Physicochemical and Biological Characterisation of Azobenzene-Containing Photoswitchable Surfactants

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Thomas completed his BSc with Honours at Monash in 2014 under the supervision of Dr Rico Tabor looking at the magnetic recovery of graphene oxide nanosheets for water purification, and returned to the Soft Materials and Colloids lab in 2015 to commence his PhD. His work explores the fundamental interactions between 2D nanomaterials and molecular surfactants, with a particular focus on small-angle neutron scattering and atomic force microscopy to understand self-assembly phenomena in complex systems. His research has been featured in The Australian newspaper along with various online news sources.

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Yingxue received her BEng Degree in Printing Engineering from Hangzhou Dianzi University (China) in 2008. She studied material science at University College London (United Kingdom) where she received her Master of Science with Distinction in 2013. From 2014–2017, she undertook her PhD studies at Monash University under Dr Brendan Wilkinson and Dr Rico Tabor. Her PhD research focused on the synthesis and characterisation of stimuli-responsive carbohydrate materials, from novel amphiphiles to complex glycodendrimers. Yingxue now works in the pharmaceutical chemical industry.

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Brendan completed his undergraduate and PhD degrees at Griffith University, Brisbane, Australia, under the supervision of Prof. Sally-Ann Poulson. He then undertook a post-doctoral position at the University of Oxford with Professor Antony Fairbanks, and a further post-doc at The University of Sydney with Professor Richard Payne. Brendan was awarded an ARC DECRA fellowship in 2012, and was later appointed as a Lecturer at Monash University. He moved to the University of New England, NSW in 2016, where he is a Lecturer in Organic Chemistry. His research interests focus on supramolecular assembly of stimuli-responsive carbohydrate and glycopeptide amphiphiles, and dynamic carbohydrate macrocycles with drug delivery applications.
Abstract
Surfactants are a versatile and widely used class of molecules, due to their valuable adsorption and self-assembly properties. In particular, surfactants that can respond to stimuli are of interest in modulating wetting, controlling delivery, and exploring mechanistic aspects of biological processes. Incorporating azobenzene into surfactants is a classic approach to rendering molecules that respond to light as an external stimulus; these molecules find wide utility in the precise spatio-temporal control of dispersed systems, from DNA to graphene. More recently, the creation of diverse libraries of such molecules has been achieved by coupling azobenzene-containing hydrophobic tail-groups to hydrophilic carbohydrate head-groups. Such a synthetic strategy offers fine control over adsorption and aggregation, as evidenced by physicochemical characterization of these molecules, uncovering rich phase behavior and diverse biological responses. This article covers recent advances in the field of both ‘traditional’ and new azobenzene-containing photosurfactants, and offers directions for future study and use of this unique class of molecule.

Keywords: Photoswitchable surfactant | Azobenzene | Photoisomerisation

1. Introduction
Responsive surfactant molecules offer unique advantages in the study of physicochemical processes, whereby an internal or external stimulus can be used to elicit a response in the system. Adding molecules that respond to internal stimuli such as changes in pH or ionic strength generally mean that the system passively responds to an internal change, a crude example of which is the function of buffer molecules to maintain constant pH; indeed, pH responsive surfactants can be used to control colloidal stability and biological processes. Molecules that respond to external stimuli are generally added to enable response to an externally applied trigger on demand, and such triggers generally take the form of thermal, magnetic or light-responsive species. Of these stimuli, light is particularly appealing as it is comparatively low energy, can be applied in a highly spatially and temporally resolved manner, and photochemical processes (particularly isomerisations) are generally fast and high yielding. In this regard, light is sometimes referred to as a ‘green’ chemical reagent.

