

Investigation of the Structure-Property Relationships of Photoactive Surfactants

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Declaration

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Elaine Kelly, B.A. Chemistry

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Abstract

Surfactants are functional and versatile molecules, common to a plethora of industries and applications as emulsifying, wetting, dispersing and foaming agents. The usefulness of surfactants is a result of their amphiphilicity; possessing both hydrophobic and hydrophilic components allows for both the adsorption of the surfactant at interfaces and the formation of self-assembled structures. In this thesis, two different classes of photoactive surfactants will be studied. In both cases, light is essential, either to exact a change in the physicochemical properties and self-assembly behaviour of the surfactant solution, or, as a visual signifier for the “switching on” of photoluminescence.

The first class of photoactive surfactants presented in this work is azobenzene photosurfactants (AzoPS). Cationic AzoPS have shown promise in a range of applications, from reversible DNA compaction to controlling the flow-type in microfluidic devices. However, despite their potential, only a handful of AzoPS structures have been reported to date. Fewer reports still are to be found regarding neutral AzoPS, despite their offering many advantages over their cationic counterparts. In Chapters 4-5, a family of four neutral AzoPS will be designed with the specific aim of studying how the molecular structure of the surfactants affects both their surface tension and self-assembly behaviour. Focus will be on the use of light as an actuator to bring about significant, measurable changes in the physicochemical properties and self-assembly behaviour of azobenzene photosurfactant systems. It will be shown that through the remote application of light, AzoPS can switch between ‘on’ and ‘off’ states with respect to their degree of surface tension lowering and self-assembled structure formation.

Chapter 6 will study the phenomenon of aggregation-induced emission (AIE), again depending on light and the photoresponse of the surfactant as a means to study the surfactant system. The inherent tendency of surfactants to self-assemble will be used to explore the aggregation and emission properties of an AIE-active surfactant, tetraphenylethylene sodium dodecyl sulfate (TPE-SDS). TPE-SDS will be combined with sodium dodecyl sulfate (SDS) to form mixed micelles, in order to probe the geometric and spatial requirements for aggregation-induced emission to occur using a combination of small-angle scattering and photoluminescence spectroscopy techniques. The structure-property relationships identified in this work will be crucial in directing the integration of photoactive surfactants into a wide range of applications and leading future studies into the mechanism behind aggregation-induced emission.

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Abbreviations

1D – one dimensional

ACQ – Aggregation-Caused Quenching

AIE – Aggregation-Induced Emission

APCI – Atmospheric Pressure Chemical Ionisation

ATR – Attenuated Total Reflection

AzoPS – Azobenzene Photosurfactant(s)

CDCl₃ – Deuterated Chloroform

CMC – Critical Micelle Concentration

cps – Counts Per Second

Cryo-TEM – Cryogenic-Transmission Electron Microscopy

D₂O – Deuterium Oxide

DCM – Dichloromethane

DLS – Dynamic Light Scattering

ESI-MS – Electron Spray Ionisation-Mass Spectrometry

FTIR – Fourier Transform Infrared

H₂O – Water

HCl – Hydrochloric Acid

IC – Internal Conversion

ISC – Inter System Crossing

K₂CO₃ – Potassium Carbonate

kcps – kilo counts per second

KI – Potassium Iodide

LED – Light Emitting Diode

LLC – Lyotropic Liquid Crystals

LSC – Luminescent Solar Concentrator

NaOH – Sodium Hydroxide

NLLS – Non Linear Least Squares

NMR – Nuclear Magnetic Resonance

OLED – Organic Light Emitting Diode

PDI – Particle Distribution Index

ppm – Parts per Millions

PSS – photostationary state

SANS – Small-Angle Neutron Scattering

SAXS – Small-Angle X-ray Scattering

SDS – Sodium Dodecyl Sulfate

SLD – Scattering Length Density

S_N2 – bimolecular nucleophilic substitution reaction

ST – Surface Tensiometry

TEM – Transmission Electron Microscopy

THF - Tetrahydrofuran

TLS – Thin Layer Chromatography

TMS – Trimethylsilane

TPE – Tetraphenylethylene

UV - Ultra Violet

Vis – Visible

List of Symbols

b – neutron scattering length

c – speed of light in a vacuum

γ – surface tension

Γ – surface excess

δ – chemical shift

$\Delta\Omega$ - unit solid angle

d - distance

D – translational diffusion coefficient

ε – molar absorptivity coefficient

η – viscosity

θ – scattering angle

h – Planck constant

I - intensity

k_B – Boltzmann Constant

$\mathbf{k}$ = wave-vector

λ – wavelength

n – refractive index

$\hat{\mu}$ - electronic dipole moment

π – electronic energy

P – packing parameter

$P(q)$ –form factor

$\mathbf{Q}$ – scattering wave vector

q – magnitude of scattering wave-vector

ρ - scattering length density

R_H - hydrodynamic radius

R_g – Radius of gyration

σ - neutron scattering cross section

S_n – nth singlet state

$S(q)$ – structure factor

T – temperature

T_n – nth triplet state

ν – frequency

Φ – time-dependent wave-function

χ^2 – chi- squared statistic

ω - angular momentum

Chapter 1

Introduction

1.1 Introduction

Light is vital for human vision and is essential for most people to interact with the world around them. Light is also critical to interact with fundamental scientific entities, such as atoms and molecules, which are too small to be seen by humans. Using light it is possible to ‘see’ things beyond the scope of the human eye, and render the invisible visible. For example, light is implicit to UV-Vis absorption spectroscopy, fluorescence spectroscopy, dynamic light scattering, and polarised light microscopy, techniques which provide information about fundamental characteristics of atoms and molecules like size, shape, chirality and the nature of electronic energy levels. Knowledge of these fundamental attributes is what has catalysed the rapid advancement and innovation in science over the last half century.

In this thesis, light is no less essential, and will be used in tandem with one class of molecules in particular, namely, *surfactants*. Surfactants are widely used molecules, ubiquitous in many industries as foaming, dispersing, emulsifying, and wetting agents.^{1,2} The usefulness of surfactants stems from their amphiphilic nature; they possess both hydrophobic and hydrophilic components which facilitates both their adsorption at interfaces and formation of self-assembled structures.³ Here, surfactants will be used as tools with light as the handle with which to grasp them. First, a family of photoresponsive azobenzene surfactants will be designed such that light can be used as an actuator to bring about significant, measurable changes in both the physicochemical properties and self-assembly behaviour of the photosurfactant system. The molecular structures of the strategically designed photosurfactants will be correlated with these changes in behaviour to unravel the specific role played by surfactant structure in the self-assembly processes.

Secondly, the inherent tendency of surfactants to self-assemble above a certain critical concentration will be used to study *aggregation induced emission* (AIE). Since its discovery in 2001 AIE has been game-changing for many fields reliant on luminescent materials.⁴ Since its initial report a variety of molecules exhibiting AIE have been developed, attracting considerable attention for solid-state light-emitting displays, solar energy conversion and optical storage.⁵ However, as yet there exists little solid experimental evidence to fully support and explain the hypothesised Restriction of Intramolecular Rotations (RIR) mechanism for AIE. In this thesis, a structure-activity study will be undertaken on mixed micelles containing an AIE-active surfactant and its non-AIE active counterpart. Light will be used as both a probe into the emission behaviour of the surfactant and as a visual signifier for the “switching on” of

the AIE mechanism. It is hoped that this investigation will lead the way to providing firm experimental evidence for the RIR mechanism.

In this chapter the fundamental concepts of surfactants will be introduced to provide context for the results presented later in Chapters 4-6 of this thesis. First, in Section 1.2, the basic principles of surfactants will be presented, with a focus on their surface tension and self-assembly behaviour. Next, in Section 1.3, azobenzene photosurfactants (AzoPS) will be discussed, specifically in relation to their spectroscopy and integration with applications. Finally, in Section 1.4, AIE will be introduced and its fundamental principles and hypothesised mechanism explained.

1.2 Surfactants

Surfactants can have many possible structures, with the only prerequisite being the co-existence of both hydrophilic and hydrophobic components on the same molecule.⁶ Typically the hydrophobic component consists of an alkyl tail, which can also incorporate an active moiety such as a fluorescence probe⁷, or as in this thesis, either a photoisomerisable or AIE-active group.⁸⁻¹⁰ The head group can be anionic (sulfates¹¹, phosphates¹²), cationic (trimethylammonium^{10,13}) or neutral (ethylene glycol¹⁴, amines¹⁵). The combination of hydrophobic and hydrophilic components within the same molecule imparts surfactants with surface tension lowering properties, which will be introduced next. In fact, the name surfactant is a portmanteau of “surface active agent”. The variety in possible molecular composition and surfactant structure leads to many different classes of surfactants (bolaform, gemini, anionic, neutral, zwitterionic^{6,10,16,17}) with this potential versatility in design leading to surfactants being integral tools for many industries, such as oil recovery, detergents, and cosmetics.^{2,16,18}

1.2.1 Surface Tension

In aqueous solutions at low concentrations, surfactant monomers dispersed in solution tend to adsorb at the air-water interface with their hydrophobic tails oriented outwards and the polar head groups immersed in the bulk water (Figure 1.1).¹⁹ This has the effect of lowering the surface tension of water by modifying the Gibbs free energy of the system. Water has a high surface tension as there is a large difference in the number of energetically favourable interactions in the bulk compared to at the interface. In the bulk, water can hydrogen bond to neighbouring water molecules in all directions, creating a network of favourable cohesive interactions throughout the liquid. At the air-water interface these hydrogen bonding interactions are not possible with the gas phase. As such, there is a high surface free energy due to these ‘missing’ interactions. To compensate for this, the air-liquid interface will tend to

minimise its interfacial surface area in an attempt to maximise the number of cohesive interactions^{19,20} Surface tension can be thought of as the energy needed to increase the interfacial surface area²¹, as shown by Equation 1.1:

$$\gamma = \left(\frac{\partial G}{\partial A} \right)_{T,P,n} \quad (1.1)$$

where γ is the surface tension (N m^{-1}), G is the Gibbs free energy (J), A is the area (m^2), T is the temperature (K), P is the pressure (Pa) and n is the number of molecules adsorbed at the interface. Surfactants act to lower surface tension by interfacial adsorption as the energetic penalty for having the hydrophobic component of the surfactant in contact with the air phase is much lower than for water molecules at an air-water interface. Surfactant adsorption allows the majority of the water molecules to exist in the bulk with maximal hydrogen bonding interactions, while also minimising the number of unfavourable surfactant hydrophobic tail-water interactions. It is in this way that surfactants can stabilise aqueous bubbles and foams of large surface area.

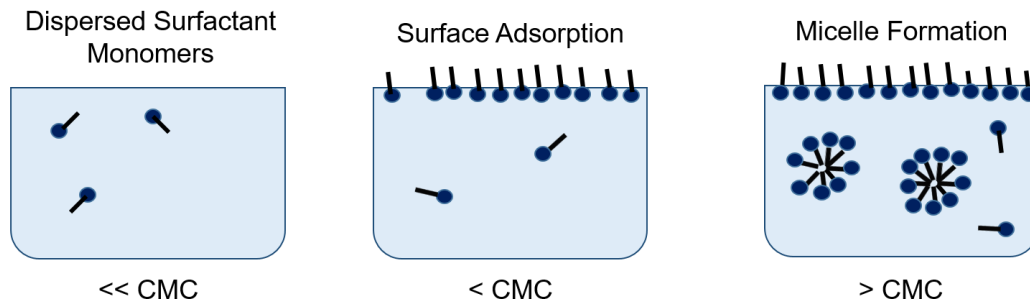


Figure 1.1 Schematic showing surfactant behaviour with increasing concentration in aqueous solution. Far below the critical micelle concentration (CMC) surfactants can be considered as dispersed unimers in solution. At higher concentrations, but still below the CMC, surfactants adsorb at the air-water interface. Above the CMC the air-water interface is saturated and micelles have formed in solution.

Surfactants have a high surface excess (Γ) in aqueous solutions, with an increase in surfactant concentration having a concurrent decrease in surface tension up to a certain critical concentration, after which surface tension is constant.^{22,23} The change in surface tension with increasing surfactant concentration is related to the amount of surfactant adsorbed at an interface by the Gibbs' adsorption equation:^{21,24}

$$\Gamma = \frac{-1}{RT} \left(\frac{d\gamma}{d \ln c} \right) \quad (1.2)$$

where Γ is the surface excess (mol m^{-2}), R is the universal gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the temperature (K), γ is the surface tension and c is the surfactant concentration (mol L^{-1}). The inverse relationship between surfactant concentration and surface tension is apparent from this equation. The surface excess, can be manipulated to allow the area per molecule at the interface

($\text{\AA}^2 \text{ molecule}^{-1}$) to be calculated. The concentration at which the surface tension becomes independent of surfactant concentration corresponds to the surface saturation point and is known as the *critical micelle concentration* (CMC).^{21,24} As the name suggests, beyond the CMC surfactant monomers in the bulk begin to self-assemble into aggregates known as *micelles* (Figure 1.1).

1.2.2 Self-Assembly of Surfactants

In aqueous solution above both the Krafft temperature (minimum temperature at which micelles can form) and the CMC, surfactant monomers spontaneously self-assemble into aggregates known as micelles. There are two main forces behind micelle formation: the long range hydrophobic effect causes the aggregation of surfactant alkyl chains, while at shorter distances repulsive forces (electrostatic, steric, hydration) from the surfactant head groups prevent large scale crystal formation or phase separation.^{25,26} At the CMC, these two opposing forces are balanced and it becomes favourable for micelles to form.²⁷ As there are no chemical bonds involved in this process, the surfactant monomers in the micelles are in equilibrium with monomers in the bulk solution.²⁷

The CMC can be identified by a change in several of the physicochemical properties of the system. As aforementioned, surface tension decreases with an increase in surfactant concentration, becoming independent of surfactant concentration above the CMC. The turbidity of the bulk solution will also increase above the CMC due to the presence of an increasing number of large (compared to monomers) self-assembled structures (Figure 1.2). Changes in conductivity, solubility, diffusion coefficient and osmotic pressure can also be used to identify the CMC.^{22,23}

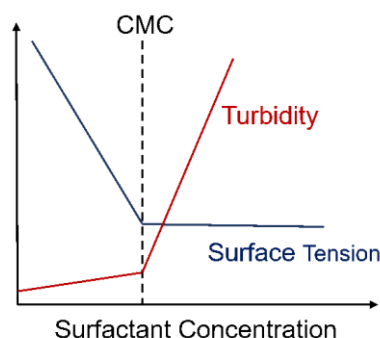


Figure 1.2 Schematic representation of the variation in surface tension (blue) and turbidity (red) with increasing surfactant concentration in aqueous solution. The CMC is indicated by the dashed vertical line.

The geometry of the self-assembled structures, or micelles, can be loosely predicted by the critical packing parameter, P , of the component surfactants given by:²⁸

$$P = \frac{V}{a_0 l_c} \quad (1.3)$$

where V is the volume of the hydrophobic chain of the surfactant monomer, a_0 is the mean cross-sectional area of the head-group and l_c is the critical chain length. Figure 1.3 shows the expected micelle structures for different values of P .²⁹ The number of surfactant monomers per micelle is given by the aggregation number (N_{agg}) and typically ranges from 50 to 10,000 monomers.²⁷ It should be noted that the packing parameter is not 100% deterministic of micellar structure and factors such as pH, salt concentration, temperature and solvent all play a role in the micellar structure adopted.

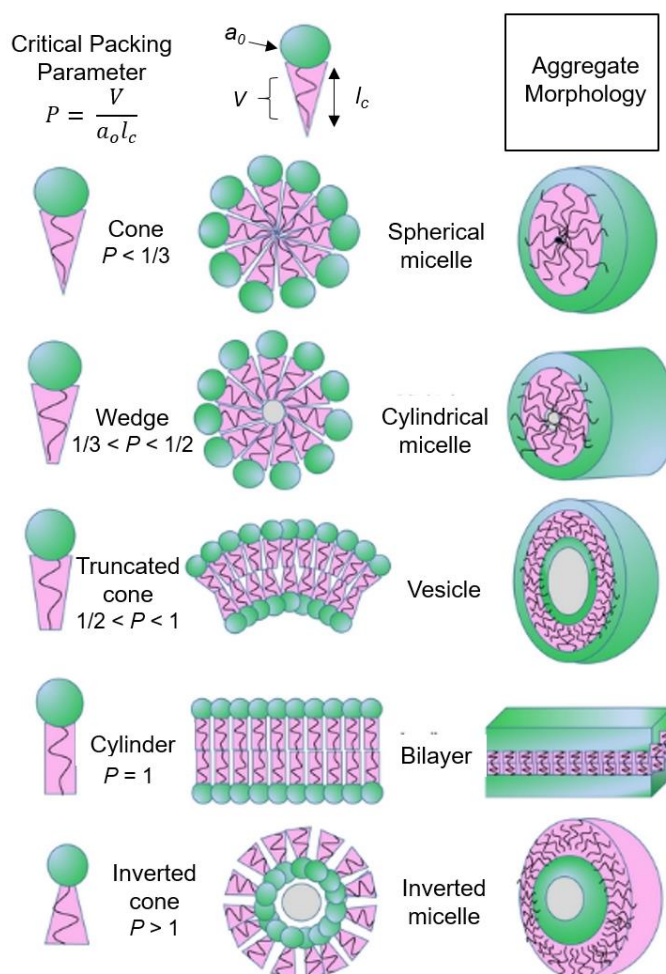


Figure 1.3 Schematic depiction of critical packing parameters and associated predicted micellar structure. Adapted from reference 29 (<http://dx.doi.org/10.1155/2015/151683>) under a creative commons licence (CC BY 4.0)

1.2.3 Surfactant Mesophases and Lyotropic Liquid Crystal Phases

As the number of micelles present in the solution increases with increasing surfactant concentration, the micelles themselves begin to interact with each other and form higher order mesophases such as vesicles, bicontinuous phases, bilayer sheets and in some cases even

lyotropic liquid crystal (LLC) phases.³⁰ The surfactant micelles arrange themselves such that hydrophilic-hydrophilic and hydrophobic-hydrophobic interactions are maximised, while steric hindrance is minimised. In this way surfactants can be thought of as primary building block and micelles as secondary building blocks.²⁷

LLC phases are particularly interesting as they impart long range order to the surfactant solutions, involving only weak intermolecular forces. LLC phases are ordered liquid phases with some degree of anisotropy as a result of molecular interactions.³¹ LLC phases can be recognised via polarised optical microscopy (POM) and diffraction techniques, as a result of the optical anisotropy (*birefringence*) and long range order in the surfactant solution.^{31–35} LLCs of surfactants can also be used to soft template materials.^{36,37} Such materials are extremely useful due to their predictable pore size and geometry, determined by the LLC phase formed by the surfactant. Several LLC phases are possible, depending on the nature of the surfactant and can be predicted from the surfactant phase diagram, provided the surfactant concentration and temperature are known^{13,32,38} (Figure 1.4).

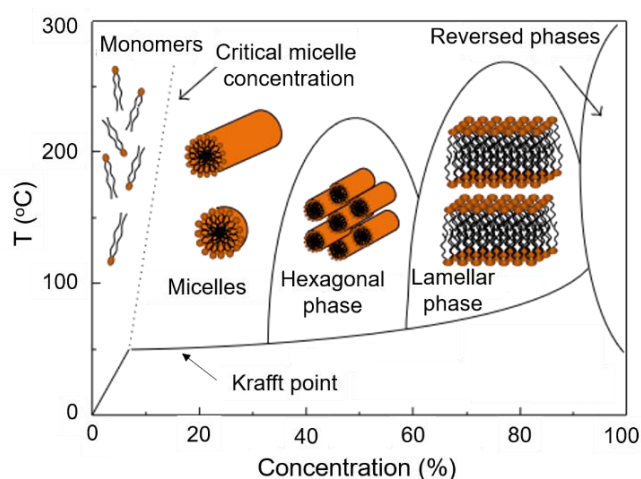


Figure 1.4 Hypothetical LLC phase diagram for a typical gemini surfactant in aqueous solution. Below the CMC dispersed monomers can be seen. As the concentration increases micelles, and eventually LLC phases (hexagonal, lamellar, reversed) can begin to form. Adapted from reference 29 (<http://dx.doi.org/10.1155/2015/151683>) under a creative commons licence (CC BY 4.0)

1.3 Photosurfactants

Photosurfactants are subclass of surfactants which contain a photoactive group. Upon irradiation with light several processes can occur depending on the chromophore: photoisomerisation³⁹, photodestruction⁴⁰ or photodimerisation^{41,42}. These light-induced structural changes can lead to an adjustment in the molecular dipole moment, geometry, and aggregation behaviour. Despite light being a cheap, non-invasive and clean stimulus photosurfactants are a relatively understudied class of materials in comparison to ‘regular’

surfactants.¹⁰ Photochromic groups investigated so far include spiropyrans⁴³, stilbenes⁴¹ and azobenzenes.⁴⁴ Photosurfactants containing an azobenzene core as the photoactive group are the most commonly studied compounds of this class¹⁰, herein to be referred to as AzoPS. Azobenzene was chosen as the photoactive group for surfactant incorporation in this work as the synthesis is versatile and straightforward and azobenzene has significant changes in conformation and physicochemical properties upon photoisomerisation, without additional side reactions like the cycloaddition and dimerisations observed for stilbenes.^{41,42}

1.3.1 Azobenzene

Azobenzene can exist in one of two isomeric states: *cis* or *trans*. Isomerisation of azobenzene substantially alters the physical properties of the molecule, such as size and dipole moment (Figure 1.5). The planar *trans*-isomer has a dipole moment of 0 D, while the non-planar *cis*-isomer has a dipole moment of 3 D.^{45,46} This leads to an increased hydrophilicity of the *cis*-isomer compared to the *trans*-isomer.⁴⁵ The latter is also thermodynamically more stable than the *cis*-isomer by about 50 kJ mol⁻¹ and so predominates at thermal equilibrium.⁴⁶

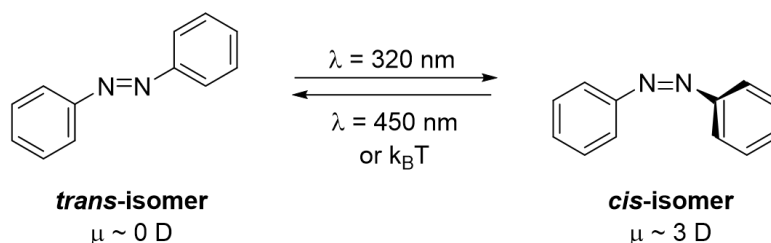


Figure 1.5 Schematic representation of the reversible *trans*- to *cis*- isomerisation of the azobenzene chromophore under irradiation with light. μ is the dipole moment.

