long-term stability, fatigue resistance, and switching efficiency under practical conditions remain insufficiently explored.

The development of multi-stimuli responsive surfactants represents another emerging direction, where light, pH, temperature, and other environmental triggers are combined to achieve enhanced control. However, the interplay between multiple stimuli is not yet fully understood, particularly in terms of synergistic versus competing effects in complex systems. In parallel, increasing attention must be paid to the environmental impact and lifecycle of these materials, especially for large scale or industrial applications. The design of inherently biodegradable and environmentally benign photo-responsive surfactants remains a significant unresolved challenge. Orthogonal photocontrol, achieved through the incorporation of multiple photoswitches within a single molecular framework., offers exciting opportunities for wavelength-selective and sequential control of processes. Nevertheless, precise control over cross reactivity and spectral overlap remains a key limitation that must be addressed.

In the context of biomedical applications, particularly drug delivery, photoresponsive surfactants have demonstrated considerable promise. However, their translation to in vivo systems is still limited by insufficient understanding of biocompatibility, toxicity, and long-term stability under physiological conditions. the integration of therapeutic and diagnostic functionalities represents a logical progression, yet challenges remain in achieving reliable, real-time monitoring without compromising system performance. Beyond biomedical applications, photo-responsive surfactants hold potential in soft matter systems, including self-healing materials, hydrogels, and microfluidic devices. While these concepts are highly promising, their practical implementation is constrained by limited control over spatiotemporal responsiveness and system robustness under repeated cycling conditions. recent advances in computational approaches, including Density Functional Theory (DFT) and machine learning, offer powerful tools for molecular design. However, their predictive capabilities are currently restricted by limited experimental datasets and the absence of standardized structure property relationships, necessitating closer integration between computational and experimental efforts. A major bottleneck for industrial translation remains the reliance on multistep, time-consuming, and costly synthetic routes, which hinder scalability and widespread adoption. The development of efficient, cost effective, and scalable synthetic strategies, along with the incorporation of green chemistry principles, remains an urgent and unresolved priority.

Overall, the future of photoresponsive lies in addressing these fundamental challenges while advancing towards increasingly complex, functional, and application-oriented systems. The coming decade is expected to witness a transition from primarily curiosity-driven research to rationally designed, robust, and scalable systems, capable of addressing real-world problems in medicine, material science, and environmental technology.