There are two main ways in which light can be used to effect changes in chemical systems: photochemical reactions (such as the formation of new bonds, or photolysis of existing bonds), or photoisomerisations (e.g. trans–cis changes of a double bond). When applied to an appropriately synthesised surfactant molecule, photochemical bond breaking allows the most significant changes in system properties to be obtained, as the surfactant can be severed into its constituent head and tail portions, rendering fragments that are no longer surface active. The drawback of this process is that it is irreversible, meaning that the original state of the system cannot be recovered. Changes offered by photoisomerisation reactions, such as the often-utilised trans–cis isomerisation of azobenzene offer significantly more subtle physical effects, but have the advantage of reversibility without loss of function. The remainder of this article will focus on recent advances in the synthesis and application of photoisomerisable surfactants.

Of the available photoisomerisable chromophores that can be incorporated into surfactant structures, azobenzene has been the most widely used. This is likely due to its facile synthesis, accessible isomerisation wavelengths in the visible and near-UV range, and ease of substitution for chemical and photochemical tuning from the raft of extant dye literature. Other chromophores such as stilbenes and spiropyrans have seen some use, although their high energy isomerisation wavelengths and complex synthesis (respectively) potentially limit their popularity compared to the ubiquitous azobenzene group.

Azobenzene was first incorporated into a surfactant geometry to intentionally obtain a surface active species in 1980 by Kunitake et al., demonstrating that such molecules exhibited different aggregate morphologies in their trans- and cis-dominated states. Tazuke et al. later showed that such molecules could variably affect surface tension due to their surfactant structure and isomeric states, and these early works spawned a new field of surfactant research. Work by Yang et al. concerning the thorough physicochemical and spectroscopic characterisation of these molecules demonstrated the extent of changes that occur during photoswitching.

Since these pioneering works, a large body of research has emerged, focused on the synthesis, characterisation and application of photosurfactants, with some recent developments summarized below.

Mixtures of azobenzene surfactants with other stabilisers or polymers can offer tailored approaches to system control. For example, Jiang et al. showed that micelles with dual response to carbon dioxide/nitrogen and light could be prepared by mixing an azobenzene surfactant with an amine-containing surfactant. Recent work has shown that a supramolecular gelator could be obtained through mixing an azobenzene surfactant with a poly(etheramine) surfactant, for enhanced and light-controlled foaming, or fibrous gels. Controlled fusion within lipid systems was recently demonstrated by doping in a small amount of cationic photosurfactant by Suzuki et al., and control of oil droplet motion could be achieved in mixtures of a conventional cationic surfactant and azobenzene gemini surfactant by Kaneko et al.

There is growing interest in the control of bubbles and foams with photosurfactants: recently, both nonionic and ionic azobenzene surfactants have also recently been applied to provide photo-control of the froth flotation of mineral particles and to control bubble stability. Similarly, the stability of droplets in emulsions can be controlled by using a cationic gemini photosurfactant. It was previously shown that fluorination of counterions had a significant effect on the assembly of azobenzene molecules. Recently, it has been seen that coupling azobenzene covalently to fluorinated chains offers new opportunities in amphiphile design, with the development of novel light-responsive layered materials.

Ionic self-assembly also provides a facile route to complex nanostructured materials. However, more recently nanoarchitectonic approaches have taken centre stage, whereby the concepts of nanoscale building blocks and supramolecular self-assembly combine to build complex or structured materials.
Here, azobenzene-containing molecules offer unique control opportunities whereby light can actuate sensors or surface phase separations. This is particularly advantageous in the creation of stimulus-responsive self-assembled monolayers.\textsuperscript{30} Attachment of such molecules to gold nanoparticles enabled a unique photomagnetic effect.\textsuperscript{31} Recent work by Martin et al. showed that an azobenzene surfactant could be employed to impart photo-control over solid-phase nanostructured particles.\textsuperscript{32} Indeed, incorporation of azobenzene into biopolymers allows for exquisite control in their folding, such as in DNA origami.\textsuperscript{33}

Specific advances in the field of photo-responsive surfactants have been reviewed in several recent works.\textsuperscript{1,34,35} Here we will focus on developments since these works, and their context within the broader literature on photo-responsive surfactant systems.