The *trans-cis* photoisomerisation of the azobenzene occurs efficiently upon UV irradiation and can be readily reversed with blue light irradiation or by gentle heating (Figure 1.5).¹⁰ Moreover, photoisomerisation can still readily occur upon incorporation of the azobenzene group into an amphiphilic surfactant molecule. The resulting changes in the shape and dipole moment of the AzoPS upon photoisomerisation have a striking influence on both the interfacial properties of the individual surfactant monomer (wettability, surface tension) and its tendency to spontaneously form molecular aggregates or micelles.^{10,47–49} In this way isomerisation allows the physicochemical properties of an AzoPS system to be dynamically manipulated.

1.3.2 Spectroscopy of Azobenzene

In its most thermodynamically stable form, azobenzene exists as the *trans*-isomer. This isomer absorbs strongly in the UV region with an absorption band centred around 320 nm corresponding to the symmetry allowed $\pi \rightarrow \pi^*$ transition ($S_2 \leftarrow S_0$ excitation).⁵⁰ Upon irradiation with UV light the *cis*-isomer is formed. The UV-Vis absorption spectrum (Figure 1.6) of the *cis*-isomer displays a less intense $\pi \rightarrow \pi^*$ transition band in the UV region, centred around 270 nm and a second absorption band at 450 nm, corresponding to the symmetry forbidden $n \rightarrow \pi^*$ transition ($S_2 \leftarrow S_0$).^{46,50,51} The Laporte selection rule states that there must be a change in symmetry upon an electronic transition, meaning that transitions can only occur between wavefunctions of different symmetry .e.g $\pi \rightarrow \pi^*$ is allowed, while $n \rightarrow \pi^*$ is forbidden. The non-planarity of the *cis*-form allows the previously Laporte-forbidden $n \rightarrow \pi$ transition to occur. The *trans*-form can be recovered by irradiation with blue light or by leaving the molecule in the dark to allow thermal relaxation to occur. The mechanism of isomerisation is disputed, with solvent choice, irradiation wavelength, temperature and nature of azobenzene substituents all playing a role in the isomerisation pathway taken.⁵¹

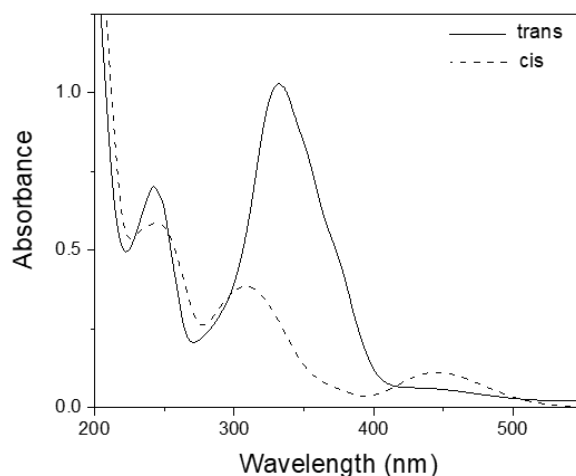


Figure 1.6 UV-Vis absorption spectra of the *trans*- (solid line) and *cis*-isomers (dashed line) of a neutral ethylene glycol AzoPS. These spectra are from the author's own work.

It should be noted that it is not possible to obtain 100% conversion from the *trans*- to the *cis*- isomer due to the overlap of their respective absorption spectra (Figure 1.6). Typically a photostationary state (PSS) of about 80-90% *cis*-azobenzene is obtained upon UV illumination, depending on the molecule.⁴⁷ Similarly, 100% *trans*-azobenzene cannot be recovered optically. When irradiated with blue light a second PSS is formed, typically consisting of ~90% *trans*-isomers.⁵¹ An assembly of 100% *trans*-isomers can only be recovered by thermal relaxation.

1.3.3 Azobenzene Photosurfactants

The impact of isomerisation on the surface activity of an AzoPS was first investigated by Shinkai *et al.* in 1982.⁵² They investigated the effect that the change in structure and hydrophilicity upon isomerisation had on the CMCs of three cationic azobenzene surfactants.⁵² It was found to be generally true that azobenzene surfactants in the *cis*-form have a higher CMC than those in the *trans*-form, owing to the increased hydrophilicity with increased dipole moment in the bent *cis*-form. Correspondingly, different values for interfacial tension, wettability, and solubility will be obtained for the *cis*- and *trans*-forms of azobenzene photosurfactants.^{47–49}

This means, using UV light, it is possible to switch an AzoPS solution of intermediary concentration between micelles (*trans*-isomer, low dipole moment, lower CMC than *cis*-) and monomers (*cis*-isomer, high dipole moment, higher CMC than *trans*-).⁸ Differences in surface tension values of up to 14 mN m⁻¹ between isomers have also been reported for some neutral azobenzene surfactants.¹⁴ It is easy to see why the ability to reversibly and promptly switch between different values for CMC, surface tension *etc.* without the addition or removal of any reagents would result in azobenzene photosurfactants showing promise in a wide range of applications, from controlling the coffee ring effect^{53–55} to reversibly compacting DNA.^{56–58} However, while the azobenzene motif is relatively easy to synthesise and functionalise,⁵⁹ surprisingly only a limited number of surfactant structures have been reported to date.¹⁰ Instead, researchers have focused their efforts on investigating the diverse potential applications for the few most common AzoPS structures.

1.3.4 Applications of AzoPS

Simple azobenzene photosurfactant structures have been used for a variety of applications, including photoresponsive foams^{60–62}, light-actuated transport in microfluidic devices^{63–65}, droplet manipulation^{66,67}, and reversible cotton dyeing processes^{68,69}, with little variation in the structure of the AzoPS used. Some recent applications of AzoPS and the corresponding molecular structure will be briefly outlined here.

By far the most common general AzoPS structures are cationic azobenzene trimethylammonium bromide surfactants, AzoTAB. Three general AzoTAB structures are shown in Figure 1.7. The alkoxy moiety between the azobenzene core and cationic head group is referred to as the spacer, with the alkyl chain the other side of the azobenzene core being referred to as the pendant tail. Diguet *et al.* studied the effect of UV and visible light illumination on liquid flows upon addition of an AzoTAB (Figure 1.7A), to the water

component of a water-in-oil continuous flow microfluidic device.⁶³ The flow type changed from laminar to a monodisperse droplet regime upon the application of UV light. Chevallier *et al.* were the first to apply photosurfactants to foaming and to attempt to control foam stability by direct manipulation of surfactant interfacial properties.⁶⁰ A slightly different AzoTAB (Figure 1.7B) was used to stabilise foams created by bubbling air through a water-AzoTAB solution. *In situ* isomerisation of the photosurfactant from *trans*- to *cis*- resulted in foam breakage, across a wide range of AzoTAB concentrations.

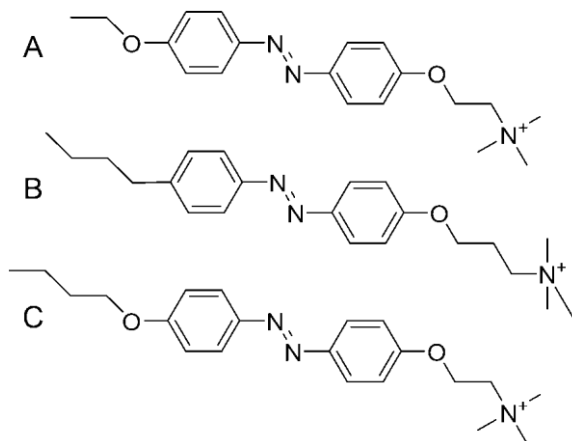


Figure 1.7 Molecular structures of three commonly used cationic AzoTABs. A is the molecular structure of the AzoTAB found by Diguët *et al.* to change the flow type in a microfluidic device upon UV illumination.⁶³ B is the structure of the AzoTAB Chevallier *et al.* used to destabilise a foam on demand using UV illumination.⁶⁰ C is the molecular structure of the AzoTAB Chen *et al.* integrated with reversible foam dyeing processes.⁶⁸

The integration of photofoams to dyeing processes was explored by Chen *et al.*⁶⁸ Cotton was dyed using a foam containing a dye-bonded blocked polyurethane dye. Dynamic photocontrol was gained over the foam by the integration of an AzoTAB (Figure 1.7C). UV illumination allowed remote breakage of the foam structure after dyeing, without the addition of defoaming agents. In each of the above cases proof of principle was demonstrated but no justification for the surfactant structure chosen was given, nor was there any significant effort made to optimise the AzoPS for a given application.

Neutral AzoPS have been much less studied and integrated with applications compared to cationic AzoPS. Yang *et al.* investigated a series of non-ionic AzoPS for creating multi-stimuli responsive hydrogels.⁷⁰ Three AzoPS were synthesised, of constant azobenzene tail lengths with hydrophilic polyetheramine head groups of varying molecular weight. It was found that all three AzoPS could form gels in aqueous solutions, and transition between gel and sol states depending on pH, temperature, and applied stress or light. Neutral AzoPS have been predominantly studied based on their capacity to form LLC phases. Peng *et al.* showed the

photo-rheological effects of an AzoPS in aqueous solutions for the first time.³⁴ Three AzoPS structures were synthesised, consisting of a hydrophilic oligoxyethylene head group in all cases, but with alkyl tails of varying spacer and pendant tail lengths. Only one of the AzoPS synthesised was useful, an AzoPS with a five carbon spacer and four carbon pendant tail (Figure 1.8a). The other two AzoPS, one short tailed (six carbon atoms total) and one long tailed (thirteen carbon atoms total) were too soluble and completely insoluble, respectively. The adequately soluble AzoPS was found to reversibly transition from a highly viscous solid-like LLC state to a low viscosity liquid-like non-LLC state upon irradiation with UV light.

Peng *et al.* further studied the effect of the spacer moiety on LLC phase formation. The same oligoxyethylene based AzoPS described above was chosen for analysis, and compared to its spacer free counterpart (Figure 1.8b) using polarised light microscopy (POM), small angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC).³⁵ It was found that the AzoPS with a spacer moiety could form more than one LLC phase depending on AzoPS concentration and temperature. For the spacer free AzoPS only one LLC phase was formed, at any temperature and concentration, and upon photoisomerisation this LLC phase was lost.

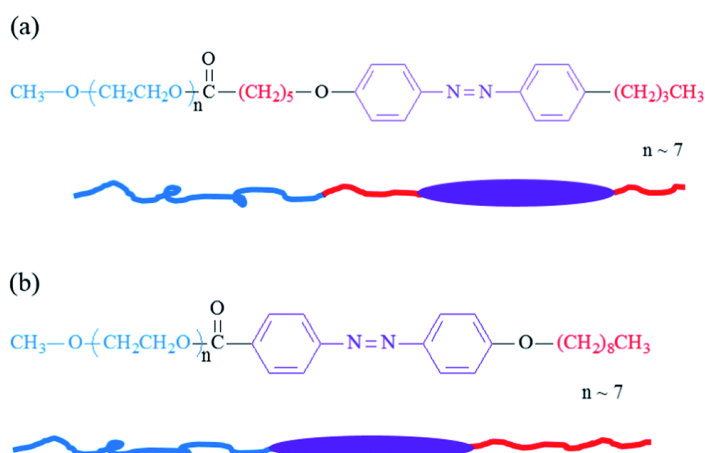


Figure 1.8 Molecular structures and schematic representations of two oligoxyethylene AzoPS synthesised by Peng *et al.*³⁵ (a) shows the variant with a spacer moiety while (b) shows the spacer free AzoPS. In both cases the carbon tail length is kept fixed at nine carbon atoms, with just the position of the azobenzene core within the tail being varied. Reproduced from ACS (J Mater Chem C, 2014, 2 (39), 8303) under a creative commons licence (Attribution 3.0 Unported Licence)

It should be apparent that while AzoPS present the possibility to be used as tools to dynamically control the physicochemical properties and LLC phase behaviour of aqueous solutions, very few studies have been carried out to consider the direct effect of molecular structure on these properties. In section 1.5, the objectives of this thesis in that regard will be outlined. In the next section, the fundamental concepts of AIE will be described in order to provide a suitable introduction to the AIE-based surfactants studied in this thesis.

1.4 Aggregation Induced Emission

Photoluminescence (fluorescence or phosphorescence) is the spontaneous emission of light from an excited electronic state as it radiatively relaxes to the ground state. Luminescent materials are integral to many technological innovations, old and new, from gas discharge lamps⁷¹ to light-emitting diodes.⁷² However, the fundamental tendency of organic dyes and luminescent molecules (luminophores) to aggregate has led to drawbacks in the efficiency of many applications reliant on these materials. In this section of the introduction, the fundamental concepts of AIE will be introduced, while the fundamental properties of light and its interaction with matter will be discussed in further detail in Chapter 2.

1.4.1 Aggregation Caused Quenching

Luminescent organic molecules have some common structural and geometric features, such as a conjugated carbon backbone, molecular rigidity, and planar aromatic rings. The conjugated backbone results in low-lying electronic states with an energy difference corresponding to the visible region, as well as increasing photoluminescence intensity due to increased electron mobility.⁷³ Molecular planarity and rigidity also helps improve fluorescence efficiency by increasing electron mobility as well as decreasing rotational-vibrational interactions, which often favour intersystem crossing (ISC) and thus population of an excited triplet state.^{73,74} The importance of molecular rigidity can be seen when the fluorescence quantum yield of biphenyl and fluorene are compared (Figure 1.9). Both molecules have the same extent of conjugation, but the more rigid and planar fluorene molecule has a fluorescence quantum yield (Φ_F) of 0.54, while the less rigid biphenyl has Φ_F of only 0.23.⁷³

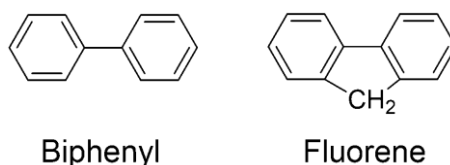


Figure 1.9 Molecular structures of biphenyl and fluorene. Both molecules are equally conjugated but the fluorescence quantum yield of fluorene ($\Phi_F = 0.54$) is over twice that of biphenyl ($\Phi_F = 0.23$).

Photoluminescence is well understood for luminophores in dilute solution, where the molecule can be considered as an isolated species with minimal intermolecular interactions. This allows the photophysics of the individual luminophore to be characterised in terms of its absorption and emission spectra, excited-state decay lifetime, emission quantum yield *etc.*^{75–80} However, most practical applications involving luminophores do not fit the assumption of the luminophore as an isolated non-interacting species, and the conclusions drawn from

measurements in dilute solutions cannot always be extended to concentrated solutions. It is the Catch-22 of luminophores that the structural characteristics that make them advantageous, in theory, for many applications (high emission quantum yield, suitable emission maxima) are those that impart luminophores with a high tendency to aggregate, and subsequently alter, their fluorescence behaviour.⁸¹ Planar aromatic rings and extensive π conjugation means luminophores are usually quite hydrophobic and also readily undergo π - π stacking. These effects result in aggregate (J- or H-aggregates)^{79,82,83} or excimer formation^{78,80,82,84} and considerably alter the emission band position, intensity and fluorescence lifetime of the luminophore solution.^{79,82} This phenomena is well known and commonly referred to as *aggregation caused quenching* (ACQ).⁸⁵ Figure 1.10 shows the onset of ACQ for two fluorescent dyes: perylene and *N,N*-dicyclohexyl-1,7-dibromo-3,4,9,10-perylenetetracarboxylic diimide (DDPD) in tetrahydrofuran (THF). As the water content of the solution increases, so does the degree of photoluminescence quenching. This has been attributed to the increased aggregation of the hydrophobic molecules in high water content solutions.^{5,86}

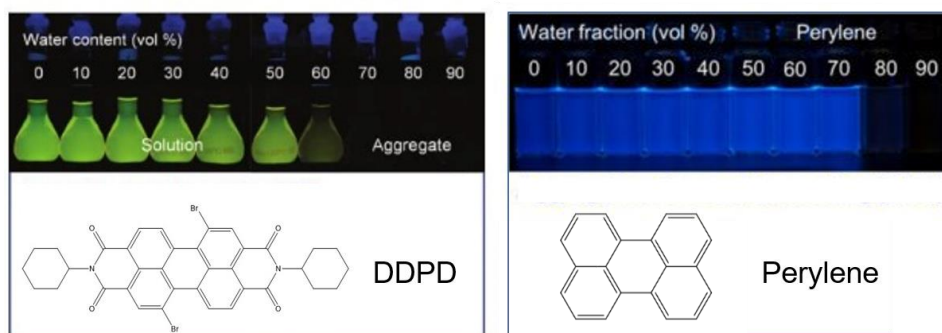


Figure 1.10 Fluorescence photographs of solutions/suspensions of DDPD (left) and perylene (right) in THF/water mixtures with different water contents. adapted with permission from the Royal Society of Chemistry (Chem. Soc. Rev., 2011, 40, 5361) and (Chem. Rev., 2015,115 (21), 11718). Copyright (2015) American Chemical Society

This ACQ effect is generally considered detrimental to the use of luminophores in many device technologies. For example, optoelectronic applications (sensors, solar cells, luminescent solar concentrators) often require the fluorescent species to be in the solid state, with luminophores held in close proximity to each other upon incorporation into polymer matrices or thin films.^{87–90} Similarly for aqueous environments, such as those necessary for ecological and biological applications, hydrophobic fluorescent dyes have a high tendency to form aggregates.^{91–93} In such cases it is imperative to control the dispersion state of the luminophore, as the properties selected for based on the behaviour of the isolated luminophore become altered upon aggregation.^{94–96} This need to control the luminophore dispersion state and prevent

aggregation can require extensive and complicated engineering approaches and usually solves one problem at the expense of introducing additional ones.^{97–101}

1.4.2 Aggregation Induced Emission

It has been established so far that fluorescent molecules are typically highly conjugated, planar, aromatic molecules and that such molecules have a universal tendency to aggregate in the solid state, in aqueous solution or at high concentrations through a combination of hydrophobic interactions and π - π stacking. Considering one of the criterion for a molecule to exhibit photoluminescence is the suppression of non-radiative deactivation *via* molecular rigidity, is there a way to both harness the natural propensity of aromatic conjugated molecules to aggregate and also establish that as a means of introducing rigidity, and perhaps photoluminescence, to the system? In 2001 Tang *et al.* reported a molecule, 1-methyl-1,2,3,4,5-pentaphenylsilole (Figure 1.11a) which exhibited fascinating behaviour, completely contrary to ACQ.⁴ It was found that in good solvents the molecule was barely luminescent ($\Phi_F \sim 0.003$) while in poor solvents it was much more emissive ($\Phi_F = 0.21$, Figure 1.11). The increased photoluminescence in poor solvent was attributed to the aggregation of the molecules, and the phenomenon referred to as *aggregation induced emission*. Tang *et al.* further investigated this phenomenon by synthesising several other bulky silole derivatives, including hexaphenylsilole (HPS, Figure 1.11b). All were found to be non-emissive in dilute solutions but highly photoluminescent in concentrated solutions or thin films, confirming that this initial discovery was not just a once-off.^{74,102}

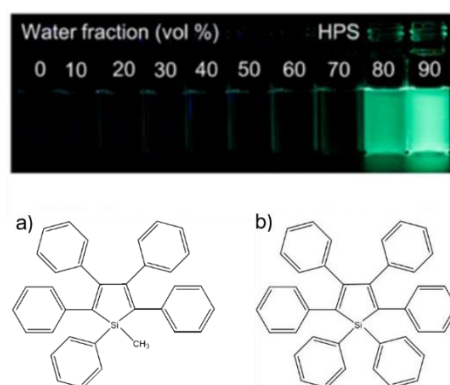


Figure 1.11 Photographs of the fluorescence of HPS in water/THF solutions and the molecular structures of two AIE active molecules. Top: Increasing fluorescence intensity of hexaphenylsilole upon increasing water fraction.⁵ Reprinted with permission from (Chem. Rev., 2015,115 (21), 11718). Copyright (2015) American Chemical Society. Bottom: Molecular structure of a) 1-methyl-1,2,3,4,5-pentaphenylsilole and b) hexaphenylsilole (HPS)

1.4.3 Mechanism of Aggregation Induced Emission

Bulky siloles are not the only family of molecules which exhibit AIE.¹⁰³ Tetraphenylethylene (TPE, Figure 1.12) is a typical AIE active molecule (or *AIEgen*), which will be used here as a case study to explain the posited mechanism for AIE. TPE possesses large rotor-like phenyl groups which are twisted out of the alkene plane by 50°. ⁸⁵ This means that in dilute solution, dynamic behaviours, such as the intramolecular rotations of the phenyl groups around the single bond axis, allow the excited state of TPE to relax non-radiatively resulting in a non-emissive molecule.^{85,104} In the aggregated state, the bulky phenyl rotors are thought to impart photoluminescence behaviour in two ways. Firstly, the phenyl groups are not coplanar, rather adopting a twisted conformation, meaning that neither π - π stacking nor the red shift and/or non-radiative recombination often associated with such stacking can occur.^{85,102} Secondly, the intramolecular rotations which previously dissipated excited state energy are suppressed due to steric hindrance of the bulky rotors between molecules.^{105,106} This latter mechanism is referred to as the *restriction of intramolecular rotations* (RIR) and is considered to be the key mechanism for AIE.^{5,107}

Several other mechanisms have been proposed to account for this aggregation-emission behaviour, such as twisted intramolecular charge transfer, J-aggregate formation and planarisation.^{85,86,107} However, none are fully supported by experimental results and theoretical calculations. For example, it was found that AIEgens are most emissive in highly viscous solutions, low temperature solutions and pressurised solids.^{102,106} These are all environments conducive to aggregation, supporting the RIR mechanism. Similarly, when sterically bulky groups or cross-locking units are tethered to AIEgens, further preventing the dissipation of excited state energy through intramolecular motions, the fluorescence intensity is enhanced.^{108–110} Studies involving theoretical calculations also seem to support the RIR mechanism.^{104,111}

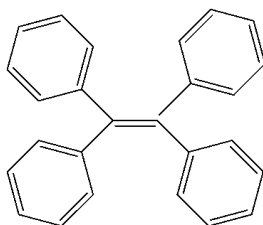


Figure 1.12 Molecular structure of Tetraphenylethylene (TPE), a prototypical AIEgen.