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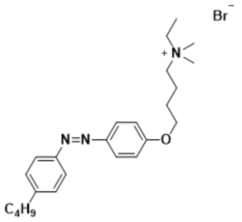
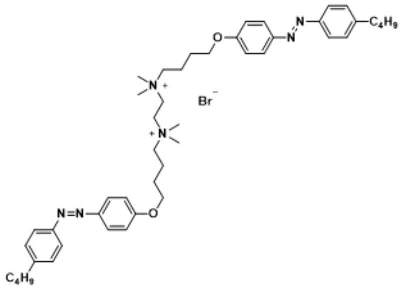
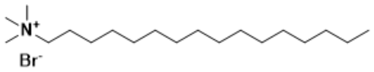
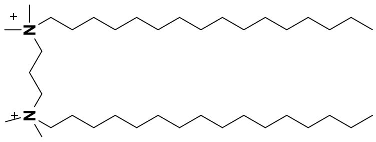
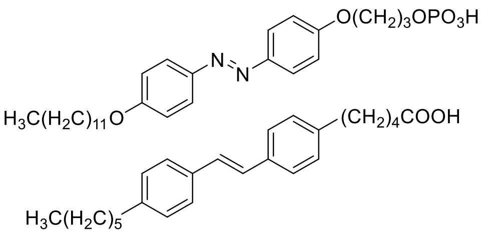
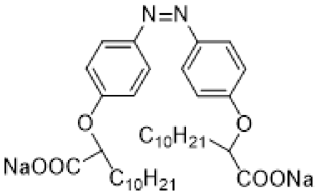
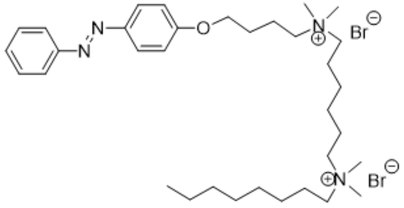
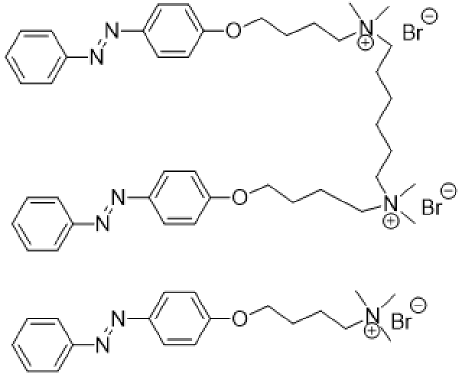
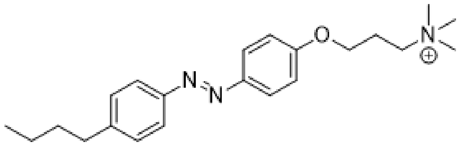
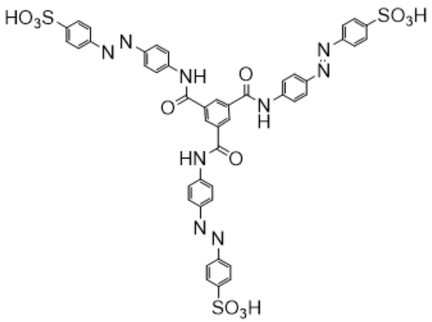
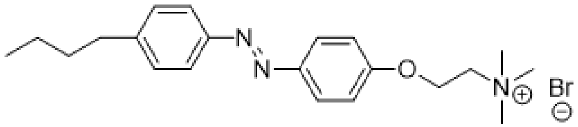
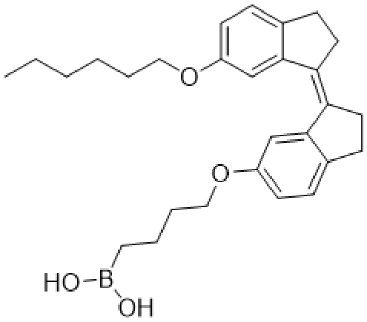
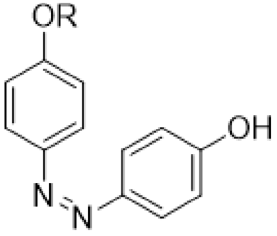
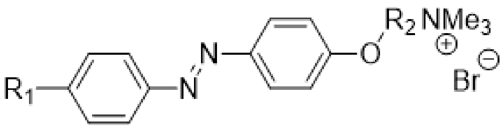
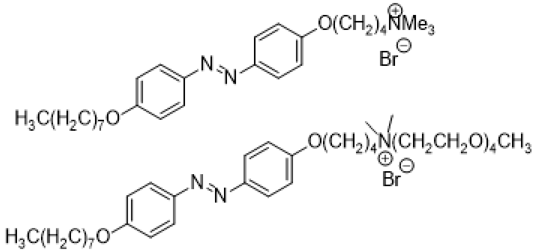
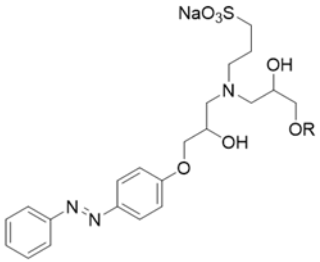
S. No.	Structure	CMC (mM)		Surface Tension (mN.m^{-1})
		Conventional Surfactant	Gemini Surfactant	
1.		Trans- 0.98 mM Cis- 1.15 mM	-	Trans- 33.06 mN.m^{-1} Cis- 37.39 mN.m^{-1}
		-	Trans-0.52 mM Cis-0.53 mM	Trans- 28.94 mN.m^{-1} Cis- 31.69 mN.m^{-1}
2.		1 mM		30-40 mNm^{-1}
			0.02 mM	35-40 mNm^{-1}