2. Molecular Architecture

The synthesis of photosurfactants is generally somewhat more complex than that of conventional surfactants, usually requiring several more steps to prepare the chromophore and incorporate it into a surface active architecture.\textsuperscript{12,36} For azobenzene molecules, a symmetrical or asymmetrical azobenzene core is generally pre-assembled bearing terminal hydroxyl moieties, which can then be readily coupled to a variety of linkers, such as alkyl groups (via displacement of a halide from a terminally halogenated alkane\textsuperscript{12,37}) or oligo(ethylene glycol) units via ether formation.\textsuperscript{36,38} This versatility allows complex molecular structures to be built up with robust and high-yielding synthetic steps, and has been used to create a variety of azobenzene-containing surfactants, from quaternary ammonium bromide single chain cations,\textsuperscript{12,37} to single chain non-ionic,\textsuperscript{38} anionics,\textsuperscript{39} bolafoil structures,\textsuperscript{40} gemini molecules,\textsuperscript{41} and complex glycodendrimers.\textsuperscript{42}

Recently, this same strategy has been applied to prepare a diverse library of different molecules with carbohydrate functionalised head-groups,\textsuperscript{36,43,44} as shown in Figure 1. In this case, it was found that an intermediate tri(ethylene glycol) spacer unit was required in order to render the molecules with sufficient flexibility and water solubility. Coupling between a tri(ethylene glycol)-functionalised butylazobenzene tail-group and the carbohydrate head-group was achieved through either Lewis-acid promoted glycosylation, or copper-mediated ‘click’ chemistry between terminal alkyne and azide groups, to render an intermediate triazole linkage. Such a modular synthesis enabled rapid prototyping of a considerable range of molecules in short order, facilitating the investigation of structure–function relationships for this new class of molecule.\textsuperscript{36}

The appeal of carbohydrates as head-groups is manifold: as well as being biodegradable and available from biological feedstocks, they are nonionic, generally biologically compatible, and may experience bio-specific interactions that can be used for targeting or recognition.\textsuperscript{45} Perhaps most usefully, a vast range of different carbohydrates exists, each with a unique molecular structure, conferring differences in physicochemical properties such as melting point, solubility, hydrophobicity, packing density, etc.\textsuperscript{46} Thus with the same chemical coupling, a range of head-groups can be linked to the same tail-group chemistry, enabling rapid prototyping of a library of molecules, and the simple elucidation of structure–performance relationships. Indeed, much of the surfactant literature addresses the exploration of different molecular architectures by changing the tail-group in a homologous series where the head-group is consistent.\textsuperscript{47} Carbohydrates offer the appealing opportunity to explore the effects of head-group size, solubility, polarity, etc., and the addition of the azobenzene tail allows further fine control of the surfactant polarity and geometry \textit{in situ}.

It is important to note that it is more correct to use the terms \textit{trans}-dominated and \textit{cis}-dominated to describe the two photo-stationary states (\textit{i.e.} the equilibrium chemical composition under a specific illumination condition) of azobenzene and molecules that contain it.\textsuperscript{7} Because of the statistical nature of the isomerisation process, the sample composition is generally around 95\% \textit{trans} for samples left in ambient conditions, and 70–95\% \textit{cis} for samples that have been irradiated with UV light for a sufficient time as to saturate the sample (\textit{i.e.} no further changes in the UV-vis spectrum are seen with additional irradiation).\textsuperscript{48,49} However, these numbers vary depending on the sample conditions, illumination power, steric hindrance within the molecule (which may favour the \textit{trans} or \textit{cis} form) and solvent effects. The precise composition of a photostationary state can be assessed spectroscopically if certain conditions are known,\textsuperscript{50} or by nuclear magnetic resonance quantification of suitably resolved protons.\textsuperscript{32,48} Once the \textit{cis}-dominated photostationary state has been reached, thermal relaxation back to the more stable \textit{trans} form inevitably occurs; the half life of this process in dark conditions is of the order 20–60 hours, depending on the specific molecule.\textsuperscript{15,44}