1.4.4 Tetraphenylethylene-based AIEgens

In the literature there is a wide variety in the structure of AIEgens to be found, from heterocarbon compounds to Schiff bases and dendrimers to metal organic frameworks.^{5,9} The number of annual AIE related publications has long surpassed 500 per year, with several comprehensive review articles to be found which detail in-depth the synthesis, mechanism and applications of AIEgens.^{5,86,106,107} One prototypical AIEgen will be focused on here, namely TPE. TPE-based AIEgens have found a use in a plethora of applications, including optoelectronic devices, optical waveguides and luminescent sensors. Recently, an AIE active sodium dodecyl sulfate (SDS) based surfactant incorporating a TPE moiety in its alkyl tail has been reported (TPE-SDS), and was found to allow direct visualisation of the micellisation process through the ‘switching on’ of luminescence upon self-assembly of the surfactant.⁹ A water-in-oil microemulsion containing TPE-SDS was created in order to theoretically calculate the shortest distance between TPE units required for the emission of light. This approach was found to support the RIR mechanism but relied heavily on assumptions about the local environment and geometry of the microemulsion droplets. The results of this study will be further detailed in Chapter 6, along with an approach new to this thesis endeavouring to use neutron scattering techniques to elucidate the TPE-TPE unit distance within TPE-SDS micelles.

1.5 Thesis Aims

The first part of this thesis will examine the physicochemical and self-assembly behaviour of a family of targeted AzoPS, with special attention being directed to the impact of light irradiation on these surfactants. Chapter 4 will focus on understanding the key structure-physicochemical property relationships of the tetraethylene glycol AzoPS up to the CMC. The synthesis of a series of strategically designed AzoPS will be outlined with their physicochemical properties as a function of light irradiation correlated with molecular structure. Chapter 5 will focus attention on the larger scale self-assembly and organisation of these AzoPS, with small-angle scattering techniques employed to elucidate the impact of molecular structure on the self-assembled structures formed.

In Chapter 6 the inherent tendency of surfactants to self-assemble will be taken advantage of to explore the aggregation and emission properties of an AIE-active surfactant, TPE-SDS. Emphasis will be on the geometric and spatial requirements for aggregation induced emission to occur, again relying on small-angle scattering techniques. Finally, Chapter 7 will summarise the main findings of this thesis and provide an outlook for future study as a result of this work. To provide a more thorough understanding of some of the techniques used and

experiments undertaken to produce this work, a brief account of the theoretical and experimental details precedes the results chapters, to be found in Chapter 2 and Chapter 3 respectively.

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Chapter 2

Theory

2.1 Interaction of Light with Matter

In the following chapter, the fundamental interactions of light with matter will be outlined as pertaining to the experiments in this thesis. As both surfactants studied in this work are photoactive (either photoisomerisable or photoluminescent), a brief description of the underlying photochemical theory behind these phenomena will be presented in Sections 2.1.1-2.2, while Section 2.2 describes the scattering techniques used to probe the self-assembled surfactant structures.

2.1.1 Wave-Particle Duality

Electromagnetic radiation is typically characterised in terms of its wavelength (λ) or frequency (ν). There is a fundamental relation between these two entities as outlined by the Planck equation:¹

$$E = h\nu = \frac{hc}{\lambda} \quad (2.1)$$

where E is energy, h is Planck's constant (6.626×10^{-34} J s) and c is the speed of light in a vacuum. In quantum theory, electromagnetic radiation is considered as consisting of discrete particles (*photons*) of quantised energy. Electromagnetic radiation can be considered as both wave-like and particle-like, with the general wave-particle duality of matter being exemplified by the de Broglie relation:¹

$$\lambda = \frac{h}{p} \quad (2.2)$$

where p is the momentum. Due to the very small value of Planck's constant, the wave behaviour of particles is only experimentally significant for very light particles such as protons and neutrons. The de Broglie relationship is the primary reason that neutrons can be used in scattering experiments, supported by a general theory that explains the scattering behaviour of light, X-rays and neutrons interchangeably.^{1,2} Scattering theory will be outlined in further detail in Section 2.2, with the next section focusing on the interaction of photons with matter.

2.1.2 Formation of Excited States

In order for an excited state to form, a molecule must absorb a photon of the correct frequency, that is, the frequency of the photon must match the frequency of an oscillating dipole within the molecule for absorption to occur.³ In general, a transition from a lower (State 1) to a higher (State 2) energy level, within the molecule is described in terms of the transition dipole moment M_{12} .

$$M_{1,2} = \int \psi_1 \hat{\mu} \psi_2 d\tau \quad (2.3)$$

where φ_1 is the time-dependent wavefunction for the electronic ground state, φ_2 is the time-dependent wave-function for the electronic excited state and $\hat{\mu}$ is the electric dipole moment. The probability of a transition occurring is given by the square modulus of the transition dipole moment, $|M_{1,2}|^2$. For this probability to be non-zero, two general rules are applied³:

- (i) *Spin selection rule*: There must be no change in angular momentum upon an electronic transition. This means that a transition between states of different multiplicities is formally forbidden. This rule is relaxed upon coupling between the spin and magnetic orbital momentums, known as *spin-orbit coupling*.
- (ii) *Laporte selection rule*: There must be a change in symmetry upon an electronic transition. This means transitions can only occur between wavefunctions of different symmetry. This rule is relevant for the absorption of AzoPS: as the *cis*- and *trans*-isomers have different symmetries (given by the point group), electronic transitions which are forbidden for one isomer may be allowed for the other.

The identity of the excited state, either singlet (S_n) or triplet (T_n), is determined by its *spin multiplicity*.^{4,5} Spin multiplicity is defined by $(2S+1)$, where S is the total spin angular momentum (the sum of the individual electron spins in the molecule).³ For a ground or excited singlet state, the spin multiplicity is 1 (as $S = 0$), while for a ground or excited triplet state the spin multiplicity is 3 (as $S = 1$). The triplet state is lower in energy than the singlet state, as it has the higher multiplicity (Hund's rule).³

The quantitative treatment of light absorption (*e.g.* UV-vis absorption spectroscopy) relies on the use of the Beer-Lambert law, which describes the light absorption efficiency of a molecule:³

$$\log_{10} \frac{I_t}{I_0} = A = \varepsilon cl \quad (2.4)$$

where I_t and I_0 are the transmitted and incident intensities respectively, A is the absorbance, ε is the wavelength dependent molar absorption coefficient (a measure of the probability of the electronic transition occurring⁵), c is the concentration of the absorbing species and l is the path length travelled by light within the absorbing medium.

2.1.3 Deactivation of Excited States

Following the formation of an excited state by absorption of a photon, a molecule can relax by means of either radiative or non-radiative processes.^{4,5} A Jablonski diagram outlining the most common deactivation pathways for organic molecules is given in Figure 2.1.⁴ Radiative relaxation (photoluminescence) involves the emission of a photon, and can be

characterised as either fluorescence or phosphorescence. *Fluorescence* is a radiative transition between electronic states of the same multiplicity, *e.g.* $S_0 \leftarrow S_1$.³ Kasha's rule states that emission can only occur from the lowest excited state of given multiplicity, explaining why fluorescence typically occurs at longer wavelengths than absorption and is generally independent of excitation wavelength.⁴ In order to reach the lowest excited state of a given multiplicity, non-radiative transitions, such as *internal conversion* (IC), must occur.⁵ IC is a transition between electronic states of the same multiplicity, *e.g.* $S_1 \leftarrow S_2$, and is typically followed by vibrational relaxation to the lowest vibrational level of the new, lower energy electronic state.⁴

Phosphorescence is a radiative transition between electronic states of different multiplicities, *e.g.* $S_0 \leftarrow T_1$.⁴ This is a formally spin-forbidden process and consequently the radiative rate is very low. To access a triplet state from a singlet state, *e.g.* $T_1 \leftarrow S_1$, a non-radiative spin-forbidden process known as *intersystem crossing* (ISC) must occur.^{3,4} Fluorescence and phosphorescence are typically characterised in terms of their excited state lifetime and quantum yield, however the details of such measurements are outside the scope of this work.

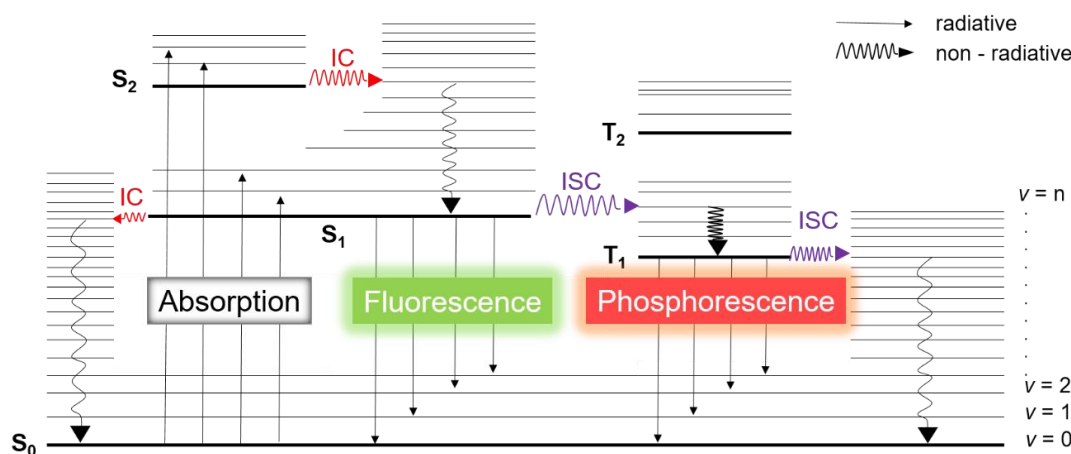


Figure 2.1 Jablonski diagram indicating formation and relaxation of a photoexcited organic species. Radiative processes (*absorption, fluorescence, phosphorescence*) are shown using black solid arrows. Non-radiative processes (*internal conversion (IC, red), intersystem crossing (ISC, purple), vibrational relaxation (black)*) are specified using wavy arrows. The lowest energy level of each state is given by a thick, black horizontal line, with the multiplicity of the state presented beside it.

2.1.3.1 Quenching of Excited States

The photoluminescence efficiency of a molecule depends in part on the degree of excited-state quenching. Fluorescence quenching refers to any process which decreases the fluorescence intensity of a material. These processes can be inherent to the molecule, such as the non-radiative decay pathways outlined previously, or can be a bimolecular process,

involving the interaction of the photoluminescent molecule (luminophore) with a second species, called a *quencher*.³ In terms of bimolecular quenching processes, there are two main quenching modes: *static* and *dynamic*. Dynamic quenching involves the quencher diffusing to the luminophore within the lifetime of the excited state, and upon contact, returning the luminophore to the ground state without the emission of a photon, that is, the quencher introduces a new non-radiative pathway along which deactivation of the excited state can occur.^{3,4} Static quenching involves the formation of a non-emissive complex between the luminophore and quencher.^{3,4} Static quenching can be extended to include ACQ, whereby the quenching process is a result of neighbouring luminophores aggregating with one another.^{6,7} ACQ has been outlined previously in the Introduction, and will be further discussed in opposition to AIE in Chapter 6.

2.1.3.2 Photoisomerisation

An additional possibility upon absorption of a photon is *photoisomerisation*, the most relevant to this thesis being the *trans-cis* isomerisation of azobenzene. In general, photoisomerisation can be considered as a non-radiative deactivation process which, in contrast to the aforementioned pathways (fluorescence, IC, phosphorescence *etc.*), results in a species which is structurally different from that of its predecessor.³ During photoisomerisation the energy supplied by light induces a large increase in the vibrational energy off the ground state.⁸ This increased energy, coupled with vibronic mixing between the ground and lowest excited state wavefunctions, ultimately resulting in a transition (typically $\pi\text{-}\pi^*$).⁸ The excess energy of this transition is accepted by the promoting vibration and can lead to complete π bond dissociation.⁸ The now excited $\pi\pi^*$ state has half-filled orbitals and adopts a twisted conformation around the remaining σ bond to minimise the electronic repulsion of the electrons in these orbitals.⁸ The excited molecule undergoes a radiationless transition back to the ground state, with the double bond being reformed either in the original planar *trans* geometry or maintaining the bent *cis* configuration. For azobenzene four possible mechanisms—rotation, inversion, concerted inversion and inversion-assisted rotation – have been proposed as pathways for photoisomerisation, the nuances of which are outside the scope of this thesis.⁹ The photoisomerisation processes of azobenzene is fundamental to Chapters 4 and 5 in this thesis, which aim to understand the physicochemical and self-assembly behaviour of azobenzene photosurfactants in both the *cis*- and *trans*- forms. Section 2.2 will now outline the scattering techniques used to characterise the self-assembly behaviour of both the AzoPS and AIE surfactants studied in Chapters 4-6.

2.2 Scattering Techniques

As mentioned previously, radiation can be considered as a beam of particles, be it neutrons, X-rays or photons. The beam of particles can either be absorbed, scattered or transmitted by the sample. Scattering techniques are widely used to characterise condensed and soft matter systems at the molecular level in terms of their structure, size and shape. Scattering techniques rely on quantifying the interaction between matter and incoming radiation or particles, specifically the deflection of the incident radiation by the sample under study.¹ By quantifying this deflection and analysing the resultant scattering pattern, a “picture” of the object under investigation can be formed. In this section the fundamental scattering theory of light, X-rays and neutrons will be reviewed, in particular as it applies to the techniques and instrumentation used in this thesis.

2.2.1 Elastic and Inelastic Scattering

Scattering processes can generally be considered as *elastic* or *inelastic*.¹⁰ *Elastic scattering* occurs when incident particles, either photons or neutrons, collide with strongly bound electrons in the sample with no energy transfer.¹ The electrons begin to oscillate synchronously at the same frequency as the incoming radiation, such that the final scattered wavelength is the same as the incident wavelength.² *Inelastic scattering* is a collision between incident particles and sample in which there is a net transfer of energy, usually with the incident particle losing energy.¹⁰ Energy is transferred to the sample, and can be used to probe the now excited vibrational and electronic levels of the sample. In this chapter only elastic scattering will be considered, as it is this type of scattering which is used for structural characterisation¹, *e.g.* small-angle neutron scattering (SANS).

As aforementioned, after an elastic scattering event the scattered radiation has the same wavelength as the incident radiation. If the incident wavelengths are coherent, *i.e.* are in phase and possess only one wavelength (or more realistically, a small spread of wavelengths), then not only does a scattered wave have the same wavelength as the incident wave, it also has the same wavelength as all other scattered waves.^{1,11} The interference of these scattered waves produces a pattern that allows structural information about the sample to be deduced.^{1,12} If this interference is in phase then *constructive interference* will be observed, seen as a bright spot on the detector. Likewise, if the scattered waves interfere out of phase, then *destructive interference* will be observed, appearing as a dark spot on the detector.

The geometry of an elastic scattering event is shown in Figure 2.2a, where the incident radiation is defined by $\mathbf{k}_i$ and $\boldsymbol{\omega}$, the incident wave vector and angular momentum, respectively.

Upon scattering through an angle of θ , the final radiation is characterised by $\mathbf{k}_f$ and ω_f , with $|\mathbf{k}_i| = |\mathbf{k}_f|$ by definition of elastic scattering.¹³ A vector diagram for this process is shown in Figure 2.2b, introducing a new parameter, $\mathbf{Q}$, which is the resultant of the incident and final wave-vectors, $\mathbf{k}_i$ and $\mathbf{k}_f$. $\mathbf{Q}$ is referred to as the scattering wave-vector. Basic trigonometry leads to the result:^{2,12,13}

$$|\mathbf{Q}| = q = \frac{4\pi \sin \frac{\theta}{2}}{\lambda} \quad (2.5)$$

where the magnitude of $\mathbf{Q}$ is designated q , θ is the scattering angle and λ is the wavelength of incident radiation (neutron or electromagnetic). Equation 2.5 links the momentum transfer to the wavelength and the scattering angle, and by substituting Equation 2.5 into Bragg's law of diffraction (Equation 2.6) the useful Equation 2.7 is yielded, which relates the wave-vector q (in reciprocal space) to real space.^{12,13}

$$\lambda = 2d \sin \frac{\theta}{2} \quad (2.6)$$

$$d = \frac{2\pi}{q} \quad (2.7)$$

where d is the distance between scattering bodies. From Equation 2.7 it is clear that a large q range allows a wide variety of distances or particle sizes to be explored, with the specific 'size' of a scattering body being ascertained rapidly from the position of any diffraction peak in q -space.^{12,13} From Equation 2.5 it is apparent that q can be adjusted by varying either the scattering angle or incident wavelength. Thus, the distances probed in real space by elastic scattering are dependent on the scattering angles or incident wavelengths chosen. This has consequences for SANS with respect to the choice of instrumentation and neutron source, and will be discussed further in Section 2.2.4.1.

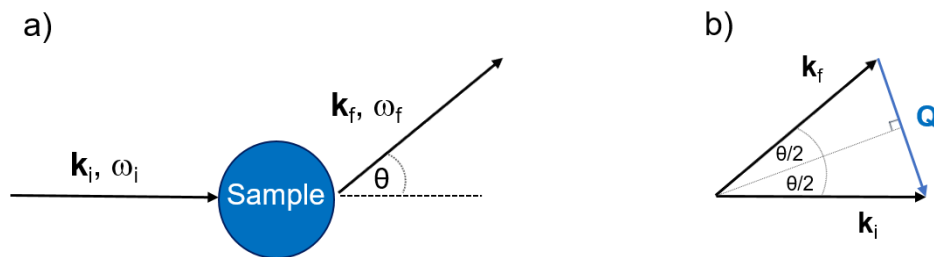


Figure 2.2 (a) Schematic representation of a particle being scattered by a sample through an angle of θ , where k_i (k_f) and ω_i (ω_f) are the incident (final) wave-vector and incident (final) angular momentum respectively. (b) Vector diagram for elastic scattering where $|\mathbf{k}_i| = |\mathbf{k}_f|$. The scattering wave-vector, $\mathbf{Q}$, ($\mathbf{k}_i - \mathbf{k}_f$) is indicated in blue.

The wavelength of incident radiation can also determine the type of scattering observed. When the wavelength of incident radiation is smaller than the diameter of the particles under study ($\sim 1/10$ the size), *Rayleigh scattering* is observed.² In this case, scattering can be considered as isotropic with the intensity of scattered light, I , being directly proportional to the particle diameter, d_p , as $I \propto d_p^6$ and inversely proportional to the wavelength of incident light as $I \propto \lambda^{-4}$.^{14,15} The assumptions of Rayleigh scattering always hold true for neutrons, where λ is on the order of 1×10^{-10} - 1×10^{-11} m, while the interacting nucleus is on the order of 1×10^{-15} m. However, for light in the visible region, wavelength starts to become comparable to molecular length scales. When the incident wavelength is on the same order as or larger than the diameter of the particle under study, *Mie scattering* is seen. Mie scattering is not strongly wavelength dependent nor isotropic, occurring predominantly in the forward direction.^{14,15} The larger the particle the more the bias towards forward scattering will be seen. Dynamic light scattering (DLS) experiments often use a He-Ne laser (630 nm) as the light source, with a back scattering configuration being selected to prevent the detector from being overwhelmed by forward scattering from large aggregates, such as dust.¹⁶

2.2.2 Properties of Light, X-Rays and Neutrons

The principal difference between different types of radiation, (*i.e.* electromagnetic or neutron), insofar as scattering experiments are concerned, lies in how the radiation interacts with the sample (Table 2.1). For example, electromagnetic radiation, such as light or X-rays, interacts with the electrons of the sample and is electrostatically repelled rapidly upon sample penetration.^{2,12} Neutrons are unaffected by the electrons in the sample, rather they are repelled by the strong nuclear force of the atomic nucleus.¹⁰ This is advantageous as it means neutrons can travel further into the material than electromagnetic radiation, and be used to probe the bulk properties of the sample.¹ The degree of neutron scattering depends on the strength of the nucleus-neutron interaction. This interaction is quantified by the *neutron scattering length* (b_n) of the atom, which is a measure of how large the nucleus appears to the incident neutron.^{10,17} b_n has a non-linear relationship to atomic number and is also isotope specific. For example, hydrogen has a neutron scattering length of 1.76×10^{-28} m², while deuterium has a neutron scattering length of 5.59×10^{-28} m².^{11,18} This means that neutron scattering experiments can distinguish between hydrogen and deuterium, while for the equivalent experiments with X-rays, these two isotopes appear identical with $Z = 1$. This has consequences for contrast-matching experiments, which will be outlined in detail in relation to SANS in Section 2.2.4.3. In this thesis, DLS and SANS techniques are employed to study self-assembled surfactant structures

in terms of size and shape. As such, these two techniques will be described in the following sections, beginning with DLS.

Table 2.1 Properties of light, X-rays and neutrons insofar as they relate to scattering experiments.