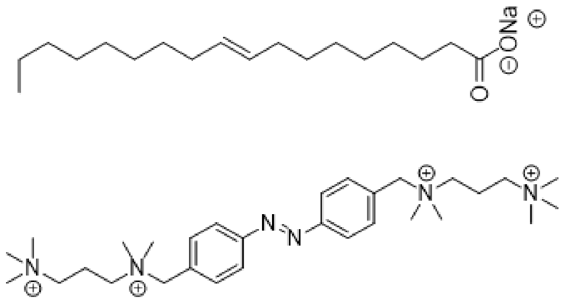
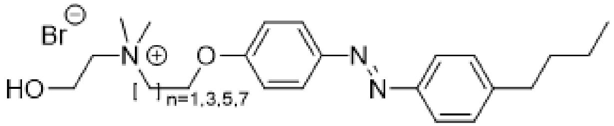
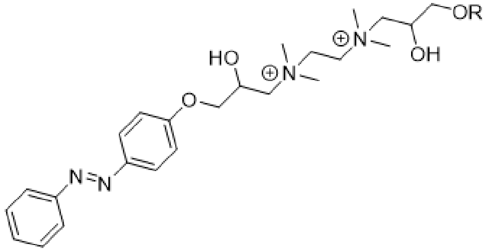
Table 1. The difference in the CMC and Surface Tension of conventional and gemini surfactants.[89,39]

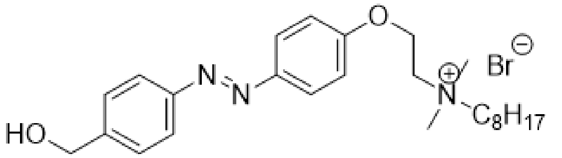
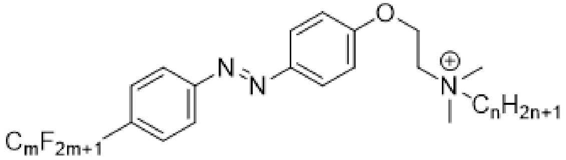
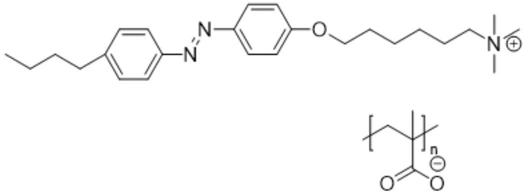
S. No.	Structure	Key Points	Applications	Ref.
1.		Compares azobenzene and stilbene surfactants as dopants in DHP bilayer membranes. They produce opposite effects on potassium ion (K+) permeability.	Model systems for photoregulated ion channels. Controlled release of ions or drugs. Creating nanodevices with opposing, light-controlled functions.	41
2.		Trans state promotes creates a high-viscosity (gel-like) fluid. Cis state converts system to a sol state.	Photorheological fluids (light-controlled viscosity). Switchable "smart" materials.	44
3.		The spacer length is crucial. The largest light-induced change in CMC was seen with moderate spacer length (n= 3,4), not the shortest one (n=2)	Light-controlled surface tension modification.	120