3. Physicochemical Characterisation

One of the most beguiling features of photoisomerisable surfactants is their complex behavior at air–water interfaces.\textsuperscript{51}
Due to the dual species present—that is, the cis and trans form of the surfactant molecule—that have different geometries and solubilities, a complex set of competing adsorption equilibria is established.\textsuperscript{50} In general, the more thermodynamically favoured trans form of these molecules tends to also be more surface active, as the lower dipole moment makes the tail-group more ‘oily’, thus driving them to the air–water interface. The bent cis configuration is not only more polar, thus partitioning more into water, but is also generally more challenging to pack at the interface, meaning that adsorbed amounts tend to be lower for this isomer.

The thermodynamics of adsorption for the trans- and cis-dominated photostationary states can be assessed (under the assumption of Gibbsonian behaviour) using standard tensiometric methods. For this purpose, pendant drop tensiometry\textsuperscript{52} is particularly appealing as it can track the surface tension in a dynamic fashion as the sample is changing (e.g. to monitor adsorption dynamics, or the effects of photosomerisation) \textit{in situ} without the creation of new interface. Indeed, this approach was used to great effect by Chevalier \textit{et al.} to explore the dynamics of changes in surface tension for a conventional cationic photosurfactant undergoing photosomerisation.\textsuperscript{50}

For air–water systems that have reached adsorption equilibrium, tensiometry gives information on the surface tension and—by application of the Gibbs adsorption isotherm—the adsorbed amount at the interface for a given bulk surfactant concentration. In doing so, comparisons are easily made between the equilibrium adsorbed states of the trans- and cis-dominated photostationary states.\textsuperscript{37} For the carbohydrate photosurfactants introduced earlier, a particularly rich picture emerges.\textsuperscript{36} In line with expectation, cis-dominated samples tend to be less surface active due to their higher polarity and poorer packing at the interface. However, it is also seen that the identity of the carbohydrate used for the head-group has a controlling effect on interfacial activity, packing and molecular area. In line with expectation, disaccharides tend to have higher solubility (and hence higher CMC values) than monosaccharides, and the oxidation of sugars to uronic acids also increases their solubility. Moreover, the uronic acid group is also pH dependent, becoming predominantly proton condensed below pH = 4 and deprotonated above this value.\textsuperscript{36} Thus a photo-surfactant with e.g. glucuronic acid as a head-group can be addressed not only using light (an external stimulus) but also pH (and internal stimulus). The effects of this are shown in Figure 2, where a single surfactant can exhibit four distinct CMC values, representing the cis and trans forms of the protonated and deprotonated acid state.

Perhaps due to their bulky tail-groups, azobenzene-containing surfactants tend not to be the most effective or efficient surfactants at the air–water interface. It has been discussed recently that the ability to form an effective interfacial film is the overriding factor that controls a surfactant’s ability to reduce surface (and presumably by inference, interfacial) tension.\textsuperscript{53} Photosurfactants generally show limiting surface tensions of 32–40 mN m\textsuperscript{-1} depending on their specific molecular architecture. Interestingly, the lower limiting surface tension value seems to be rather consistent for azobenzene photosurfactants regardless of the head-group chosen: ammonium bromide (AzoTAB) \(37\) mN m\textsuperscript{-1},\textsuperscript{34} poly(ethylene glycol) (C\textsubscript{4}AzoOC\textsubscript{6}E\textsubscript{2}) \(32\) mN m\textsuperscript{-1},\textsuperscript{38} carbohydrate (GlcU-Azo) \(34\) mN m\textsuperscript{-1}.\textsuperscript{56} indicating that the film packing argument is indeed a good description of the interface.