	Light	X-rays	Neutrons
Wavelength	400-800 nm ¹⁴	0.01-0.2 nm ²	0.01-2 nm ¹
Penetration Depth ¹	>0.01 µm	nm-µm	nm-cm
Scattering Depends On:	Refractive index ¹⁴	Electron density ¹²	Neutron scattering length ¹

2.2.3 Dynamic Light Scattering

DLS, also known as *photon correlation spectroscopy* or *quasi-elastic light scattering*, is a scattering technique useful for determining both the average size and size distribution of particles in the sub-micrometer range in terms of their hydrodynamic radius (R_H) and polydispersity index (PDI).¹⁹ DLS quantifies the speed at which particles diffuse in solution as a result of Brownian motion, and relates this to the effective size of the particles.²⁰ Brownian motion is the random movement of particles in a liquid or gas as a result of the particles colliding with the rapidly moving solvent or vapour molecules.²¹ DLS is concerned only with the measurement of particles suspended within a liquid. The extent of Brownian motion is given by the translational diffusion coefficient, D , which relates to R_H through the Stokes-Einstein equation:²¹

$$D = \frac{k_b T}{6\pi\eta R_H} \quad (2.8)$$

where k_b is the Boltzmann constant, T is the temperature and η is solvent viscosity. Larger particles will be displaced by shorter distances through Brownian motion than smaller particles, resulting in a slower rate of diffusion, as exemplified by the inverse relationship between D and R_H in Equation 2.8. The hydrodynamic radius obtained is the radius of a sphere with the same translational diffusion coefficient as the particle under study.²⁰ As such, the size values obtained by DLS can only be unequivocally ascribed to spherical objects.

A DLS experiment typically consists of a solution of particles illuminated by a monochromatic light source, such as a laser.¹⁶ The beam of light will be scattered by the particles in solution with the particle size (and the magnitude of Brownian motion) affecting the rate at which the intensity of scattered light fluctuates.¹⁵ Small particles cause the intensity of scattered light to fluctuate more rapidly than large particles. This is quantified using a digital auto-correlator, which measures the degree of similarity between two signals at the same time or between one signal at different time intervals.^{15,14} The latter approach is taken for DLS, with

the signal of scattered light intensity at time t compared to the signal at a later time $(t + \delta t)$, where δt is a very short time interval. For larger particles, where the intensity of scattered light fluctuates slowly, the correlation between signals persists for a relatively long time.¹⁴ Conversely, for small particles the correlation decays rapidly as the signal of scattered light intensity fluctuates quickly. From this, a correlation function of the scattered intensity, $G^2(t)$, can be established. For a large number of monodisperse particles in Brownian motion, $G^2(t)$ is an exponentially decaying function of the delay time δt , as shown in Equation 2.9:¹⁹

$$G^2(t) = \int_0^\infty I(t)I(t + \delta t) = B + Ae^{-2q^2 D\delta t} \quad (2.9)$$

where B is the baseline of the correlation function, A is the intercept of the correlation function and q is the scattering wave-vector. The correlation function is analysed *via* cumulants analysis, whereby a single exponential is fitted to the correlogram, yielding a value for the diffusion coefficient and subsequently R_H .^{14,16} The PDI can also be ascertained, which is an estimate of the width of the size distribution obtained from the cumulants analysis.¹⁴

2.2.4 Small-Angle Neutron Scattering

While light scattering is a convenient and straightforward technique to rapidly ascertain the hydrodynamic diameter of aggregates > 10 nm, neutrons allow for a wider length scale to be explored. SANS experiments can also be used to probe particle shape, structure and surface properties as well as inter-particle interactions.¹³ In this section the basic instrumentation, theory and data analysis employed for SANS will be outlined, in particular as relevant for the experiments in this thesis.

2.2.4.1 SANS Instrumentation

SANS experiments typically explore length scales of 1.4 – 630 nm, making SANS an ideal technique for studying soft matter systems such as micelles.¹² From Equation 2.7, which relates q -spacing to distance, it can be deduced that this length scale corresponds to a q -range of 0.001–0.45 Å⁻¹. The q -range can be reached by varying either θ or λ (evident from Equation 2.5), the choice of which will depend on the neutron source used. Neutrons are generated either *via* the fission of uranium-235 at a nuclear reactor^{10,17} or from a spallation source. At a spallation source a synchrotron accelerates a high-energy proton beam and uses it to bombard a heavy metal target such as tantalum.²² The metal target fragments and releases a certain number of neutrons for every incident proton. Neutrons from either a continuous reactor source or a spallation source must be moderated initially to reduce their velocity and increase the wavelength. At a reactor source, a bandpass will then be used to select one particular neutron

wavelength,¹⁰ while at a synchrotron source a pulse containing a broad range of wavelengths will be maintained.

A basic scattering experiment consists of the initial radiation (either a single wavelength or a band) passing through a collimator to align the beam and a detector to determine the initial intensity, before interacting with the sample. After passing through the sample the scattered intensity is determined by a second detector. For neutrons generated at a spallation source, the initial broadband pulse determines the q -range, with θ fixed by having a fixed final detector distance. The neutron λ is calculated by measuring the length of time taken for a neutron from the broad pulse to reach the detector.²² This configuration is called a *time of flight* (TOF) instrument. For neutrons generated at a continuous reactor source, a fixed wavelength configuration is preferred. In this set-up, the q -range is determined by varying θ by using a series of detector distances, with a single wavelength selected by the velocity selector and chopper.²³ All the SANS experiments described in this thesis were carried out at the continuous source KWS-2 instrument (Figure 2.3) in JCNS, Garching, Munich.^{23,24}

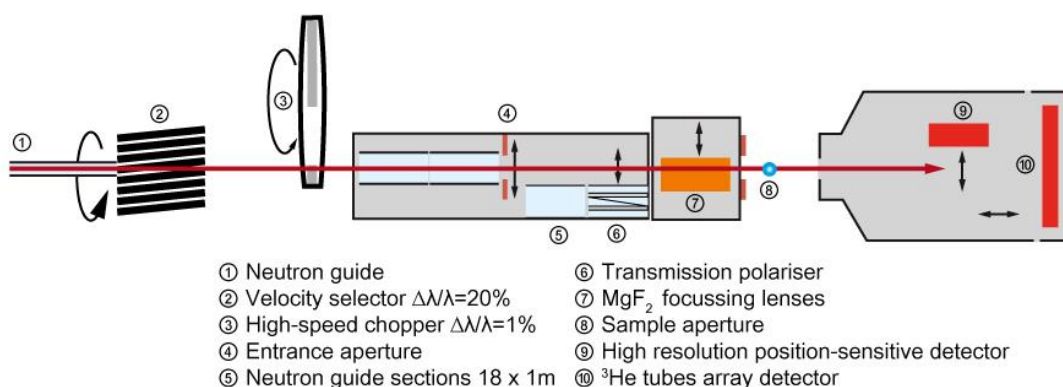


Figure 2.3 A schematic representation of the KWS-2 instrument at JCNS, Munich. The neutron wavelength is determined by the velocity selector (1) and chopper (2), while the sample is held in position at (8). The intensity of scattered radiation is determined by the detectors at (9) and (10).

2.2.4.2 Theory of Small-Angle Neutron Scattering

The basic aim of a scattering experiment is to measure the proportion of incident particles that emerge in various direction having undergone elastic scattering. The differential cross-section (Equation 2.10) is an experimental parameter which can describe this phenomenon in terms of measurable entities.^{1,25}

$$\frac{d\sigma}{d\Omega}(q) = I(q) = NV^2(\Delta\rho)^2P(q)S(q) + BG \quad (2.10)$$

where $(d\sigma/d\Omega)(q)$ is the differential cross section, N is the number of scattering bodies per unit volume, V is the volume of a single scattering body, $\Delta\rho$ is the contrast, $P(q)$ is the form factor, $S(q)$ is the structure factor and BG is the isotropic, incoherent background. The contrast, form factor and structure factor will be outlined in more detail below.

2.2.4.3 Contrast and Contrast-Matching in SANS Experiments

The *contrast* in scattering experiments refers to how the incoming radiation scatters differently depending on the nature of the sample. For example, in light scattering experiments the contrast depends on the difference in refractive indices within the sample, while for X-ray scattering experiments the contrast arises from differences in electron density, with heavy atoms contrasting highly with lighter atoms.¹² As neutron scattering relies on the interaction of the neutron and nucleus *via* the strong nuclear force, the contrast relies on differences in neutron scattering length densities (SLD), with the neutron SLD being determined from Equation 2.11 as follows:¹

$$\rho = \frac{\sum_i^N b_i}{V_m} \quad (2.11)$$

where ρ is SLD, b_i is the scattering length of the i th atom and V_m is the molar volume. The atomic scattering length, b , as aforementioned, quantifies the strength of the interaction between the incident neutron and bound atomic nucleus and is isotope dependent. The contrast, $(\Delta\rho^2)$, in SANS is then the difference between the SLD of the sample (ρ_s) and the SLD of the matrix (ρ_m) squared, as shown in Equation 2.12.^{1,12}

$$(\Delta\rho)^2 = (\rho_s - \rho_m)^2 \quad (2.12)$$

Should $\rho_s = \rho_m$ the contrast will be zero and no scattering profile will be seen.¹³ When this condition is met, the scatterer is said to be *contrast-matched*. The scattering profile from a multi-component sample system can be simplified significantly by employing contrast matching. As hydrogen and deuterium have dramatically different SLDs using a deuterated solvent will achieve a contrast between the hydrogenated sample scatter and the deuterated solvent matrix scatter. Figure 2.4 portrays some of the contrast matching possibilities for selective deuteration of a core-shell sample dispersed in either a deuterated or hydrogenated solvent.

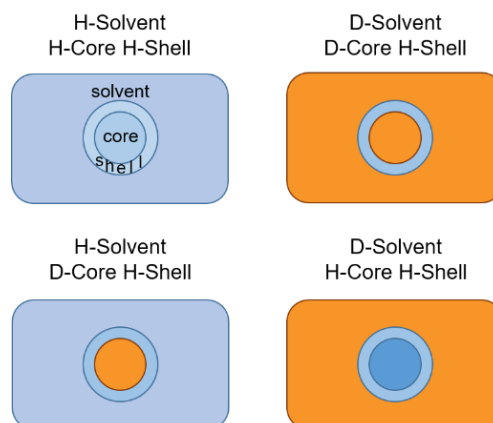


Figure 2.4 Schematic representation of the contrast variation possibilities for a core-shell micelle dispersed in a solvent. The hydrogenated and deuterated components are indicated in blue and orange respectively. In cases where the contrast of the core and/or shell of the micelle matches that of the solvent, the core and/or shell is said to be contrast-matched, with scatter from the non-contrast matched component(s) dominating the scatter profile.

2.2.4.4 $P(Q)$: The Form Factor

The scattering of a particle made up of many different atoms can be considered as the interference pattern produced by the interaction of all the scattered waves from every atom in the particle that reaches the detector.¹³ As such, information about the sample shape, size, wetness and structure can be deduced from this interference pattern. The scattering profile is constructed from the addition and squaring of all the wave amplitudes at the detector position. This addition and squaring is known as a 1D reduction and is performed by the instrumental software, in this case QtiKWS.²⁶ The shape of the resulting scattering profile is characteristic of the shape of the scattering particle and is called the *form factor*.^{1,12} Figure 2.5 shows form factors characteristic of scattering from a lamellar sheet, a sphere and a cylinder. The observed scattering pattern can be considered as corresponding to the form factor for one particle only if the sample is monodisperse, *i.e.* the particles are all identical in shape and size, and sufficiently dilute, meaning that the particles are far enough away from each other such that the form factors of all illuminated molecules can be summed.²⁵ The scattering pattern observed will then correspond to the individual particle form factor multiplied by the number of particles within the sample area illuminated by the incident neutron beam.

The wetness of the sample, χ_{sol} , gives a measure of the proportion of water present within the self-assembled structure and can be obtained from the fitting of a suitable form factor to the scattering profile. It is calculated from the SLD of the solvent, $\text{SLD}_{\text{solvent}}$, the SLD of the dry sample, SLD_{dry} , and the SLD of the measured sample, $\text{SLD}_{\text{measured}}$, as shown in Equation 2.13.

$$\chi_{sol} = \frac{SLD_{measured} - SLD_{dry}}{SLD_{solvent} - SLD_{dry}} \quad (\text{Eq. 2.13})$$

The SLD of the dry sample and pure solvent are readily determined from the summing of the individual atomic scattering lengths, as described previously by Equation 2.11, while the SLD of the measured sample is an outputted parameter from the correct fitting of a form factor to the scattering profile.

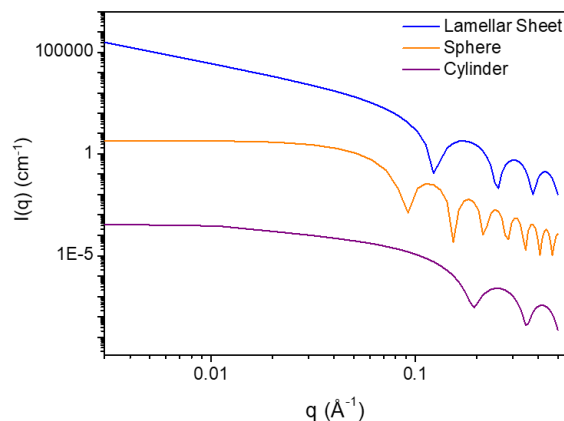


Figure 2.5 Graph of scattering intensity ($I(q)$) vs q showing the form factors ($P(Q)$) for a lamellar sheet (blue), a sphere (orange) and a cylinder (purple). The y-axes have been offset for clarity.

2.2.4.5 $S(Q)$: The Structure Factor

If a scattering system is highly concentrated, the magnitude of inter-particle distances becomes comparable to the magnitude of intra-particle distances. As a result, the interference pattern obtained will have contributions from neighbouring particles, with the form factor alone no longer being sufficient to describe the data.²⁵ The form factor must be multiplied by a *structure factor* to account for the additional interference.²⁵ In general, a decrease in scattering intensity, typically at low q values, indicates repulsive interactions between molecules, while an increase in scattering intensity typically indicates attractive inter-particle interactions, such as aggregation. Eventually, upon increasing concentration, the scattering intensity can increase and develop into pronounced peaks. This is representative of a highly ordered or periodic arrangements of particles, such as in a crystal.²⁵ The increased scattering intensity is referred to as a *Bragg peak*, the position of which in q -space can be used to calculate the distance, d , between the ordered particles using Equation 2.3. In Chapters 5 and 6, scattering profiles obtained from self-assembled aggregates of AzoPS and AIE surfactants will be fit with form factor and structure factor models using non-linear least squares analysis. The descriptions of $P(Q)$ and $S(Q)$ used in the model-dependent SANS data analysis within this thesis are outlined in the Experimental section (Chapter 3).

2.2.4.6 Model-Independent Analysis: Standard Plots

Fundamental parameters about the scattering particle, such as size and shape, can also be obtained *via* model-independent analysis, which involves directly manipulating the data in accordance with standard plots, rather than fitting form factors and structure factors as outlined above. The two most commonly used model independent analyses are Guinier analysis and q -scaling. Guinier proposed that at low q the following expression could be used to describe the scattered intensity, $I(q)$:¹²

$$I(q) = I_0 e^{\frac{-(qR_g)^2}{3}} \quad (2.14)$$

where I_0 is the incident intensity and R_g is the radius of gyration of the scattering particle. A Guinier plot ($\ln I(q)$ vs. q^2) should include a linear section up to the limit $qR_g < 1.3$. The slope of this linear plot corresponds to $-(qR_g)^2/3$ allowing R_g to be determined. R_g is a measure of the effective size of the scattering particle. Guinier analysis is only suitable for analysing scattering profiles of monodisperse samples with no inter-particle interactions.¹

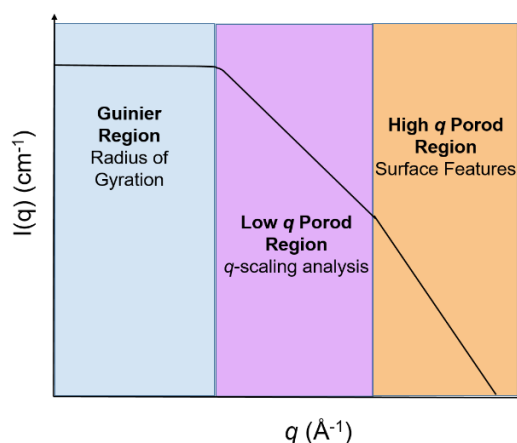


Figure 2.6 Schematic representation of the different regions within a typical scattering profile. The plateau in the Guinier region (blue) at low q gives information about the overall aggregate size, the slope of the scattering profile in the low q Porod region provides information about the fractal dimension of the scattering body, while in the high q Porod region details regarding the surface features of the scattering body can be determined.

q -scaling analysis is based on analysis of a specific region in a $\text{Log} I(q)$ vs $\text{Log}(q)$ plot, namely the low q Porod region (Figure 2.6). This region corresponds to a range smaller than the scattering objects themselves, such that the radiation is exploring the local structure.¹³ The slope of the Porod plot in this region (typically from the Guinier plateau, if seen, to $0.04 \text{ \AA}^{-1}$.) is indicative of the fractal dimension of the scattering objects. For example, a Porod slope of 1 is indicative of scattering from rigid rods, a Porod slope of two corresponds to scattering from sheet-like entities, a Porod slope of 3-4 indicates scattering from rough interfaces and a Porod slope of 4 characterises scattering from a smooth surface or sharp interface.^{13,27}

2.3 References

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Chapter 3

Experimental

3.1 Materials

3.1.1 Chemicals

Sodium dodecyl sulfate (SDS, $\geq 99\%$), 4-ethylaniline, 4-butaniline (97%), 4-octylaniline, sodium nitrite ($\geq 99\%$), 1,2-dibromoethane, anhydrous potassium carbonate ($\geq 99\%$), potassium iodide (99%), sodium sulfite (98%), sodium carbonate, sodium hydride (60% w/w in mineral oil), tetraethylene glycol (99%), hydrochloric acid (conc. 37%), ethanol (HPLC grade), tetrahydrofuran (HPLC grade), diethyl ether ($\geq 99.5\%$), deuterated chloroform ($> 99.8\%$ atom) dichloromethane, acetone and hexane were purchased from Sigma Aldrich. 1,4-dibromobutane ($> 98\%$) and 1,8-dibromooctane ($> 98\%$) were purchased from Alfa Aesar. 4-hexylaniline (90%), 1,6-dibromohexane (96%) were purchased from ChemCruz. d-25 Sodium dodecyl sulfate ($> 98\%$) was purchased from Santa Cruz Biotechnology. Sodium hydroxide ($\geq 97\%$) and chloroform ($> 99\%$) were purchased from Fisher Scientific and phenol ($> 99\%$) was purchased from BDH Chemical Ltd. England. TPE-SDS was a kind gift from Prof. Ben Zhong Tang of The Hong Kong University of Science and Technology. All reagents were used as received. All solvents for reactions were analytical grade while those used for characterisation were HPLC grade.

3.2 Instrumentation

3.2.1 UV-Vis Absorption Spectroscopy

UV-Vis absorption spectra for AzoPS and TPE-SDS characterisation were recorded on a Perkin Elmer Lambda 35 spectrometer with a slit width of 0.5 nm. Measurements were carried out using quartz cells with path lengths of 1 cm.

UV-Vis measurements to confirm the *trans-cis* photoisomerisation of the AzoPS during SANS measurements were carried out on a NanoDrop 2000c spectrophotometer (ThermoScientific), with a Hamamatsu Lightning Cure LC8 lamp ($\lambda = 365$ nm) used as the UV illumination source.

3.2.2 Photoirradiation

Photoisomerisation of each AzoPS from *trans* to *cis* for CMC and ST measurements was obtained by exposing the AzoPS to a UV light emitting diode (LED) (LedEngin[®]) with an illumination wavelength of 365 nm and a power output of 7 mW cm^{-2} , when placed at 2 cm from the sample. Reverse *cis* to *trans* isomerisation was performed using a white LED (Prolight[®]) with a blue filter, resulting in an illumination wavelength of 465 nm and a power output 0.5 mW cm^{-2} , when placed at 2 cm from the sample.

3.2.3 Solution Phase Nuclear Magnetic Resonance (NMR) Spectroscopy

Solution NMR spectroscopy was performed using a Bruker DPX 400 NMR instrument and 20 °C. ^1H and ^{13}C NMR spectra were recorded using operating frequencies of 400 and 151 MHz respectively. Chemical shifts were calibrated against a trimethylsilane (TMS) signal and reported in parts per million (ppm). CDCl_3 ($\delta_{\text{H}} = 7.25$ ppm, singlet; $\delta_{\text{C}} = 77.16$ ppm, triplet) was used as the deuterated solvent.

3.2.4 Fourier Transform Infrared (FT-IR) Spectroscopy

FT-IR spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer with an ATR accessory. All spectra were recorded at room temperature over a range of 4000-650 cm^{-1} with a resolution of 4 cm^{-1} .

3.2.5 Electrospray Ionisation Mass Spectrometry (ESI-MS)

Electrospray ionisation mass spectra were acquired using a Bruker microTOF-Q III spectrometer interfaced to a Dionex UltiMate 3000 liquid chromatography system, in negative and positive modes as required. The instrument was calibrated using a tune mix solution, (Agilent Technologies ESI-I low concentration tuning mix). Masses were recorded over the range 100-1200 m/z. Samples were prepared in HPLC CHCl_3 .

3.2.6 Melting Point Analysis

Measurements were performed on a Stuart melting point apparatus, SMP3. The heating block possesses 3 capillary tube holders. The heating rate was set at 0.5 °C/min.

3.2.7 Dynamic Light Scattering

DLS experiments were performed using a Malvern Instruments Zetasizer Nanoseries nano-ZS. The apparatus is equipped with a He-Ne laser emitting at 633 nm and with a 4 mW power source. Detection of the scattering intensity was done at a backscattering angle of 173°. All results (R_{H} , counts *etc.*) were obtained from an average of three runs, each run being of approximately 20 measurements. The autocorrelation function, $G(t)$ was determined from the fluctuation of the scattering intensity with time.

3.2.8 Photoluminescence Spectroscopy

Steady state emission spectra were recorded on a Fluoroog-3 (Horiba JobinYvon) spectrophotometer. Samples were measured in 3 path length quartz cuvettes in a right angled configuration. Spectra were corrected for the wavelength response of the system using correction factors supplied by the manufacturer. The emission and excitation slits widths were varied depending on the nature of the sample under investigation.

3.2.9 Surface Tensiometry

Experiments were performed on a Kibron EZ-Piplus surface tensiometer using 3 mL DyneCups and a DyneProbe. Millipore water was used as a reference sample. Surface tension values as a function of surfactant concentration were recorded on the Aquapiplus software.