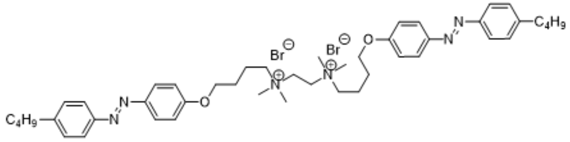
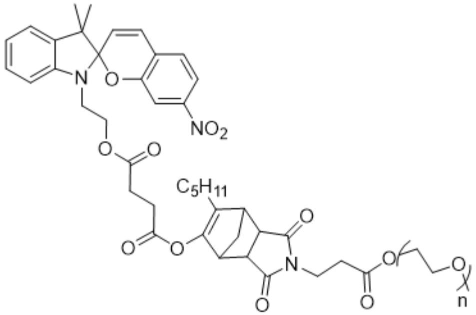
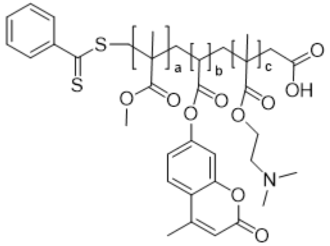
				
4.		Demonstrates a "pumping-out" mechanism where light irreversibly removes surfactant from the air-water interface.	Light-induced, irreversible destabilization of foams and emulsions.	24
5.		The surfactant acts as both a stabilizer (capping agent) and a shape-directing agent during the synthesis of gold nanoparticles (AuNPs).	Photocontrol of nanoparticle morphology. Fabricating materials with tunable plasmonic properties.	2

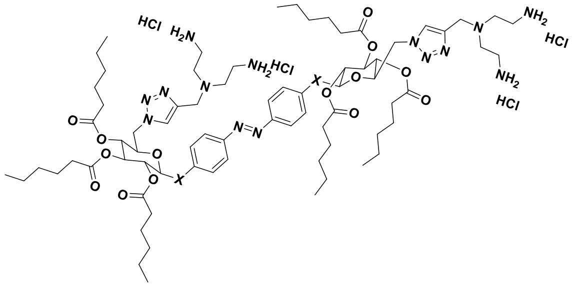
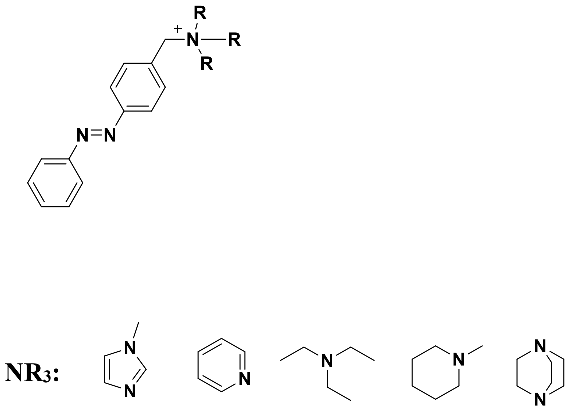
6.		Demonstrates reversible "catch-and-release" of Polycyclic Aromatic Hydrocarbons (PAHs).	Removing toxic PAH pollutants from water. Controllable release systems for hydrophobic "guest" molecules.	1
7.		The trans molecule forms heterodimers, which effectively transport protons through a lipid bilayer. The cis isomer disrupts this dimerization, significantly inhibiting proton transport.	Artificial, light-controlled ion channels. Photoregulation of pH inside vesicles or liposomes.	30
8.		The tail length is crucial. Longer-chain surfactants (C_{10}, C_{12}) showed the most significant and effective light-control over foam stability.	Light-controlled foaming and defoaming agents for industrial processes.	32

9.		Spacer length is more dominant than tail length in controlling the trans isomers self-assembly. Short spacer (n=3) forms small, spherical micelles regardless of tail length. Long Spacer (n=11) forms large, ellipsoidal/wormlike micelles, especially with longer tails.	Smart materials with predictable, light-controlled nanostructures.	121
10.		Instead of affecting the main, strong π-π* band (~350 nm), Hg²⁺ binding specifically interacts with and enhances the very weak n-π* transition band (~436 nm).	Selective and colorimetric detection of Hg²⁺ ions in aqueous solutions.	13
11.		Incorporated an azobenzene group and a sulfonic acid headgroup. The series varies the hydrophobic tail length.	Photo-switchable foaming agents.	34