### 3.1 Aggregation Properties

The first photoswitchable azobenzene-containing surfactants were based around the robust, cationic trimethylammonium bromide headgroup.\textsuperscript{12} A wide range of molecules sharing these two molecular features have been synthesized and explored over the intervening 38 years, providing detailed structure–function relationships that inform the adsorption and aggregation of such surfactants in both dynamic and equilibrium conditions. Indeed, due to their reliable behavior, these molecules have found utility in the formulation of systems that utilize surfactant self-assembly mediated control of stability to gather and disperse DNA,\textsuperscript{55} control micelle and vesicle formation and geometry,\textsuperscript{48,56,57} catalytic reactions,\textsuperscript{58} and modulate solution viscosity.\textsuperscript{59} These cationic azobenzene surfactants tend to form small, highly charged and nearly spherical micelles, the dimensions of which do not change a great deal on irradiation.\textsuperscript{49} This behavior can be mostly attributed to the cationic head-group, which limits micelle size due to the unfavourable condition of having too many charge residues in close proximity. Different aggregate morphologies can be attained in mixed systems with cationic photosurfactants, where an additive is used to modulate packing or inter-head-group interactions.\textsuperscript{60,61}

Due to the absence of head-group charge, nonionic surfactants tend to favour larger aggregation numbers in general, and are therefore able to form rod-like and even wormlike micellar...
structures comprising many thousands of monomers without additives.\(^{37}\) Indeed, nonionic carbohydrate head-groups coupled to azobenzene-containing tail-groups enable an extraordinarily diverse selection of micelle geometries to be attained, from near-spherical to elongated flexible cylinders (Figure 3).\(^{36,43}\)

Crucially, these aggregation structures are obtained when using the surfactants as a single component, with no additives present, and thus the structure is dictated by the innate packing of the surfactant monomers. Some expected results emerge, such as charged uronic acid-headed surfactants favouring smaller ellipsoidal micelles compared to their uncharged counterparts.\(^{36}\)

Interestingly however, there is little correlation between the carbohydrate size (monosaccharide, disaccharide) and solubility with the eventual self-assembly geometry, indicating that a number of complex factors (monomer packing, interactions, polarity) influence aggregation for these surfactants.\(^{43}\)

One of the obvious appeals of photoswitchable surfactants is the ability to change the molecular structure by application of light as a stimulus. The change in molecular geometry from the linear/planar trans state to the bent cis state has been shown previously to induce commensurate changes in molecular packing.\(^{51}\) This can manifest as changes in micelle size and shape,\(^{57}\) or more elaborate aggregation changes such as rupture of vesicles.\(^{48,56}\)

Small-angle neutron scattering (SANS) is a powerful tool for the interrogation of self-assembly structures on scales of typically one to several hundred nanometres—ideally suited for micelles and related phases.\(^{62}\) Due to the highly penetrating nature of neutrons (which interact with sample nuclei as opposed to X-rays, which interact with electron density), SANS can be used to interrogate a wide variety of soft and self-assembled systems. Crucially, the opportunity for contrast variation through selective isotopic labelling of solvents or molecules means that different contrast conditions can be used to isolate structural elements or interactions within systems. Although small-angle X-ray scattering (SAXS) generally allows for much quicker data acquisition, SANS is particularly advantageous in the study of dilute systems such as micelles, where precise quantification of the size, shape, hydration and solvent penetration can be achieved. SANS has been widely applied to the study of photosurfactant systems, providing insight into the shape, size and interactions present in samples comprising micelles,\(^{49}\) vesicles,\(^{39}\) microemulsions\(^{39}\) and other structures.

We recently showed that by using a weak UV illumination source in the form of a light-emitting diode, it was possible to monitor directly using SANS the changes in aggregate morphology that accompany trans–cis isomerisation.\(^{57}\) For a typical azobenzene-containing carbohydrate surfactant far above the CMC of both trans and cis forms, rodlike cylindrical micelles were formed. On photoswitching to the cis-dominated state, the micelles became slightly thinner (presumably as a result of the shorter dimensions and weaker packing of the bent cis molecules) and their aggregation number reduced modestly. At a concentration of a few times the CMC, changes in aggregation were more pronounced, with micelles decreasing from short rods of aggregation number 290 to spheres comprising 110 monomers.