3.2.10 Small-Angle Neutron Scattering

Small-angle neutron scattering experiments were performed using the KWS-2 instrument in the Juelich Centre for Neutron Science (JCNS) at Maier Leibnitz Zentrum (MLZ) in Garching, Germany. The measurements were performed using sample-to-detector distances of 1.5, 8 and 20 m and a neutron wavelength of 5 (or 3) Å ($\Delta\lambda/\lambda = 20\%$), to optimise both the q -range (~ 0.004 – 0.2 Å⁻¹) and the beam flux. Each raw scattering data set was corrected for detector sensitivity, electronics background and sample transmission and converted to scattering cross-section data using instrument software QtiKWS. This data was converted to the absolute scale (cm⁻¹) through reference to the scattering from a secondary standard sample (Plexiglas). The samples were prepared in deuterium oxide (D₂O) to provide good neutron scattering contrast and were transferred to Hellma quartz glass cuvettes with path length of 1 mm for measurements.

3.2.11 Transmission Electron Microscopy (TEM) and cryo-TEM

TEM measurements were performed by Dr. Marie-Soussai Appavou, using the EOL 200 kV JEM-FS2200 instrument in the Juelich Centre for Neutron Science (JCNS) at Maier Leibnitz Zentrum (MLZ) in Garching, Germany. Room temperature TEM was carried out using a G677 multi-position specimen holder, with EFTEM contrast at zero loss and the minimum dose system employed to avoid beam damage as much as possible. A MultiA holey carbon coated grid was used as the substrate. The preparation method involved depositing a 10 µL drop of sample on the grid, blotting after several minutes and leaving to dry in air before insertion into the specimen holder and introduction into the instrument.

Cryo-TEM was carried out on the same instrument using a G910 multi-position specimen holder, with EFTEM contrast at zero loss and the minimum dose system employed to avoid beam damage as much as possible. Measurements were carried out at -178°C. A MultiA holey carbon coated grid was used as the substrate. The preparation method involved depositing a 10 µL drop of sample on the grid, blotting by hand after several minutes, leaving the sample in the cryo-plunge chamber at 20°C and 80% relative humidity for 30 seconds, blotting again with the Cryo-plunge device, before finally plunging in liquid ethane.

3.3 Data Fitting

3.3.1 Non-Linear Least Squares Fits

Every fitting procedure used in this thesis relies on the method of *Non-Linear Least Squares* (NLLS) analysis. The goal of NLLS analysis is to fit the measured data, to test whether a given mathematical model is consistent with the data and to determine the parameter values for that model which best match the measured data (y_i) and the calculated fit (f_{ic}), assuming initial parameter values.¹ The minimisation of the goodness-of-fit parameter χ^2 (Equation 3.1) allows this to be achieved:

$$\chi^2 = \sum_{i=1}^n \frac{(y_i - f_{ic})^2}{\sigma_i^2} \quad (3.1)$$

where σ_i is the standard deviation and n is the number of data points. If the deviation of the experimental data from the theoretical model is proportional to the value of the data it can be said that²:

$$\chi^2 = \sum_{i=1}^n \frac{(y_i - f_{ic})^2}{y_i} \quad (3.2)$$

In this way χ^2 is the sum of the squared difference between the measured data, y_i , and the value expected from the model, f_{ic} , with each squared difference divided by the measured data. The fit is run in iterations until the smallest sum is found. Depending on the results and parameters produced by preceding fits, the iterative process can involve small variations in the fitting parameters for each subsequent fit and re-evaluation of χ^2 until a minimum value is reached.^{1,2}

3.3.2 SANS models

The scattering profiles obtained from SANS measurements were fitted by appropriate form factor models using NLLS analysis in SASview (Version 4.0.1).³ The scattered SANS intensity for each shape of the assembled aggregates is given by:

$$I(q) = NV^2P(Q)S(Q) + BKG \quad (3.3)$$

where N is the number of particles per unit volume, V is the volume of the aggregate, $P(Q)$ is the form, $S(Q)$ is the structure factor and BKG is the isotropic incoherent background. In the absence of interparticle interactions $S(Q)$ is taken to be 1. Figure 3.1 provides a schematic representation of each of the form factor models discussed in this thesis. The mathematical descriptions of each model used will be outlined next.

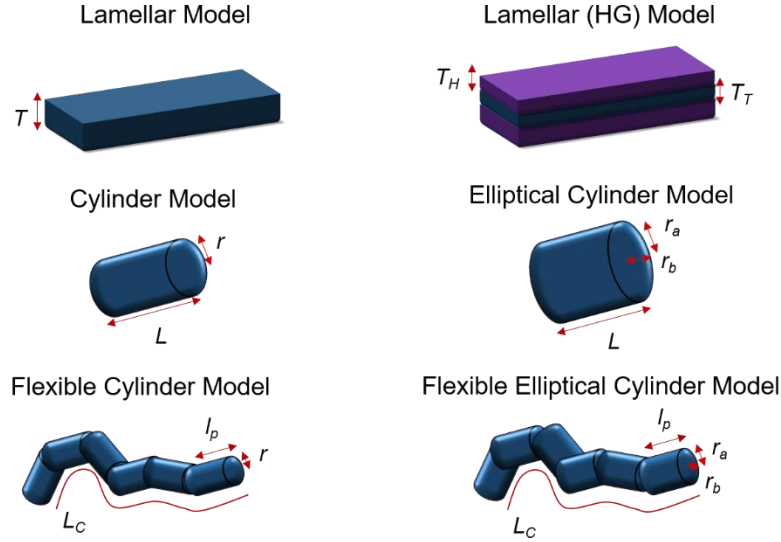


Figure 3.1 Schematic representation of the form factors, $P(Q)$, used to fit the SANS scattering profiles in this thesis. T is the thickness of a lamellar sheet, with T_H and T_T being the thickness of the head and tail layers in the Lamellar (HG) model. r is cylinder radius, with r_a and r_b being the major and minor radii of an elliptical cylinder respectively. L is the cylinder length, L_c is the contour length of a flexible cylinder and l_p is the persistence length of a flexible cylinder.

3.3.2.1 Lamellar Models

The Lamellar model describes a lyotropic lamellar phase with a uniform SLD and random distribution. The scattering intensity $I(q)$ is defined as:⁴

$$I(q) = \frac{2\pi V P(q)}{T q^2} \quad (3.4)$$

where V is the scattering volume, T is the sheet thickness and $P(q)$ is the form factor, in this case given by:⁴

$$P(q) = \frac{2\Delta\rho^2}{q^2} (1 - \cos(qT)) e^{-\frac{q^2\sigma^2}{2}} \quad (3.5)$$

where $\Delta\rho$ is the scattering contrast and σ is arbitrarily set to $T/4$. The Lamellar (HG) model, which describes a random lyotropic lamellar phase comprised of head and tail groups, has equations for intensity (Equation 3.6) and form factor (Equation 3.7) very similar to Equations 3.4 and 3.5, but adjusted for the presence of distinctive head and tail components.⁴ In the case of the Lamellar (HG) model the scattered intensity is given by:

$$I(q) = \frac{2\pi V P(q)}{2(T_T + T_H) q^2} \quad (3.6)$$

where T_T and T_H are the tail and head group thicknesses respectively. In this case, the total lamellar thickness is $2\delta_T + 2\delta_H$. The form factor for the Lamellar (HG) model is described by:

$$P(q) = \frac{4}{q^2} \{ \rho_H [\sin(q(\delta_H + \delta_T)) - \sin(q\delta_T)] + \rho_H \sin(q\delta_T) \}^2 \quad (3.7)$$

where ρ_H is the contrast of the head group and ρ_T is the contrast of the tail group.

3.3.2.2 Cylinder Models

The cylinder model in SASview describes a right circular cylinder with uniform scattering length density. The output of the 1D scattering intensity function for randomly oriented cylinders is given by:^{5,6}

$$P(q, \alpha) = \frac{scale}{V} \int_0^{\pi} F^2(q, \alpha) \sin(\alpha) d\alpha \quad (3.8)$$

where *scale* gives a measure of the amount of sample present in solution, α is the angle between the axis of the cylinder and the vector $\mathbf{Q}$, and V is the volume of the cylinder. For randomly oriented cylinders $F^2(q)$ is described by:

$$F^2(q) = \int_0^{\pi} F(q, \alpha) \sin(\alpha) d\alpha \quad (3.9)$$

And $F(q, \alpha)$ is given by:

$$F(q, \alpha) = 2(\Delta\rho)V \frac{\sin(\frac{qL\cos(\alpha)}{2})J_1(qR\sin(\alpha))}{\frac{qL\cos(\alpha)}{2}qR\sin(\alpha)} \quad (3.10)$$

where $\Delta\rho$ is the contrast, L is the length of the cylinder, J_1 is the first order Bessel function and R is the radius of the cylinders.

For an elliptical cylinder, where the angles θ and ϕ define the orientation of the axis of the cylinder, and the angle ψ is defined as the orientation of the major axis of the ellipse with respect to the vector $\mathbf{Q}$, the treatment is slightly different.⁷ In this case, the scattering intensity is given by:

$$I(q) = \frac{1}{V} \int d\psi \int d\phi \int p(\theta, \phi, \psi) F^2(q, \alpha, \psi) \sin(\alpha) d\alpha \quad (3.11)$$

$$\text{where} \quad F^2(q, \alpha, \psi) = 2 \frac{J_1 \sin(a) \sin(b)}{ab} \quad (3.12)$$

$$\text{and} \quad a = qr' \sin(\alpha) \quad (3.13)$$

$$b = \frac{L}{2} q \cos(\alpha) \quad (3.14)$$

$$r' = r_a \sqrt{2(1 + v^2) + (1 - v^2)\cos(\psi)} \quad (3.15)$$

where r_a is the minor axis of the elliptical cylinder. The form factor is then obtained by averaging over all possible orientation before normalized by the particle volume, V , as follows:⁷

$$P(q) = scale \langle F^2 \rangle / V \quad (3.16)$$

Where $\langle F^2 \rangle$ denotes the average value of Equation 3.12 over all orientations.

2.3.2.3 Flexible Cylinder Models

The Flexible (Elliptical) Cylinder models are based on the form factors for rigid cylinders (spherical or elliptical). The flexible cylinder is considered as a chain of contour length, L_C comprised of a number of locally stiff segments, the length of which is given by the persistence length, l_p . The Kuhn length, L_K is the length over which the flexible cylinder can be considered as a rigid rod and is given by $L_K = 2l_p$. The cross-sectional radius of the cylinder segment is given by R_{CS} . The non-negligible diameter of the cylinder is included by accounting for excluded volume interactions within the walk of a single cylinder. The scattering function, $I_{WC}(q, L_C, L_K, R_{CS})$, for the flexible cylinder model is described by:⁸⁻¹⁰

$$I_{WC}(q, L_C, L_K, R_{CS}) = c\Delta\rho^2 M_w S_{WC}(q, L_C, L_K) P_{CS}(q, R_{CS}) + BKG \quad (3.17)$$

where c is the concentration, M_w is the average molecular weight of the cylinder, $P_{CS}(q, R_{CS})$ is the scattering cross section of a rigid rod given by:

$$P_{CS}(q, R_{CS}) = \left[\frac{2J_1(qR_{CS})}{qR_{CS}} \right]^2 \quad (3.18)$$

where J_1 is the first order Bessel function. $S_{WC}(q, L_C, L_K)$ is the scattering function of a single semi-flexible chain with excluded volume effects given by:

$$\begin{aligned} S_{WC}(q, L_C, L_K) = & [1 - w(qR_g)] S_{Debye}(q, L_C, L_K) + \\ & w(q, R_g) \left[1.22(qR_g)^{-\frac{1}{0.585}} + 0.4288(q, R_g)^{-\frac{2}{0.585}} - 1.651 \left(q, R_g \right)^{-\frac{3}{0.585}} \right] + \\ & \frac{C(n_b)}{n_b} \left\{ \frac{4}{15} + \frac{7}{15u} - \left(\frac{11}{15} + \frac{7}{15u} \right) \times e^{-u(q, L_C, L_K)} \right\} \end{aligned} \quad (3.19)$$

where R_g is the radius of gyration of the flexible cylinder with excluded volume effects and $w(qR_g)$ is the empirical cross-over function given by Equation 3.20:

$$w(qR_g) = \frac{1 + \tanh\left[\frac{qR_g - 1.532}{0.1477}\right]}{2} \quad (3.20)$$

$S_{Debye}(q, L_C, L_K)$ is the Debye function with $u = \langle R_g^2 \rangle q^2$ as follows:

$$S_{Debye}(q, L_C, L_K) = \frac{2}{u(q, L_C, L_K)} \{ e^{-u(q, L_C, L_K)} + u(q, L_C, L_K) - 1 \} \quad (3.21)$$

$$u(q, L_C, L_K) = \frac{L_C L_K}{6} \left\{ 1 - \frac{3}{2n_b} + \frac{3}{2n_b^2} + \frac{3}{4n_b^3} [1 - e^{-2n_b}] \right\} q^2 \quad (3.22)$$

$$\langle R_g^2 \rangle = \alpha(n_b)^2 \frac{L_C L_K}{6} \quad (3.23)$$

$$u(q, L_C, L_K) = \alpha(n_b)^2 \frac{L_C L_K}{6} q^2 \quad (3.24)$$

where $n_b = L_C/L_K$ (for $L_C > 10L_K$, $C(n_b) = 3.06n_b^{-0.44}$ and for $L_C \leq 10L_K$, $C(n_b) = 1$) and $\alpha(n_b)$ is the expression factor which follows the empirical expression:

$$\alpha(x) = \sqrt{\left[1 + \left(\frac{x}{3.12}\right)^2 + \left(\frac{x}{8.67}\right)^3\right]^{0.176/3}} \quad (3.25)$$

The flexible elliptical cylinder model calculates the form factor for a flexible cylinder with an elliptical cross section and a uniform scattering length density. The treatment follows the same procedure as above for the flexible elliptical cylinder but is slightly adjusted to account for the existence of both major and minor radii within the cylinder cross-section.^{8,9} Ultimately, the resulting form factor is normalized by the particle volume such that:^{8,9}

$$P(q) = \text{scale} \left(\frac{\langle F^2 \rangle}{V} \right) + BKG \quad (3.26)$$

3.4 References

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Chapter 4

The Impact of Molecular Structure on the Physicochemical Properties of Tetraethylene Glycol AzoPS Systems

4.1 Introduction

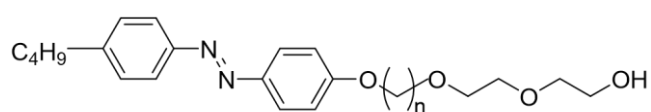
Photoisomerisation is the driving force behind the use of azobenzene photosurfactants as tools in a multitude of surface tension related applications.^{1–5} For example, the variation of the hydrophobic-hydrophilic balance upon photoisomerisation has a significant enough impact to alter the flow type in a microfluidic device,^{6–8} or to destabilise a foam on demand.^{9–11} Changes in physicochemical behaviour upon photoisomerisation can be attributed to the difference in molecular size and polarity between the *cis*- and *trans*-isomers.^{12,13} For this reason, it would be expected that modifying the substituents on the azobenzene group within the surfactant would have a corresponding impact on its physicochemical properties upon isomerisation.

For commercial or industrial applications it would be desirable to use an AzoPS that exerts a significant difference in physicochemical properties upon photoisomerisation, and that displays surface activity at low concentrations. In this manner, the AzoPS could be used as a switch, with the *trans*- and *cis*-isomers representing “on” or “off” states, with light as the actuator for the system. While proof-of-principle studies have shown that it is possible for AzoPS to act as such switches there have been few systematic investigations into the effect of molecular structure on AzoPS physicochemical properties.^{4,6,12,14–16} In fact, as described in the Introduction, most studies to date focus on the application of only a handful of AzoPS structures. The development and advancement of technologies, such as photo-controlled microfluidic devices^{1,7,8} and green, reversible foam dyeing processes,^{16,17} will depend on the availability of flexible methods for controlling surface tension, such as a wide catalogue of well-characterised photosurfactants. Knowledge of the impact of chemical structure on the physicochemical properties and self-assembly behaviour of the photosurfactants will be a key factor in the advancement of these applications on a commercial or industrial scale.

Some general structural trends for AzoPS have been established. Yang *et al.* found that the *cis*-form of a cationic AzoTAB (4-ethylazobenzene 4'-(oxyethyl)trimethylammonium bromide) had a lower surface activity than the *trans*-isomer, and correspondingly, had a higher CMC.¹⁸ In general, the more hydrophilic *cis*-isomer would be expected to have a higher CMC than the *trans*-isomer. Kang *et al.* reported that for a series of cationic azobenzene photosurfactants (4-alkylazobenzene-4'-(oxy-2-hydroxypropyl)trimethylammoniummethyl sulfate, alkyl varied from H to methyl, ethyl, butyl and octyl) the CMC decreased as the number of carbons in the alkyl tail increased, due to the increased hydrophobicity of the AzoPS.¹⁹ It should be noted that almost all AzoPS studied to date are cationic,²⁰ which may render them

unusable for some applications, such as foam colouring using negatively-charged adhesives or dyes.¹⁶ Ionic AzoPS also have higher CMC values¹⁹ (due to their increased polarity) compared to neutral AzoPS,¹² meaning more material would be required for a given application.

Neutral AzoPS have been studied by Shang *et al.* who synthesised a series of diethylene glycol AzoPS (Figure 4.1) of constant pendant tail length (C_4H_9) but varying spacer length n .¹² In this case the hydrophobic component is the composite alkyl tail comprised of the pendant tail, azobenzene core and spacer. It was found that spacer length plays a key role in the surface tension by facilitating structural changes upon photoisomerisation that greatly impacts surface activity for both *cis*- and *trans*-isomers.



$$n = 2, 4, 6 \text{ or } 8$$

Figure 4.1 General structure of the diethylene glycol AzoPS synthesised by Shang *et al.*¹² The pendant tail length (C_4H_9) and head group (E_2) was kept constant, while spacer length, $(CH_2)_n$, was varied.

Other examples of neutral AzoPS are those synthesised by Tan *et al.* who created a series of multi-stimuli responsive AzoPS based hydrogelators.²¹ The AzoPS structure consisted of a polyetheramine head group of varying molecular weight bound to azobenzene-based alkyl tails of constant length. The AzoPS solutions transitioned between gel and sol states depending on the temperature, pH, mechanical stress or light illumination of the system.

The aim of this chapter is to investigate the impact of molecular structure on the physicochemical properties of a family of neutral AzoPS, specifically in relation to surface activity. In the first instance, the design strategy and synthesis for a family of four neutral tetraethylene glycol AzoPS of varying pendant tail and spacer length will be discussed. The molecular structure of each will then be correlated with photoresponse, CMC and surface activity. By characterising these AzoPS in terms of their physical properties this study will act to broaden the catalogue of AzoPS available for integration with applications, particularly for areas where charged AzoPS would be undesirable. In this chapter, focus will be directed toward identifying differences in the nature and extent of physicochemical response of individual surfactant monomers and molecular assemblies (*i.e.* micelles) to photoisomerisation, at the CMC or below, while the impact of the molecular structure on the bulk self-assembly behaviour of AzoPS, at concentrations above the CMC, will be further investigated in Chapter 5.

4.2 Experimental

4.2.1 Materials

4-Ethylaniline, 4-butaniline (97%), 4-octylaniline, sodium nitrite ($\geq 99\%$), 1,2-dibromoethane, anhydrous potassium carbonate ($\geq 99\%$), potassium iodide (99%), sodium sulfite (98%), sodium carbonate, sodium hydride (60% w/w in mineral oil), tetraethylene glycol (99%), hydrochloric acid (conc. 37.5%), ethanol (HPLC grade), tetrahydrofuran (HPLC grade), diethyl ether ($\geq 99.5\%$), dichloromethane, acetone and hexane were purchased from Sigma Aldrich. 1,4-diisobutane ($>98\%$) and 1,8-dibromooctane ($>98\%$) were purchased from Alfa Aesar. 4-hexylaniline (90%), 1,6-dibromohexane (96%) were purchased from ChemCruz. Sodium hydroxide ($\geq 97\%$) and chloroform ($>99\%$) were purchased from Fisher Scientific and phenol ($>99\%$) was purchased from BDH Chemical Ltd. England. All reagents and solvents were used as received with the exception of tetraethylene glycol which was dried *via* azeotropic distillation with toluene.

4.2.2 Instrumentation

The instrumentation used for UV-Vis absorption spectroscopy, surface tensiometry, dynamic light scattering, NMR spectroscopy, FT-IR spectroscopy and mass spectrometry are described in Chapter 3.

4.2.3 Methods

UV-Vis Absorption Spectroscopy: Stock solutions ($0.065 \text{ mmol L}^{-1}$) of each AzoPS were prepared in Millipore water ($18.2 \text{ M}\Omega \text{ cm}$).

Critical Micelle Concentration Titrations: Stock solutions (0.5 mmol L^{-1}) of each AzoPS were prepared in triple filtered Millipore water ($18.2 \text{ M}\Omega \text{ cm}$).

Surface Tensiometry: Aliquots of the AzoPS stock solutions (0.5 mmol L^{-1}) were added to Millipore water (total volume = 3 mL) to form solutions of varying concentration. Surface tension was measured *via* the Du Noüy-Padday method of maximum pull force as a function of concentration, with Millipore water ($18.2 \text{ M}\Omega \text{ cm}$) used as a reference sample.

Dynamic Light Scattering: Aliquots of the AzoPS stock solutions (0.5 mmol L^{-1}) were added to Millipore water (total volume = 1 mL) to form solutions of varying concentration. The intensity of scattered light (kcounts) was measured as a function of concentration at fixed attenuator positions.