12.		Used a light-switchable "pseudo-tetramer" assembly as the builder for the wormlike micelles, offering a new route to photorheological fluids.	Switchable "smart" gels and materials.	122
13.		A Pickering emulsion, stabilized by solid nanoparticles (Pd@SiO$_2$), and light-responsive surfactants.	Phase-transfer catalysis, acting as a nanoreactor.	116
14.		The gemini structure results in exceptionally low CMCs compared to similar conventional photosurfactants.	High-efficiency, photo-switchable wetting agents.	26

15.		Forms vesicles (bilayers), not just simple micelles in solution. These are further loaded with anticancer drug doxorubicin (DOX).	On-demand, site-specific drug release.	11
16.		The hybrid surfactant shows superior surface activity (lower CMC, lower surface tension) than either of the pure hydro or pure fluoro chain versions, due to the unique packing of the two different tails.	Light-controlled foaming and emulsification (especially for fluorinated systems).	91
17.		Demonstrates reversible, high efficiency solubilization of PAHs.	Remediating PAH-contaminated groundwater.	4

18.		Provides multi-stage, stepwise photocontrol (trans-trans to cis-trans to cis-cis). This stepwise isomerization allows for a wider and more tunable range of properties.	Photo-switchable foaming agents with tunable foam stability.	39
19.		Uses a photoresponsive surfactant inside an aqueous droplet placed on a Liquid-Infused Surface (LIS/SLIPS). Achieves precise, dynamic manipulation (movement) of the droplet using only light employing Marangoni effect.	Microfluidics / Lab-on-a-chip with light-based pumps. Micro-cargo transport using droplets as light-guided carriers.	37
20.		A triple-stimuli-responsive polymer, responding to temperature, pH, and light, that forms reversibly cross-linked micelles.	Smart nanocarriers for targeted cancer therapy	51

21.		Each glucose scaffolds is functionalized with specific components to facilitate gene delivery: ionizable headgroups that electrostatically interact with pDNA, and lipophilic tail that drive self-assembly. This "Janus" design having distinct polar and non-polar faces enables the molecule to form stable, single-component nanocomplexes with nucleic acid.	Light-responsive, single-component molecular vectors for the spatiotemporally controlled and organ-selective delivery of plasmid DNA (pDNA) in gene therapy	106
22.		Ionic groups are added to the structure to make the fuel water-soluble. Internal cation-π interactions help the fuel store more energy for over 30 days.	Water-soluble solar thermal fuels show great potential for fabricating advanced solar energy storage devices that capture and store solar energy to be later released as heat.	119

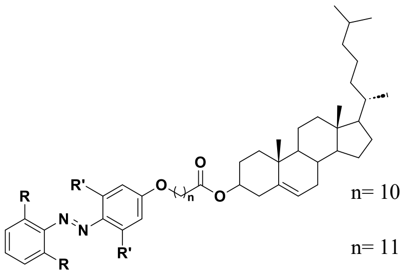
23.	 n= 10 R= R' = F, Cl n= 11 R= R' = H, F, Cl R= F, R'= Cl	The molecular design incorporates an alkyl spacer of varying lengths (n= 10, 11) connecting the two moieties, along with ortho-substitutions on the azobenzene ring to modulate the materials properties and changing efficiency	These liquid crystal-based solar-thermal fuels can be integrated as coatings for solar blankets, deicing systems, and functional fibers to provide on-demand heat release	117

Table 2: Structure of azobenzene containing surfactants with various applications

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Author contributions

Mittal Gunjan Lokesh and **Shivank Sharma** contributed equally to this work and share first authorship. Both authors were involved in literature survey, conceptualization, writing, and revision of the manuscript. **Amit Kumar Tiwari:** conceptualization, validation, resources, writing– review & editing, visualization, and supervision.

Conflicts of interest

There are no conflicts to declare.

Data availability

No data were used for the research described in the article

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