By photoswitching the sample at a concentration between the CMC values of the cis and trans forms (i.e. a concentration above the CMC of the trans dominated photostationary state, but below the CMC of the cis photostationary state) complete disaggregation of the micelles can be achieved (Figure 4). Naturally, this process is reversible and on reversion to the trans-dominated state, micelles re-form. This has obvious implications for the light-stimulated delivery of molecules hosted within the micelles. Indeed, it was shown that such a disaggregation strategy could be used to release a model hydrophobic cargo in the form of ethylbenzene by Sakai and co-workers.\(^{49,64}\)

4. Applications

Due to the complexity of their synthesis and cost of manufacture, photoswitchable surfactants are unlikely to find application in large scale processes where surfactants are widely used, for example in mineral flotation or oil recovery. However, in smaller scale systems where fine control is required, they offer unique advantages. Perhaps most usefully, the ability to change their geometry and polarity in situ makes them powerful mechanistic probes for biological and physicochemical processes. In this context, they can provide insight into a range of phenomena from self-assembly to bacterial adhesion. Additionally, for highly valuable systems where fine spatiotemporal control is required, such as the dispersion and deposition of nanomaterials for microelectronic systems and sensing, or of biological materials for separations and diagnostics, such surfactants offer a unique route to precisely controlling stability.

4.1 Responsive Colloids and Nanomaterial Systems. One of the most appealing aspects of responsive surfactants is the ability to change the dispersion state of a colloidal system when they are used as stabilisers. Utilising the subtle change in
surfactant geometry, polarity and/or solubility, systems near a stability edge or phase boundary can be separated, with important applications in recovery of valuable nanomaterials, catalytic nanoparticles, etc. Soft colloids such as vesicles and microemulsions can also be controlled in this way, although locating a phase boundary with sufficient precision can prove challenging. We previously showed that a critical separation could be induced in a microemulsion stabilised primarily by a conventional anionic surfactant (bis-2-ethylhexyl)sulfosuccinate, AOT) when only 2% of an anionic azobenzene-containing surfactant was added (Figure 5a). This result provided the optimistic outlook that with precise tuning, small amounts of photosurfactant could be used to control overall system stability at low cost, increasing the prospect of their use in larger scale separations. Using a gemini photosurfactant that contained azobenzene as a bridge between two cationic headgroups, Takahashi et al. were able to achieve complete separation of an oil-in-water (macro) emulsion induced by light.

Aqueous processing of many nanomaterials is facilitated by the addition of surface active species, and indeed for hydrophobic materials such as graphene, this is essential. Many applications for such materials require that they can be not only dispersed, but also deposited on demand, for coating, fabrication and device production. Thus, the appeal of externally addressable surfactants to achieve this aim is clear. McCoy recently showed that by addition of a cationic azobenzene-containing photosurfactant, dispersion of carbon nanomaterials could be readily controlled (Figure 5B). By adding low concentrations of the photosurfactant and switching between the trans- and cis-dominated photostationary states, reversible aggregation and dispersion could be achieved. The effect was most significant for reduced graphene oxide, which is closest to a stability edge; graphene oxide itself is sufficiently hydrophobic as to be well dispersed in water, and therefore more difficult to aggregate using this approach. Carbon nanotubes could be reversibly recovered by addition of the photosurfactant, although the size dispersity of the nanotubes meant that a clear phase boundary was not readily achieved, and the separation was thus not as ‘clean’ (i.e. complete) as for reduced graphene oxide.

In order to better understand the interactions between nanomaterials and photosurfactants that result in such changes in system stability, McCoy later explored the interfacial activity of carbon nanomaterials in the presence of photosurfactants. In this context, the photosurfactant provides insight into the mechanistic aspects of how carbon nanomaterials are enriched at interfaces, relevant for their use in Pickering emulsification, Pickering polymerisations, and nanomaterial foams/aerogels. It was seen that a small amount of photosurfactant significantly enhanced the surface activity of graphene oxide, allowing for highly effective emulsification at low energy input. However, further addition resulted in the surfactant re-stabilising the graphene oxide sheets into the bulk, rendering them less interfacially active. Only modest changes were seen upon trans-cis isomerisation of the surfactant, likely indicating that once at the interface, graphene oxide is irreversibly adsorbed—a unique mechanistic insight only possible when using a surfactant that can be externally addressed in situ at the interface, and demonstrating the utility of photosurfactants as probes for physical phenomena.