4.2.4. Synthesis and Characterisation

4.2.4.1 General Procedure for the Synthesis of the Bromoprecursor

The family of ethylene glycol azobenzene photosurfactants was synthesised in three main stages: the preparation of a hydroxyl precursor, **1**, of the desired alkyl tail length, modification of **1** to a bromoprecursor, **2**, incorporating the desired alkyl spacer, followed by addition of the polar tetraethylene glycol head group to form the final AzoPS, **3**. The synthetic strategy will be discussed in detail in Section 4.3.1, with only the experimental details being provided here. All intermediates and products were characterised by ^1H and ^{13}C NMR spectroscopy, FTIR spectroscopy, mass spectrometry and melting point analysis. Spectroscopic and analytical data are summarised below, with assigned NMR and FTIR spectra available in the appendix. (Figures A.4.1-11).

Synthesis of $C_m\text{AzoOH}$ (4-alkyl-4'-hydroxyl azobenzene, replace alkyl with ethyl ($C_2\text{AzoOH}$), hexyl ($C_6\text{AzoOH}$) or octyl ($C_8\text{AzoOH}$) as appropriate for desired tail length)

In a 100 mL round-bottom flask, 4-alkylaniline (20 mmol: 4-ethylaniline: 2.49 mL; 4-butaniline: 3.16 mL; 4-hexylaniline: 3.85 mL; 4-octylaniline: 4.57 mL) was dissolved in an acetone: water mixture (1:1, 50 mL) and HCl (37.5%, 0.048 mol, 4 mL) added. The resulting orange/brown solution was placed in an ice bath and kept at 0 °C. Sodium nitrite (20 mmol, 1.38 g) was dissolved in distilled water (20 mL), cooled to 1-2 °C and added dropwise to the acidic alkylaniline solution. The orange solution was left to stir over ice for 5 min, to allow for the formation of the diazonium salt. The solution was then placed in the freezer until required. Separately, NaOH (20 mmol, 0.8 g), Na_2CO_3 (20 mmol, 2.12 g) and phenol (20 mmol, 1.88 g) were dissolved in distilled water (50 mL) and placed in an ice bath until the solution temperature reached 1-3 °C. To this basic solution the acidic diazonium salt solution was added dropwise, maintaining a temperature below 8 °C. An aqueous NaOH solution (6.5 mL, 2.5 mmol L^{-1}) was added dropwise to the basic phenol solution along with the acidic diazonium salt solution, in order to maintain a final pH of 10. The resulting yellow/orange precipitate was left to warm to room temperature, filtered and washed with cold distilled water. **$C_m\text{AzoOH}$** was recovered in the form of a yellow/orange powder with an average yield of 70%.

$C_2\text{AzoOH}$ (1a**)**

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ = 1.31 (t, J = 8 Hz, 3H), 2.75 (quart., J = 8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 7.34 (d, J = 8.2 Hz, 2H), 7.82 (d, J = 8.3 Hz, 2H), 7.88 (d, J = 8.8 Hz, 2H) ppm.

^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ = 15.4, 28.8, 115.8, 122.6, 124.9, 128.5, 147.2, 150.9, 158.0 ppm.

FTIR: ν = 3163 (br.), 2960 (w), 2927 (m), 2848 (w), 1583 (s), 1505 (s), 1242 (s), 1131 (s) cm^{-1} .

Mass Spectrometry (CH_3Cl , m/z : APCI $^+$): Exact mass calculated: 226.1106 [M], Exact mass obtained: 227.1168 [M+H] $^+$.

Melting Point: 85.1 – 86.2 °C.

Yield: 68%

C₆AzoOH (1b)

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ = 0.91 (t, J = 8 Hz, 3H), 1.34 (m, 6H), 1.68 (m, 2H), 2.67 (t, J = 9 Hz, 2H), 5.06 (s, br.), 6.98 (d, J = 7 Hz, 2H), 7.33 (d, J = 8.4 Hz, 2H), 7.81 (d, J = 7.2 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H) ppm.

^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ = 14.1, 22.6, 28.9, 31.3, 31.7, 35.9, 115.8, 122.5, 124.8, 129.1, 146, 147.2, 150.9, 158.2 ppm.

FTIR: ν = 3547 (w), 3292 (b), 2956 (s), 2916 (s), 2849 (s), 1646 (w), 1586 (s), 1478 (C-H, s), 1404 (s), 1290 (s), 1142 (s), 830 (s) cm^{-1} .

Mass Spectrometry (CH_3Cl , m/z : APCI $^+$): Exact mass calculated: 282.1732 [M], exact mass obtained: 281.1659 [M-H] $^+$.

Melting Point: 86.9 – 88.81 °C.

Yield: 74%

C₈AzoOH (1c)

^1H NMR (CDCl_3 , 400 MHz, 25 °C): δ = 0.90 (t, J = 7 Hz, 3H), 1.33 (m, 8H), 1.66 (m, 4H), 2.69 (t, J = 7 Hz, 2H), 5.5 (s, br.), 6.96 (d, J = 7.2 Hz, 2H), 7.32 (d, J = 9 Hz, 2H), 7.81 (d, J = 7.2 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H) ppm.

^{13}C NMR (CDCl_3 , 100 MHz, 25 °C): δ = 14.2, 22.7, 29.3, 29.5, 31.3, 31.9, 35.9, 115.9, 122.5, 125.1, 129.1, 146.1, 147.1, 150.6, 158.3 ppm.

FTIR: ν = 3427 (br), 2956 (s), 2923 (s), 2856 (s), 1586 (s), 1465 (s), 1243 (s), 1135 (s), 833 (s), 558 (s) cm^{-1} .

Mass Spectrometry (CH_3Cl , m/z : APCI $^+$): Exact mass calculated: 310.2045 [M], exact mass obtained: 309.1977 [M-H] $^+$.

Melting Point: 87.2 – 88.8 °C.

Yield: 66%

Synthesis of bromoprecursor $C_m\text{AzoOC}_n\text{Br}$ (4-alkyl-4'-(4/6/8-bromo)alkoxy azobenzene, replace alkyl with ethyl, hexyl and octyl as relevant, and select 4/6/8 accordingly):

$C_2\text{AzoOH}$ (1 eq., 10 mmol, 2.26 g), was dissolved in acetone (25 mL). 1,4 di-bromobutane (2 eq., 20 mmol, 2.39 mL), K_2CO_3 (2 eq., 20 mmol, 2.76 g) and KI (0.1 eq., 1 mmol, 0.17 g) were added to the reaction flask and the resulting dark red solution was stirred under reflux at 65 °C for 2 days with monitoring *via* thin layer chromatography (TLC, 9:1 cyclohexane: ethyl acetate). When the reaction reached completion acetone was removed *via* rotary evaporation and the product was dissolved in dichloromethane (DCM, 20 mL) and washed with water several times to remove the co-salt. DCM was removed *via* rotary evaporation and $C_4\text{AzoOC}_2\text{Br}$ was recovered as an orange solid upon recrystallisation from ethanol.

For the synthesis of $C_6\text{AzoOC}_4\text{Br}$ and $C_8\text{AzoOC}_4\text{Br}$ the appropriate hydroxyl precursor (1 eq., 10 mmol, $C_6\text{AzoOH}$: 2.82 g, $C_8\text{AzoOH}$: 3 g) was reacted with 1,4 di-bromobutane (2 eq., 20 mmol, 2.39 mL) as outlined above for $C_2\text{AzoOC}_4\text{Br}$. For the synthesis of $C_8\text{AzoOC}_8\text{Br}$ $C_8\text{AzoOH}$ (1 eq., 10 mmol, 3.1 g) was reacted with 1,8 di-bromooctane (2 eq., 20 mmol, 3.68 mL) as outlined above for $C_2\text{AzoOC}_4\text{Br}$.

$C_2\text{AzoOC}_4\text{Br}$ (2a)

^1H NMR: ($CDCl_3$, 400 MHz, 25 °C): δ = 1.31 (t, J = 8 Hz, 3H), 2.02 (m, 2H), 2.13 (m, 2H), 2.74 (m, J = 8 Hz, 2H), 3.53 (mt, J = 6 Hz, 2H), 4.11 (t, J = 6 Hz, 2H), 7.01 (d, J = 9 Hz, 2H) 7.34 (d, J = 8.36 Hz, 2H) 7.83 (d, J = 8.32 Hz, 2H) 7.92 (d, J = 9 Hz, 2H) ppm.

^{13}C NMR: ($CDCl_3$, 400 MHz, 25 °C): δ = 15.4, 27.8, 28.82, 29.4, 33.4, 67.2, 114.7, 122.6, 124.6, 128.5, 147.1, 147.1, 151, 161.1 ppm.

FTIR: ν = 2966 (w), 2920 (m), 2861 (w), 1609 (s), 1497 (s), 1236 (s), 1138 (s) cm^{-1} .

Mass Spectrometry: (CH_3Cl , m/z : $APCI^+$): Exact mass calculated: 360.0837 [M], exact mass obtained: [M+H] 361.0910.

Melting Point: 115.4 – 117.3 °C

Yield: 82%

$C_6\text{AzoOC}_4\text{Br}$ (2b)

^1H NMR: ($CDCl_3$, 400 MHz, 25 °C): δ = 0.92 (t, J = 8 Hz, 3H), 1.35 (m, 6H), 1.68 (m, 2H), 2.06 (m, 4H), 2.7 (t, J = 6.6 Hz, 2H), 3.47 (m, 2H), 4.11 (t, J = 6 Hz, 2H) 7.03 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.2 Hz), 7.81 (d, J = 8.3 Hz 2H), 7.9 (d, J = 8.9 Hz, 2H) ppm.

^{13}C NMR: (CDCl_3 , 400 MHz, 25 °C): δ = 14.1, 22.62, 27.9, 29, 31, 31.3, 32.5, 33.4, 35.9, 67.2, 119.7, 122.6, 124.6, 129.1, 145.9, 147.1, 151, 161.1 ppm.

FTIR: ν = 2914 (s), 2848 (w), 1602 (s), 1498 (s), 1380 (w), 1256 (s), 1133 (s) cm^{-1} .

Mass Spectrometry (CH_3Cl , m/z: APCI): Exact mass calculated: 416.1463 [M], exact mass obtained: 417.154 [M+H]⁺

Melting Point: 136.2 - 137.5 °C

Yield: 85%

$\text{C}_8\text{AzoOC}_4\text{Br}$ (2c)

^1H NMR: (CDCl_3 , 400 MHz, 25 °C): δ = 0.91 (t, J = 7 Hz, 3H) 1.3 (m, 10H), 1.66 (m, 2H), 2.02 (m, 2H), 2.11 (m, 2H), 2.7 (t, J = 8 Hz, 2H), 3.54 (t, J = 7 Hz, 2H) 4.11 (t, J = 7 Hz, 2H), 7.01 (d, J = 8.9 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H), 7.92 (d, J = 8.9 Hz, 2H) ppm.

^{13}C NMR: (CDCl_3 , 100 MHz, 25 °C): δ = 14.1, 22.7, 27.9, 29.2, 29.3, 29.4, 29.5, 31.3, 31.9, 33.4, 35.9, 67.2, 114.7, 122.5, 124.6, 129.1, 145.9, 147.1, 151.2, 161.1 ppm.

FTIR: ν = 2929 (s), 2838 (m), 1606 (s), 1498 (m), 1452 (m), 1393 (w), 1250 (s), 1141 (s) cm^{-1} .

Mass Spectrometry (CH_3Cl , m/z: APCI): Exact mass calculated: 444.1776 [M], exact mass obtained: 445.1849 [M+H]⁺.

Melting Point: 138.4 – 140.1 °C

Yield: 67%

$\text{C}_8\text{AzoOC}_8\text{Br}$ (2d)

^1H NMR: (CDCl_3 , 400 MHz, 25 °C): δ = 0.91 (t, J = 8 Hz, 3H), 1.29-1.35 (m, 10H), 1.4 – 1.47 (m, 8H), 1.66 (quint., 2H), 1.86 (m, 4H), 2.69 (t, J = 7 Hz, 2H), 3.44 (m, 2H), 4.05 (t, J = 7 Hz, 2H), 7.01 (d, J = 9 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 7.81 (d, J = 8.6 Hz, 2H), 7.9 (d, J = 8.7 Hz, 2H) ppm.

^{13}C NMR: (CDCl_3 , 100 MHz, 25 °C): δ = 14.1, 26, 29.2, 28.1, 28.5, 28.6, 28.7, 29.3, 29.3, 29.5, 31.4, 31.9, 32.7, 33.9, 35.9, 68.3, 114.7, 122.5, 124.6, 129.1, 145.8, 147, 151.1, 161.4 ppm.

FTIR: ν = 2983 (s), 2916 (s), 2849 (s), 1600 (s), 1492 (s), 1470 (s), 1256 (s), 1122 (s), 833 (s), 550 (s) cm^{-1} .

Mass Spectrometry (CH_3Cl , m/z: APCI⁺): Exact mass calculated: 500.2402 [M], exact mass obtained: 501.2473 [M+H]⁺.

Melting Point: 119.8 - 121.2 °C

Yield: 80%

Synthesis of $C_m\text{AzoOC}_n\text{E}_4$ (4-alkyl-4'-(mono-tetraethylene glycol) alkoxy azobenzene, replace alkyl with ethyl, hexyl and octyl and alkoxy with butyl and octyl as relevant)

Tetraethylene glycol (5 eq., 28.1 mmol, 5.41 mL) was dried azeotropically by distillation with toluene (20 mL) at 170 °C. Dry tetraethylene glycol was then dissolved in dry THF (25 mL) in a round-bottomed flask (50 mL) under an inert N_2 atmosphere. To this NaH (60% in oil (w/w), 1.5 eq., 8.4 mmol, 0.346 g) was added and left to stir for 1 h under N_2 . The desired bromoprecursor (1.0 eq, 5.6 mmol, $\text{C}_2\text{AzoOC}_4\text{Br}$: 2.02 g, $\text{C}_6\text{AzoOC}_4\text{Br}$: 2.3 g, $\text{C}_8\text{AzoOC}_4\text{Br}$: 2.5 g, $\text{C}_8\text{AzoOC}_8\text{Br}$: 2.8 g) was dissolved in dry THF (10 mL) and added to the reaction flask. The resulting red/orange solution was refluxed at 65 °C for 24 h. Acetone was removed *via* rotary evaporation and the resulting red oil dissolved in DCM (20 mL) and washed with water. The DCM layer was dried using MgSO_4 , filtered and the solvent was removed *via* rotary evaporation. Excess bromoprecursor was removed using a silica plug and washing with chloroform. The product was recovered with acetone and the solvent removed *via* rotary evaporation to yield $C_m\text{AzoOC}_n\text{E}_4$ as a red oil.

$C_2\text{AzoOC}_4\text{E}_4$ (3a)

^1H NMR: (CDCl_3 , 400 MHz, 25 °C): δ = 1 (t, J = 8 Hz, 3H), 1.81 (m, 2H), 1.9 (m, 2H), 1.98 (m, 2H), 2.74 (t, J = 8 Hz, 2H), 3.65 (m, 16H), 4.09 (t, J = 6 Hz, 2H), 7.01 (d, J = 8.92 Hz, 2H), 7.33 (d, J = 8.24 Hz, 2H), 7.82 (d, J = 8.24 Hz, 2H), 7.9 (d, J = 8.92 Hz, 2H) ppm.

^{13}C NMR: (CDCl_3 , 600 MHz, 25 °C): δ = 15.5, 26, 26.1, 28.8, 61.7, 68, 70.2-70.9 (7 peaks) 72.64, 114.69, 122.6, 124.6, 128.49, 146.97, 147.04, 151.05, 161.38 ppm.

FTIR: ν = 3404 (br.), 2965 (w), 2933 (s), 2874 (w), 1589 (s), 1492 (m), 1249 (s), 1315 (s) cm^{-1} .

Mass Spectrometry (CH_3Cl , m/z : APCI $^+$): Exact mass calculated: 474.2730. Exact mass obtained: 475.2779 $[\text{M}+\text{H}]^+$.

Yield: 38%

$C_6\text{AzoOC}_4\text{E}_4$ (3b)

^1H NMR: (CDCl_3 , 400 MHz, 25 °C): δ = 0.9 (t, J = 8 Hz, 3H), 1.22 (d, 2H), 1.33 (m, 6H), 1.66-1.9 (m, 6H), 2.69 (t, J = 8 Hz, 2H), 3.63 (m, 16H), 4.09 (t, J = 7 Hz, 2H), 7 (d, J = 8.88 Hz, 2H), 7.3 (d, J = 8.16 Hz, 2H), 7.8 (d, J = 8.2 Hz, 2H), 7.89 (d, J = 8.8 Hz, 2H) ppm.

^{13}C NMR: (CDCl_3 , 600 MHz, 25 °C): δ = 14.1, 22.6, 26.1, 28.9, 30.9, 31.3, 31.7, 35.4, 61.7, 68, 70-70.9 (7 peaks), 72.65, 114.68, 122.51, 124.55, 129.03, 145.8, 146.9, 151, 161.4 ppm

FTIR: ν = 3175 (br.), 2959 (w), 2926 (m), 2873 (w), 1603 (s), 1490 (m), 1256 (s), 1131 (m) cm^{-1} .

Mass Spectrometry (CH_3Cl , m/z : APCI^+): Exact mass calculated: 530.3356. Exact mass obtained: 531.3442 $[\text{M}+\text{H}]^+$.

Yield: 39%

$\text{C}_8\text{AzoOC}_4\text{E}_4$ (3c)

^1H NMR: (CDCl_3 , 400 MHz, 25 °C): δ = 0.79 (t, J = 8 Hz, 3H), 1.18-1.23 (m, 12H), 1.55 (m, 2H), 1.71 (m, 2H), 1.8 (m, 2H), 2.57 (t, J = 8 Hz, 2H), 3.49 (m, 12H), 3.62 (m, 4H), 3.97 (t, J = 8 Hz, 2H), 6.9 (d, J = 8.92 Hz, 2H), 7.2 (d, J = 8.24 Hz, 2H), 7.7 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 8.88 Hz, 2H) ppm.

^{13}C NMR: (CDCl_3 , 600 MHz, 25 °C): δ = 14, 22.6, 26, 25.9, 29.2, 29.4, 30.7, 31.2, 31.8, 35.73, 61.4, 67.9, 70-70.8 (7 peaks), 72.5, 114.3, 122.7, 124.5, 129.0, 145.2, 146.8, 151.1, 160.9 ppm.

FTIR: ν = 3175 (br.), 2965 (w), 2926 (m), 2866 (w), 1596 (s), 1497 (s), 1248 (s), 1135 (s) cm^{-1} .

Mass Spectrometry (CH_3Cl , m/z : APCI^+): Exact mass calculated: 558.3669. Exact mass obtained: 559.3714 $[\text{M}+\text{H}]^+$.

Yield: 42%

$\text{C}_8\text{AzoOC}_8\text{E}_4$ (3d)

^1H NMR: (CDCl_3 , 400 MHz, 25°C): δ = 0.84 (t, J = 8 Hz, 3H), 1.26 – 1.54 (m, 24H), 1.78 (m, 2H), 2.63 (t, J = 8 Hz, 2H), 3.64 (m, 16 H), 3.99 (t, J = 7 Hz, 2H), 6.95 (d, J = 9 Hz, 2H), 7.25 (d, J = 8.32 Hz, 2H), 7.75 (d, J = 8.36 Hz, 2H), 7.84 (d, J = 8.96 Hz, 2H) ppm.

^{13}C NMR: (CDCl_3 , 600 MHz, 25°C): δ = 14.06, 22.61, 25.93, 29.2, 29.3, 29.2, 29.3, 29.3, 29.3, 30.9, 31.3, 31.8, 33.6, 35.8, 61.5, 68.3, 70.2-70 (7 peaks), 72.8, 114.6, 122.5, 124.5, 129, 145.8, 146.9, 151, 161.1 ppm.

FTIR: ν = 3169 (br.), 2971 (w), 2928 (m), 2867 (w), 1594 (s), 1498 (s), 1247 (s), 1139 (s) cm^{-1} .

Mass Spectrometry (CH_3Cl , m/z : APCI^+): Exact mass calculated: 614.4295 $[\text{M}]$. Exact mass obtained: 615.439 $[\text{M}+\text{H}]^+$.

Yield: 47%

4.3 Results and Discussion

4.3.1 Strategic Design of Azobenzene Photosurfactants

A homologous series of four neutral azobenzene photosurfactants were designed and synthesised, of general formula $C_m\text{AzoOC}_n\text{E}_4$, as represented in Figure 4.2. Each AzoPS consists of a hydrophilic tetraethylene glycol head group (E_4) and a hydrophobic azobenzene-based tail. The hydrophobic tail of each AzoPS can be considered in terms of three components: the azobenzene core, fundamental to all AzoPS; an alkoxy spacer moiety (OC_n , indicated in green) which links the azobenzene core to the tetraethylene glycol head group at the *para* position of one aryl group; a pendant alkyl tail (C_m , indicated in blue) at the *para* position of the other aryl group. The spacer and pendant tail lengths are readily modifiable through judicious selection of precursor materials, with spacer lengths of 4 to 8 carbon atoms and pendant tail lengths of 4, 6 or 8 carbon atoms being chosen here. The resulting AzoPS are **$C_2\text{AzoOC}_4\text{E}_4$** , **$C_6\text{AzoOC}_4\text{E}_4$** , **$C_8\text{AzoOC}_4\text{E}_4$** and **$C_8\text{AzoOC}_8\text{E}_4$** . These strategically designed AzoPS will enable the impact of the molecular structure on both the physicochemical properties and self-assembly processes of the AzoPS to be studied.

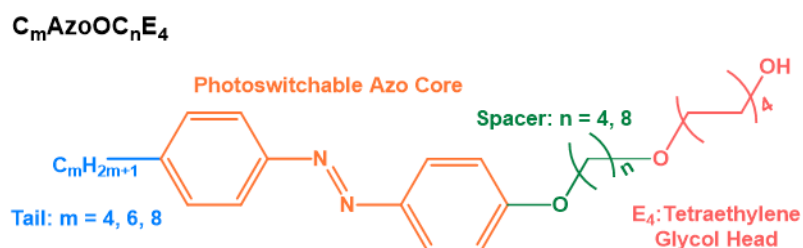


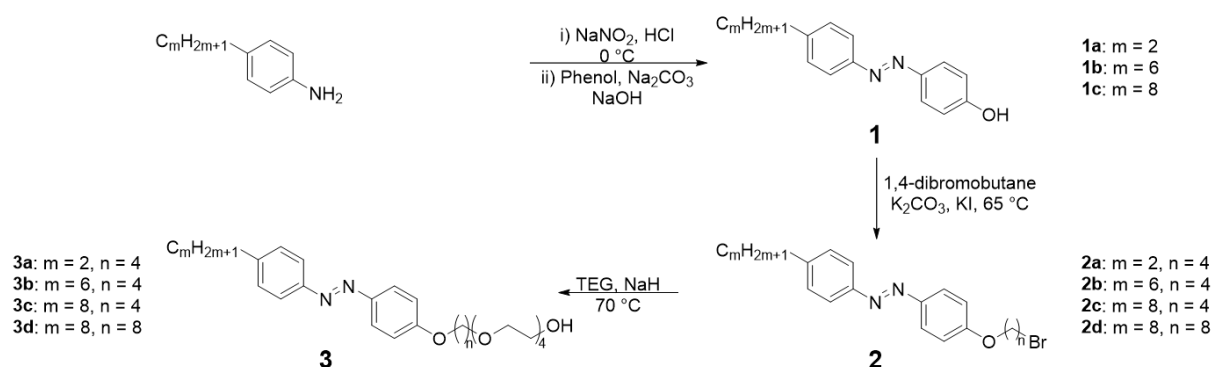
Figure 4.2 General chemical structure of the AzoPS synthesised in this chapter, where m refers to carbon tail length (blue), n to the carbon spacer length (green) and E_4 to the polar tetraethylene glycol head group (pink). The azobenzene core is indicated in orange.

Peng *et al.* reported an interesting change in the self-assembled structure and bulk properties of a neutral AzoPS (with an oligooxyethylene head group) upon photoisomerisation when a spacer was present.²² Multiple LLC phases were seen for the oligooxyethylene-based AzoPS with a spacer moiety, while no difference in LLC phase upon photoisomerisation was seen for an AzoPS of the same general structure without a spacer moiety. The present study involves a different polar head group (tetraethylene glycol) to that used by Peng *et al.* but based on their results, a spacer moiety was incorporated into all AzoPS designed. The spacer was chosen to vary between 4 and 8 carbon atoms to investigate how the increased molecular flexibility of the 8 carbon long spacer (**$C_8\text{AzoOC}_8\text{E}_4$**) alters the surface activity and self-assembly behaviour of the AzoPS.

The effect of the pendant tail on the physicochemical properties and self-assembly behaviour was studied by varying the length of the pendant tail for a fixed spacer length, producing **C₂AzoOC₄E₄**, **C₆AzoOC₄E₄** and **C₈AzoOC₄E₄**. Changing the length of the hydrophobic tail is anticipated to lead to major differences in the physicochemical properties, as the structural changes (size, shape *etc.*) associated with isomerisation of the azobenzene group cause changes in surface tension behaviour and CMC. It would be expected that as the number of carbon atoms in the hydrophobic tail increases there would be a corresponding decrease in the CMC due to the increased hydrophobicity of the AzoPS. The wide variety in total tail lengths studied here, from the short -tailed **C₂AzoOC₄E₄** to the extremely long-tailed **C₈AzoOC₈E₄**, should provide an array of differing physicochemical behaviours.

4.3.2 Synthetic Route to AzoPS

Scheme 4.1 shows the synthetic route to the targeted photosurfactants. All steps are based on literature procedures, modified according to the desired AzoPS.^{12,23} The initial step is an azo-coupling reaction with the second and third steps both relying on bimolecular nucleophilic substitution S_N2 reactions (Scheme 4.6). All four AzoPS synthesised here are novel compounds.



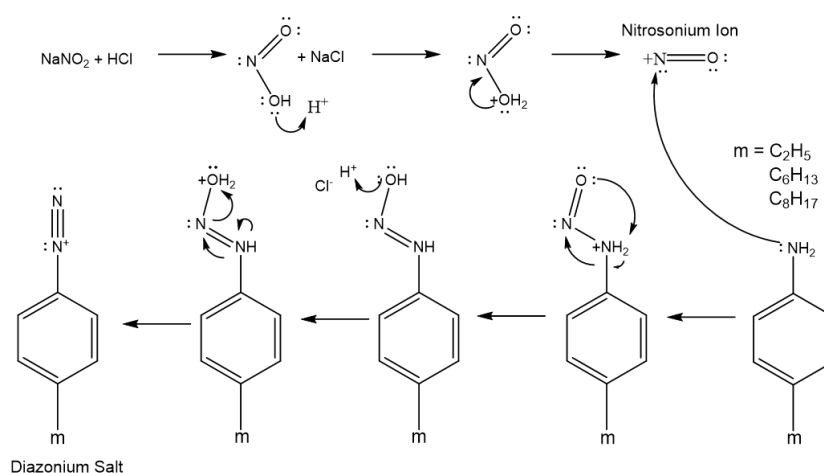
Scheme 4.1 Synthetic route to the azobenzene photosurfactants. **1a**, **1b** and **1c** refer to the three hydroxyl precursors (C₂AzoOH, C₆AzoOH and C₈AzoOH respectively), **2a**, **2b**, **2c** and **2d** to the four bromoprecursors (C₂AzoOC₄Br, C₆AzoOC₄Br, C₈AzoOC₈Br and C₈AzoOC₈Br respectively) and **3a**, **3b**, **3c** and **3d** to the final four AzoPS (C₂AzoOC₄E₄, C₆AzoOC₄E₄, C₈AzoOC₈E₄ and C₈AzoOC₈E₄ respectively).

4.3.2.1 Formation of Azobenzene Hydroxyl Precursor 1: Choosing Pendant Tail Length

Formation of the azobenzene core with a specific pendant tail length to yield **1** occurs *via* a low temperature azo coupling reaction. Diazotisation of an alkyl aniline to form a diazonium salt intermediate occurs first, followed by reaction with an electron rich aromatic nucleophile, in this case sodium phenoxide. This is a versatile reaction and allows for the

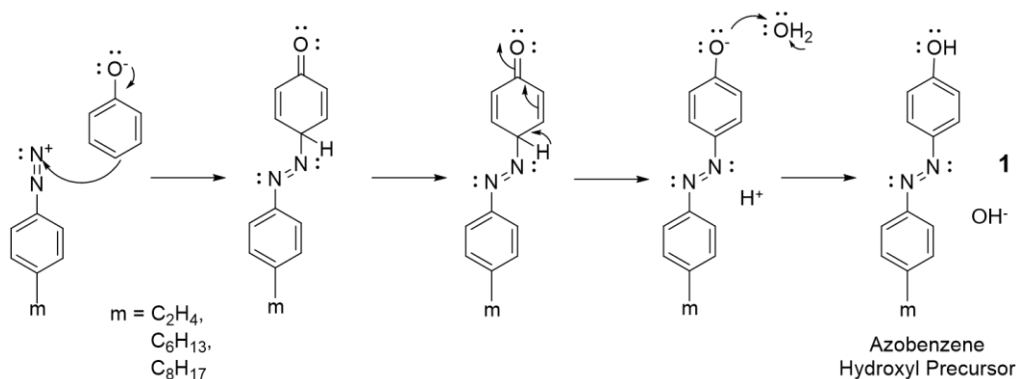
number of carbon atoms in the pendant alkyl tail (m) to be selected by choosing the appropriate alkyl aniline. In this case, 2, 6 and 8 carbon tailed azobenzene structures, were synthesised by using 4-ethylaniline, 4-hexylaniline and 4-octylaniline respectively (Scheme 4.2).

Control over both pH and temperature is crucial for this reaction to proceed effectively. Acid is required for the *in situ* formation of the nitrosonium ion (NO^+) electrophile from sodium nitrite (NaNO_2), for double protonation of NaNO_2 followed by water elimination. The lone pair on the aniline then attacks the NO^+ cation, which after loss of water yields the diazonium salt.²⁴ This diazonium salts is quite unstable and can readily decompose to form a phenol derivative.²⁵ As such, it is crucial to maintain a low temperature, of 1-3 °C.



Scheme 4.2 Synthetic scheme showing the *in situ* generation of the nitrosonium ion followed by formation of a diazonium salt intermediate.

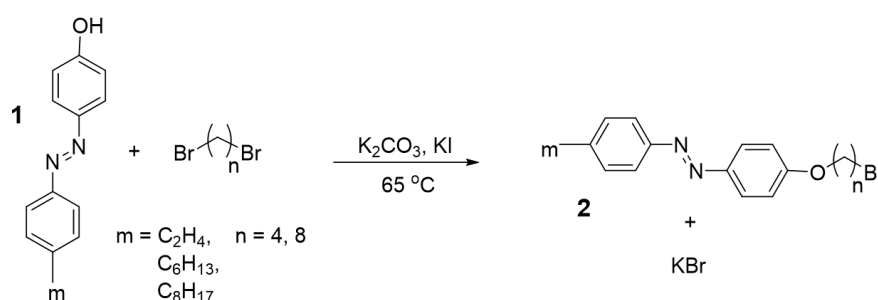
Separately, a basic solution is needed in order to deprotonate phenol and form the more nucleophilic phenoxide anion.²⁴ Typically aqueous sodium hydroxide is used for this purpose. The diazonium salt acts as a weak electrophile and undergoes electronic aromatic substitution at the *para* position of sodium phenoxide upon addition to this mildly basic solution, yielding the azobenzene hydroxyl precursor **1**. (Scheme 4.3)



Scheme 4.3 Synthetic route to formation of **1**, the azobenzene hydroxyl precursor, from the diazonium salt (Scheme 5.2) and sodium phenoxide.

4.3.2.2 Formation of the Azobenzene Bromo-Precursor 2: Selecting the Spacer Moiety

The second step in the synthesis of targeted AzoPS is a bimolecular substitution (S_N2) reaction between the hydroxyl precursor **1** and a di-bromoalkane. The di-bromoalkane chosen determines the spacer length, n , of the AzoPS. In this instance, spacers of length 4 and 8 carbons were selected by using 1,4-dibromobutane and 1,8-dibromooctane, respectively. Potassium carbonate (K_2CO_3) and potassium iodide (KI) are also combined with the hydroxyl precursor **1** and the di-bromoalkane in acetone. K_2CO_3 provides a basic environment for deprotonation of the hydroxyl precursor **1**, turning it into a better nucleophile. A catalytic amount of KI is used to facilitate a halogen exchange with the one of the bromine atoms in the di-bromoalkane *via* a Finkelstein reaction.²⁶ This is an S_N2 reaction, driven towards product formation by the insolubility and precipitation of KBr in acetone.²⁷ This step is included to improve leaving group ability, as the larger iodide is a more favourable leaving group for an S_N2 reaction.²⁵ Backside attack of the deprotonated nucleophile **1** upon the alkyl halide ultimately yields bromoprecursor **2** (Scheme 4.4).

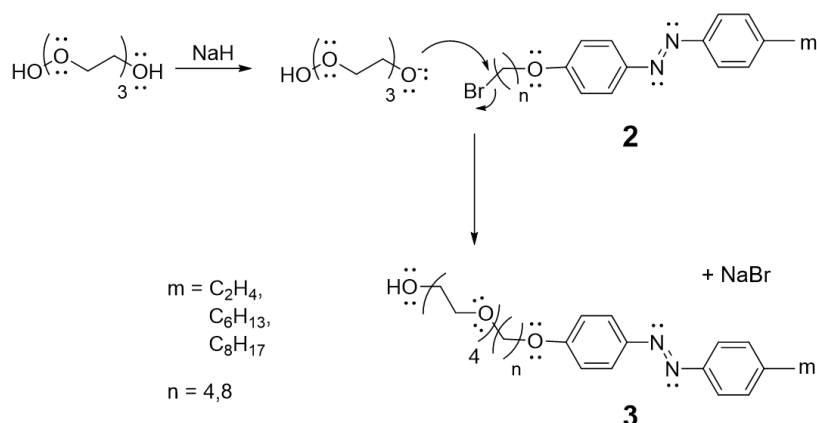


Scheme 4.4 Synthetic scheme for the introduction of the AzoPS spacer and formation of azobenzene bromoprecursor **2** *via* an S_N2 reaction.

4.3.2.3 Addition of the polar head group and formation of targeted AzoPS

With the tail and spacer length selected and the azobenzene core formed the hydrophobic component of the AzoPS can be considered complete. The final synthetic step is to impart amphiphilicity to the structure by addition of a polar tetraethylene glycol (TEG) head group, thus yielding the AzoPS. A modified Williamson ether synthesis was used for this purpose (Scheme 4.5). This synthesis is very useful for creating asymmetric ethers and proceeds *via* an S_N2 route. Sodium hydride (NaH) is used to deprotonate one of the TEG hydroxyl groups, as the conjugate base of TEG makes a much better nucleophile than TEG itself, due to the higher electron density on the deprotonated oxygen atom. Backside attack occurred on bromoprecursor **2**, with minimal steric hindrance from the azobenzene core due to the presence

of 4-8 carbon atoms in the spacer component. Release of the bromide leaving group results in the completed AzoPS.



Scheme 4.5 Synthetic route from bromoprecursor 2 and TEG to the AzoPS 3 via a Williamson Ether synthesis.

4.3.3 Observation of Photoisomerisation Using UV-Vis Absorption Spectroscopy

The photoswitching capabilities of the four AzoPS were investigated using UV-Vis absorption spectroscopy. Figure 4.3 shows the UV-Vis absorption spectra for the *trans*- and *cis*-isomers of **C₈AzoOC₈E₄** in H₂O at 25 °C. Similar optical properties were observed for the other three AzoPS, **C₂AzoOC₄E₄**, **C₆AzoOC₄E₄**, and **C₈AzoOC₄E₄** (shown in the Appendix, Figure A.4.12-4.14). The optical properties for all four AzoPS are summarised in Table 4.1.

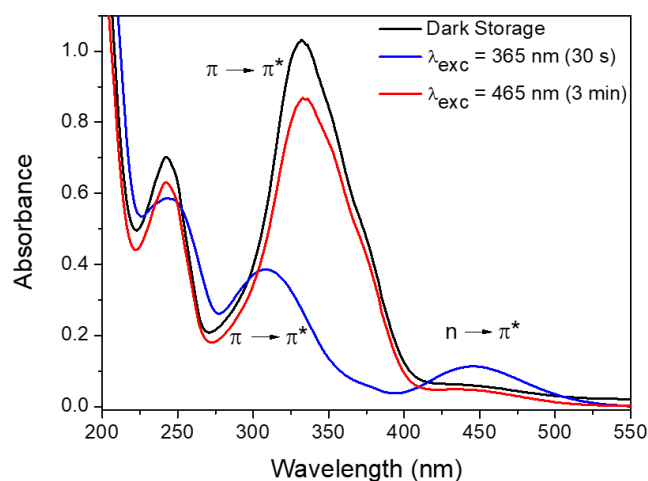


Figure 4.3 UV-Vis absorption spectra of **C₈AzoOC₈E₄** in water (0.065 mmol L⁻¹, below CMC) at 20 °C. The spectra correspond to the *trans*-form (dark storage, black line), the majority *cis* photostationary state (after UV irradiation for 30 seconds, blue line), and the majority *trans* photostationary state (blue light illumination, red line).

The *trans*-isomer of azobenzene is the more thermodynamically stable form,²⁸ and when stored in the dark or heated gently the azobenzene photosurfactant exists fully in the *trans*-state. This is recognisable from the wavelength of maximum absorption ($\lambda_{\max}$) at 332 nm (Figure 4.5), assigned to the $\pi \rightarrow \pi^*$ transition of the chromophore.²⁹ This absorption maximum for the *trans*-AzoPS is shifted to a longer wavelength than that of pure *trans*-azobenzene, with the general observation that the $\pi \rightarrow \pi^*$ transition of azobenzenes depends on the nature of their substituents.³⁰ Electron donating groups (EDG), such as alkyl and alkoxy groups, are known to cause a decrease in the $\pi \rightarrow \pi^*$ transition energy as increased electron density decreases the S_0 - S_1 energy gap. This causes $\lambda_{\max}$ to become red-shifted compared to pure azobenzene, which has a maximum absorption at 320 nm.³⁰ The strongly electron-donating alkoxy substituent in particular (the spacer moiety for AzoPS), shifts the $\pi \rightarrow \pi^*$ transition to longer wavelengths, such that it overlaps with the $n \rightarrow \pi^*$ transition.³¹

Isomerisation to the *cis*-form occurs upon illumination with UV light, identified by a blue shift in $\lambda_{\max}$ to 320 nm with a concurrent decrease in intensity, and the appearance of a new band at 445 nm (Figure 4.5).³¹ This isomerisation occurred within 30 seconds of UV irradiation (LED wavelength: 365 nm, power output: 7 mW). The solution was irradiated for a further 10 minutes with no change in the absorption spectrum. This new band at 445 nm corresponds the $n \rightarrow \pi^*$ transition that is symmetry forbidden by the Laporte selection rule for the planar *trans*-azobenzene (symmetry group C_{2h}).³² Despite π -conjugated systems typically favouring planar conformations, *cis*-azobenzene adopts a non-planar conformation (symmetry group C_2) due to the steric hindrance of the phenyl groups and repulsion of the non-bonded electrons on the nitrogen atoms in the N=N bond.³³ This reduction in symmetry means the $n \rightarrow \pi^*$ transition becomes allowed.²⁹

As aforementioned the $\pi \rightarrow \pi^*$ transition overlaps with the $n \rightarrow \pi^*$ transition, meaning that 100% *cis*-azobenzene cannot be obtained. The overlap of the *cis*- and *trans*- absorption spectra is clear from Figure 4.5. Rather than 100% *cis*-AzoPS being obtained, a photostationary state (PSS) which consists of a ratio of the two isomers emerges.²² The *cis*-PSS can be calculated from the ratio of the *cis*-PSS absorbance to 100% *trans*-absorbance, at a given wavelength. This is referred to as the degree of isomerisation (ID)²²:

$$ID_{trans-cis} = \frac{A(0)_{365} - A(PSS)_{365}}{A(0)_{365}} \times 100\% \quad (4.1)$$

where $A(0)_{365}$ refers to the absorbance of the 100% *trans* isomer at 365 nm and $A(PSS)_{365}$ refers to the absorbance of the *cis* isomer at 365 nm, in the PSS. Similarly, for reverse isomerisation

back to the *trans* isomer, a majority *trans*-PSS is obtained upon illumination with blue light ($\lambda = 465$ nm). 100% *trans*-azobenzene is only accessible thermally/or via dark storage.³¹ The *trans*-PSS state can be calculated in an analogous manner to the *cis*-PSS:

$$ID_{cis-trans} = \frac{A(PSS)_{365}}{A(0)_{365}} \times 100\% \quad (4.2)$$

where $A(0)_{365}$ still refers to the absorbance of the 100% *trans*-isomer at 365 nm and $A(PSS)_{365}$ now refers to the absorbance of the *trans*-PSS at 365 nm. The degrees of isomerisation obtained for each of the four AzoPS synthesised are summarised in Table 4.1

Table 4.1 UV-vis absorption properties of the photosurfactants **C₂AzoOC₄E₄** (6.5×10^{-5} mol L⁻¹), **C₆AzoOC₄E₄** (6.5×10^{-5} mol L⁻¹), **C₈AzoOC₄E₄** (6.5×10^{-5} mol L⁻¹), and **C₈AzoOC₈E₄** (6.5×10^{-5} mol L⁻¹), at 25 °C. ϵ_{trans} is the molar absorption coefficient for the *trans*-isomer, λ_{max} is the wavelength at which an absorption maximum is seen, $ID_{trans-cis}$ and $ID_{cis-trans}$ are the isomerisation degrees for the *trans-cis* and *cis-trans* photoisomerisations respectively.

AzoPS	ϵ_{trans} at 332 nm (L mol ⁻¹ cm ⁻¹)	<i>trans</i> - λ_{max} (nm)	<i>cis</i> - λ_{max} (nm)	$ID_{cis-trans}$ (%)	$ID_{trans-cis}$ (%)
C₂AzoOC₄E₄	12,350	348	312, 438	87.7	89.6
C₆AzoOC₄E₄	15,640	331	308, 443	95.2	84.1
C₈AzoOC₄E₄	15,874	332	308, 445	90.2	87.0
C₈AzoOC₈E₄	12,306	332	308, 443	93.7	61.1

C₂AzoOC₄E₄, **C₆AzoOC₄E₄** and **C₈AzoOC₄E₄** gave a *trans-cis* ID of 89.6%, 84.1% and 87.0% respectively in good agreement with literature values for similar neutral AzoPS (86-89%).²² Strikingly, the value for **C₈AzoOC₈E₄** is much lower, at 61.1%. All four AzoPS demonstrated a high degree of *trans*-isomer recovery upon irradiation with blue light. Reverse ID values of 87.7%, 95.2%, 90.2% and 93.7% were found for **C₂AzoOC₄E₄**, **C₆AzoOC₄E₄**, **C₈AzoOC₄E₄** and **C₈AzoOC₈E₄** respectively. These values are quite high in comparison to other AzoPS in the literature, such as 4-alkylazobenzene-4'-(oxy-2-hydroxypropyl)-trimethylammoniummethysulfate (AZMS) which had a *trans*-recovery of only 72-77% upon irradiation with blue-light ($\lambda_{ex} = 465$ nm).¹⁹

4.3.4 Determination of Critical Micelle Concentrations

The concentration at which surfactants form aggregates is a crucial parameter in the physical characterisation of surfactants, as it is at this point that a dramatic change in the physicochemical properties occurs. The CMC represents the point at which monomers begin to form self-assembled aggregates, or micelles. A corresponding change in physicochemical

properties (*i.e.* turbidity, conductivity, surface tension, solubility) is seen at this point. DLS and surface tensiometry are two techniques used here to determine the CMC for the four AzoPS synthesised.

4.3.4.1 CMC Determination Method 1: Dynamic Light Scattering

DLS measures the intensity of light scattered from a sample, and can be used to determine the CMC. In aqueous solutions below the CMC, dispersed surfactant monomers scatter very little light due their small size. In this low concentration region, the intensity of scattered light will increase slowly in a linear fashion with concentration as the number of monomers in solution increases. As the concentration of surfactant increases above the CMC, a break in the slope is seen when scattering intensity increases dramatically, indicative of the formation of micelles.