4.2 Controlling Processes in Biological Systems. Photosurfactants show great promise in the exploration of processes within biological systems, wherein the ability to externally address a surfactant can provide not only a means to control the system, but also explore mechanistic aspects of processes.
Here, nonionic surfactants – in particular those bearing carbohydrate head-groups – offer significant advantages in terms of their higher permeability and lower toxicity in biological systems. Previous researchers have explored the use of photosurfactants to control the aggregation state of biomolecules such as DNA, and modulate amyloid protein fibril growth.

Hu et al. recently synthesised a panel of carbohydrate-headed azobenzene photosurfactants where the tail group was functionalised to bear a terminal trifluoromethyl substituent. The molecules were seen to exhibit dose-dependent, selective toxicity against the bacterium *Staphylococcus aureus*, although were non-toxic to *Escherichia coli*. Subsequent work showed such partially fluorinated carbohydrate photosurfactants could be also used to control ice recrystallization during freeze–thaw processes relevant to cryopreservation; some *trans* vs *cis* effects were seen that could not be simply explained as a function of solubility or aggregation, indicating that geometric or binding effects may play a role. Indeed, the trifluoromethyl tip was seen to be non-essential (although potentially advantageous) in rendering the ice recrystallization inhibition effects; *n*-butyl tipped carbohydrate photosurfactants also exhibited this propensity, with a mannose-headed surfactant proving the most effective.

Further control of biological systems using carbohydrate photosurfactants was demonstrated in the ability of these molecules to modulate the biofilm formation ability of bacteria on surfaces (Figure 6). The effects of *trans*–*cis* isomerisation were found to elicit control over bacterial growth, protective biofilm formation, and bacterial motility, again without a clear correlation to any obvious physical parameter such as solubility or CMC. In this study, small-angle neutron scattering demonstrated again a wide range of aggregation morphologies controlled by the selection of carbohydrate head-group, from small ellipsoidal micelles (arabinoose), to large flexible, worm-like structures (xylose).

More advanced azobenzene-containing molecules in the form of glycodendrimers have also been synthesised, and were shown to be effective multivalent inhibitors of lectins expressed on the surface of *Pseudomonas aeruginosa* bacterial cells. The glycodendrimers produced in this work showed some particularly unusual physical properties, whereby they were seen to be effectively non-surface active, but strongly aggregated into ‘giant micelle’ type geometries, with either near-spherical or elongated, rod-like shapes. Thus the onset of their aggregation was described by a critical aggregation concentration as determined by encapsulation of a fluorescent dye molecule.

5. Conclusion and Outlook

Over the last four decades, the field of surfactants that can be addressed by light has developed from a curiosity into a mature set of materials and an accompanying conceptual framework to understanding their behaviour. Their utility in the control of fluid interfaces and dispersed materials has been demonstrated, and new applications in the control of valuable carbon nanomaterials indicates new scope for their deployment in colloidal systems.

In particular, the motivation to produce carbohydrate-functionalised surfactants for use in biological systems offers new opportunities for fine spatiotemporal control of biological processes and as mechanistic probes for uncovering the role of surface active species in biomolecular phenomena. Future potential includes using more diverse biological motifs to impart specific targeting and recognition of the molecules, whereby they can be used to explore and control a wide range of biochemical and biophysical processes.

To explore the utility of photosurfactants as mechanistic probes in tissue samples or even *in vivo*, the weakly penetrating nature of UV radiation in these circumstances must be addressed. A possible solution is the design of chromophores such as highly substituted azobenzenes that can be isomerized by radiation in the red or infra-red regions of the spectrum, and recent work in the field indicates that this is indeed possible.

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