Figure 4.6 shows the intensity of scattering (kcounts per second) as a function of concentration for **C₈AzoOC₈E₄** before and after UV irradiation. The corresponding plots for **C₂AzoOC₄E₄**, **C₆AzoOC₄E₄** and **C₈AzoOC₄E₄** are shown in the appendix (Figure A.4.15). In the *trans*-form, **C₈AzoOC₈E₄** exhibits a CMC of $102.7 \times 10^{-6} \text{ mol L}^{-1}$. After illumination this value increases to $128.4 \times 10^{-6} \text{ mol L}^{-1}$. Similarly, the CMC values for **C₆AzoOC₄E₄** increased from $22.9 \times 10^{-6} \text{ mol L}^{-1}$ to $23.7 \times 10^{-6} \text{ mol L}^{-1}$ and **C₈AzoOC₄E₄** increased from $11.4 \times 10^{-6} \text{ mol L}^{-1}$ to $12.4 \times 10^{-6} \text{ mol L}^{-1}$ before and after UV illumination. In all three cases, the *cis*-isomers display a CMC greater than the *trans*-isomers. However, for **C₂AzoOC₄E₄** almost identical values were obtained for the *cis*- and *trans*-CMCs, of $34.4 \times 10^{-6} \text{ mol L}^{-1}$ before UV illumination and $34.1 \times 10^{-6} \text{ mol L}^{-1}$ after. There is quite a large error associated with the *cis*-CMC value, which likely accounts for the deviation of **C₂AzoOC₄E₄** from the general trend $\text{CMC}_{\text{cis}} < \text{CMC}_{\text{trans}}$. The CMC values for all four AzoPS are summarised in Table 4.2.

In addition, the values of CMC were found to decrease as the number of carbon atoms in the pendant tail increased for both *cis*- and *trans*-isomers, with the exception of **C₈AzoOC₈E₄**. Therefore, these values are generally in good agreement with the fact that the AzoPS with longer alkyl tails have a higher hydrophobicity and subsequently lower CMCs.¹⁹ The nonconformity of **C₈AzoOC₈E₄** to this trend is very similar to results reported by Shang *et al.* For a series of diethylene glycol (E₂) AzoPS it was found that the CMC of the *trans* form decreased monotonically with increasing number of carbon atoms in the tail, with the exception of an AzoPS with a long spacer, C₄AzoOC₈E₂.¹² Hydrophobicity alone is clearly not enough to rationalise the high CMC values seen for molecules with long spacer lengths. It is apparent

that molecular structure, in particular the spacer moiety, plays a fundamental role in determining the physicochemical behaviour of the surfactant.

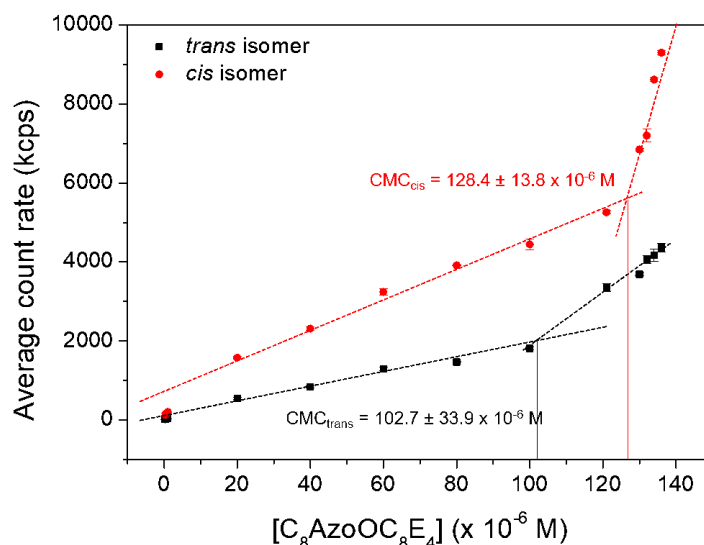


Figure 4.6 Effect of AzoPS concentration on the intensity of scattered light for an aqueous solution of **C₈AzoOC₈E₄** for both *trans*- and *cis*-isomers at 25 °C. The CMC values are obtained from the intersection of the two linear trend-lines. The error bars, which are on the same order as the count rate values, show the standard deviation of the mean average count rate obtained over 3 measurement.

Table 4.2 Critical micelle concentrations of the *trans*- and *cis*-isomers of the photosurfactants, determined from the point at which a break in slope was seen for a graph of kcounts vs concentration. kcounts were measured for a variety of concentrations using DLS. The associated errors are given in brackets (std. dev. of three measurements).

AzoPS	CMC _{trans} (μmol L ⁻¹)	CMC _{cis} (μmol L ⁻¹)
C₂AzoOC₄E₄	34.4 (5.7)	34.1 (19.1)
C₆AzoOC₄E₄	22.9 (4.2)	23.7 (5)
C₈AzoOC₄E₄	11.4 (1.6)	12.4 (1.2)
C₈AzoOC₈E₄	102.7 (33.9)	128.4 (13.8)

4.3.4.2 CMC Determination Method 2: Surface Tensiometry

Thorough determination of the CMC requires that at least two methods be used. For this reason a second technique was employed, namely surface tensiometry (ST). In surface tension terms, the CMC can be considered as the point at which the air-water interface becomes saturated with surfactant monomers.³⁴ After this surface saturation point, the surfactant monomers in the bulk solution begin to self-assemble into micelles. Accordingly, surface tension should decrease with increasing AzoPS concentration up to a point, at which surface tension becomes independent of AzoPS concentration.^{35,36} This point indicates the CMC.

The equilibrium surface tension of all four AzoPS in water was measured over a range of concentrations, using pure water as the reference (72.80 mN m⁻¹ at 25 °C). Surface tension

values were obtained *via* the Du Noüy-Padday maximum pull force method, whereby a rod is first immersed and then slowly withdrawn from the AzoPS solution, while the force exerted on the rod is measured.^{37,38} Figure 4.7 shows the surface tension as a function of concentration for **C₈AzoOC₈E₄**, before and after UV irradiation. The CMC was determined from the point at which surface tension became independent of concentration, for both isomers. The plots for **C₂AzoOC₄E₄**, **C₆AzoOC₄E₄**, **C₈AzoOC₄E₄** are presented in the Appendix (Figure A.4.16). The CMC values for all four AzoPS are summarised in Table 4.2.

In the *trans*-form, **C₈AzoOC₈E₄** exhibits a CMC of $108.6 \times 10^{-6} \text{ mol L}^{-1}$, which increases to $125.9 \times 10^{-6} \text{ mol L}^{-1}$ after photoisomerisation. Similarly, the CMC values for **C₈AzoOC₄E** increased from $17.8 \times 10^{-6} \text{ mol L}^{-1}$ to $19.9 \times 10^{-6} \text{ mol L}^{-1}$ and **C₂AzoOC₄E₄** increased from 52.5 to $56.8 \times 10^{-6} \text{ mol L}^{-1}$ after UV illumination. **C₆AzoOC₄E₄** has a lower CMC for the *cis*-form than the *trans*-. However, the values for *cis*- and *trans*-isomers are within error, with $37.1 \pm 6.3 \times 10^{-6} \text{ mol L}^{-1}$ obtained before UV illumination and $29.5 \pm 1.8 \times 10^{-6} \text{ mol L}^{-1}$ obtained after. The values obtained by ST are compared with those obtained from DLS in Table 4.3.

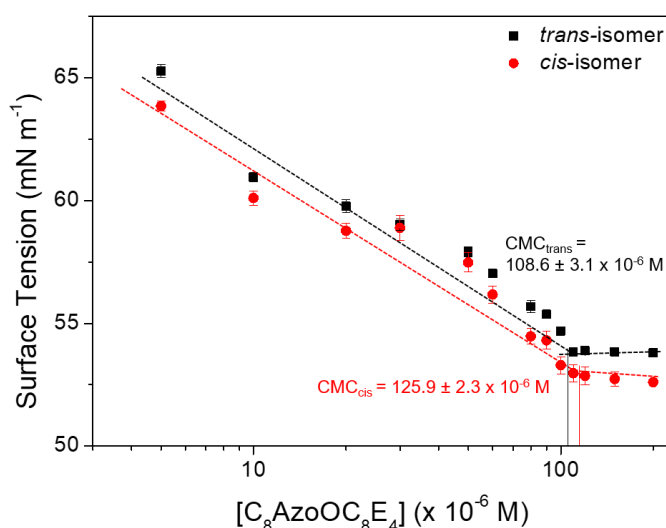


Figure 4.7 Surface tension as a function of concentration for the *trans*- and *cis*-forms of **C₈AzoOC₈E₄** at 25 °C. The CMC values are obtained from the intersection between the two linear trend-lines. The error bars show the standard deviation of the mean surface tension obtained over 3 measurements.

Table 4.2 Critical micelle concentrations of the *trans*- and *cis*-isomers, determined from the point at which a break in slope was seen for a graph of surface tension vs concentration. The surface tension of the AzoPS in aqueous solution were measured for a variety of concentrations using ST. The associated errors (given in brackets) are the std. dev. of three measurements.

AzoPS	CMC _{trans} ($\mu\text{mol L}^{-1}$)	CMC _{cis} ($\mu\text{mol L}^{-1}$)
C₂AzoOC₄E₄	52.5 (2.4)	56.8 (2.1)
C₆AzoOC₄E₄	37.1 (6.3)	29.5 (1.8)
C₈AzoOC₄E₄	17.8 (2.1)	19.9 (1.8)
C₈AzoOC₈E₄	108.6 (3.1)	125.9 (2.3)

The CMC values recorded *via* surface tensiometry are in very good agreement with the values obtained *via* dynamic light scattering (Table 4.3). In almost all cases the CMCs resulting from ST are higher than those obtained from dynamic light scattering. This highlights how the CMC value is dependent on the technique employed. The CMC is a transitional region, rather than a hard boundary; micelle formation does not occur instantaneously upon reaching the CMC.³⁹ The slightly different CMC values found for surface tensiometry and dynamic light scattering thus gives an indication of the width of this CMC region. Figure 4.8 and Table 4.3 summarise the CMC values obtained from both DLS and ST for all four AzoPS in both isomeric forms, as a function of carbon atoms in the pendant tail and spacer. It is clear that for a fixed spacer length of 4, the CMC decreases as the total number of carbon atoms in the tail increases from 6 to 12, owing to increased hydrophobicity of the molecule, while for long spacer lengths of 8 carbons (total tail length = 16 carbon atoms), this trend is not observed.

Table 4.3 Critical micelle concentrations of the *trans*- and *cis*-isomers of the photosurfactants in water compared for DLS and ST. The associated errors are given in brackets (std. dev. of three measurements).

AzoPS	CMC by DLS ($\mu\text{mol L}^{-1}$)		CMC by ST ($\mu\text{mol L}^{-1}$)	
	<i>trans</i> -isomer	<i>cis</i> -isomer	<i>trans</i> -isomer	<i>cis</i> -isomer
C₂AzoOC₄E₄	34.4 (5.7)	34.1 (19.1)	52.5 (2.4)	56.8 (2.1)
C₆AzoOC₄E₄	22.9 (4.2)	23.7 (5)	37.1 (6.3)	29.5 (1.8)
C₈AzoOC₄E₄	11.4 (1.6)	12.4 (1.2)	17.8 (2.1)	19.9 (1.8)
C₈AzoOC₈E₄	102.7 (33.9)	128.4 (13.8)	108.6 (3.1)	125.9 (2.3)

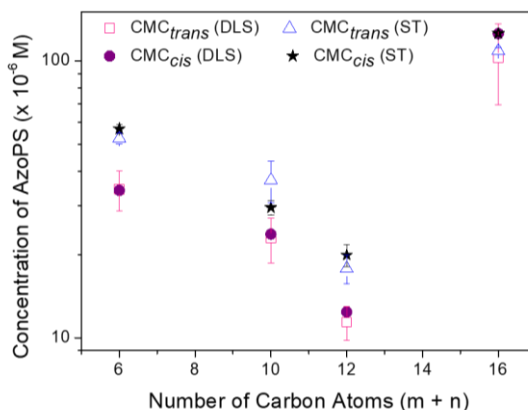


Figure 4.8 CMC as a function of the number of carbon atoms in the pendant tail (m) and spacer moiety (n) combined. *trans*-CMCs are indicated by open symbols, and *cis*-CMCs by solid symbols. CMC determinations done by DLS are given by pink squares and purple circles, while CMC determinations by ST are indicated by blue triangles and black stars.

4.3.5 Using AzoPS to Control the Surface Tension with Light

It is clear that changes in molecular structure upon photoisomerisation impacts the CMC, and not just in terms of additional carbon atoms imparting additional hydrophobicity; the spacer moiety in particular appears to play a key role in controlling the physicochemical properties of the AzoPS. In this section the equilibrium surface tension behaviour of all four AzoPS, measured by ST as outlined previously in section 4.3.4.2, will be discussed in more detail.

Figure 4.9 displays the equilibrium surface tension behaviour of all four AzoPS as a function of surfactant concentration and illumination conditions. The different responses of the individual surfactants to changes in illumination conditions demonstrate how sensitive the interfacial properties of AzoPS are to small changes in surfactant structure. For the shortest AzoPS, **C₂AzoOC₄E₄**, (Figure 4.9a) isomerisation changes both the shape of the surface tension curve and the equilibrium surface tension value. The surface tension values for the *trans*-form start to decay more rapidly with concentration than those of the *cis*-, with the greatest difference obtained being 16.1 mN m⁻¹, before ultimately the *trans*- isomers reaches a saturated surface tension value 14.8 mN m⁻¹ lower than that of the *cis*-isomer. For **C₆AzoOC₄E₄** (Figure 4.9b) the *cis*-form initially lowers the surface tension more than the *trans*-form at low surfactant concentrations. However, close to the CMC the *trans*-form begins to present values lower than those of this *cis*-form, with the saturated surface tension being on average 4.2 mN m⁻¹ lower than the *cis*-form.

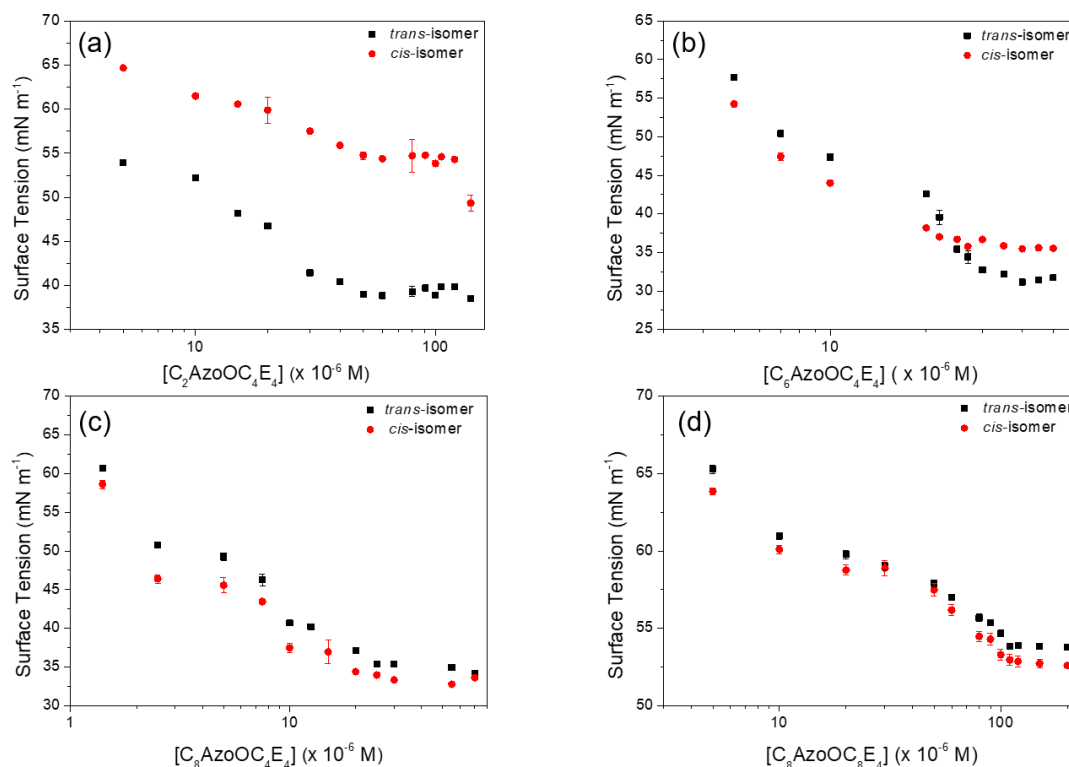


Figure 4.9 Concentration dependence of the equilibrium surface tension for a series of four AzoPS at 20 °C under both visible (black squares) and UV (red circles) light illumination. (a) **C₂AzoOC₄E₄**, (b) **C₆AzoOC₄E₄**, (c) **C₈AzoOC₄E₄**, (d) **C₈AzoOC₈E₄**

In the case of **C₈AzoOC₄E₄** the *cis*-isomer always gives surface tension values lower than the *trans*-isomer, with the saturated surface tensions above the CMC having the smallest difference between isomers yet, of 2.6 mN m⁻¹. **C₈AzoOC₈E₄** shows both *cis*- and *trans*- surface tension curves having a very similar shape and equilibrium surface tension. Again, the *cis*-isomer is always lower in surface tension value than the *trans*-isomer, but in this case they are almost identical, with saturated surface tension differences of only 1 mN m⁻¹ between them. Both **C₈AzoOC₄E₄** and **C₈AzoOC₈E₄** seem relatively unaffected by UV illumination, while for the AzoPS with fewer carbon atoms more significant differences are seen upon illumination, with surface tension differences of 4.2 mN m⁻¹ and 14.8 mN m⁻¹ possible in the low concentration regime of **C₆AzoOC₄E₄** and **C₂AzoOC₄E₄**, respectively.

The surface excess and area per molecule for both isomeric forms of each AzoPS were calculated to help further rationalise these results. The surface excess represents the relative accumulation of a substance at the interface of the solution in which it is dissolved. The surface excess concentration can be found from the slope of the surface tension curve with respect to the surfactant concentration by using the Gibb's adsorption isotherm^{35,36}:

$$\Gamma = \frac{-1}{RT} \left(\frac{d\gamma}{d \ln c} \right) \quad (4.3)$$

where Γ is the surface excess, R is the universal gas constant, T is temperature, γ is the surface tension and c is surfactant concentration. The area occupied per molecule at the surface is calculated by taking the inverse of this surface excess concentration as follows:

$$A = \frac{1 \times 10^{20}}{\Gamma N_A} \quad (4.4)$$

where A is the area per molecule and N_A is Avogadro's constant. Table 4.4 summarises the values obtained for the bulk and interfacial properties of all four AzoPS.

Table 4.4 Interfacial and bulk properties of **C₂AzoOC₄E₄**, **C₆AzoOC₄E₄**, **C₈AzoOC₄E₄** and **C₈AzoOC₈E₄** under varying illumination conditions, where γ is average saturated surface tension value, Γ is surface excess, A is area per molecule and the CMC is as determined *via* ST.

	C₂AzoOC₄E₄		C₆AzoOC₄E₄		C₈AzoOC₄E₄		C₈AzoOC₈E₄	
	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>
γ (mN m ⁻¹)	39.9	54.5	31.2	35.4	35.4	32.8	53.8	52.8
Γ (μmol m ⁻²)	2.9	1.7	4.8	3.4	3.3	3.3	1.8	1.7
A (Å ²)	57	98	34	49	50	50	90	96
CMC (μM)	52.5	56.8	37.1	29.5	17.8	19.9	108.6	125.9

Surface excess concentration can be seen to decrease with increasing spacer length, as the surface excess values of both the *cis*- and *trans*-forms of **C₂AzoOC₄E₄**, **C₆AzoOC₄E₄** and **C₈AzoOC₄E₄** (2.9-4.8 μmol m⁻² for *trans*- and 1.7 – 3.3 μmol m⁻² for *cis*-) are all higher than those for **C₈AzoOC₈E₄** (1.8 and 1.7 μmol m⁻² respectively). For AzoPS of a fixed spacer length but varying pendant tail length the surface excess generally increases with increasing pendant tail length, for both *cis*- and *trans*-isomers. This could perhaps be attributed to the increasing hydrophobicity of the molecules with increasing number of carbon atoms. In which case, the same behaviour as for the CMC is seen, with **C₂AzoOC₄E₄**, **C₆AzoOC₄E₄** and **C₈AzoOC₄E₄** all following a trend of increased surface excess concentration and decreasing CMC with increasing pendant tail length, while **C₈AzoOC₈E₄** bucks this trend and presents both a low surface excess and a high CMC, despite it being a highly hydrophobic molecule. This is very similar to results reported by Shang *et al.* for diethylene glycol AzoPS of varying spacer length.¹² In their case, the surfactant with the longest spacer, **C₄AzoOC₈E₂**, presented both the lowest surface excess and highest CMC.

In all cases the surface excess concentration was the same if not lower for the *cis*-form than for the *trans*-form. The most significant difference was seen for **C₂AzoOC₄E₄**, ($\Gamma_{cis} \sim 70\%$

lower than Γ_{trans}) with the difference in surface excess concentrations between isomers becoming much less pronounced as the number of carbons in the alkyl tail increased. For **C₈AzoOC₄E₄** and **C₈AzoOC₈E₄** there is almost no difference between surface excess concentrations for each isomer, and both *cis*- and *trans*-isomers occupy roughly the same area per molecule. Correspondingly, the difference in saturated surface tension values is also very small, 2.4 mN m⁻¹ and 1 mN m⁻¹ respectively. This can be attributed to the increased molecular flexibility with increasing alkyl tail length. Isomerisation changes the shape and conformation of the molecule less significantly when the molecule has the freedom to arrange itself in a preferred orientation, facilitated by the many methylene groups in the pendant tail and/or spacer. The large area of **C₈AzoOC₈E₄** (90 Å² and 95 Å² for *trans* and *cis* respectively) can be used to rationalise why surface tension values plateau for this AzoPS at only 53.8 and 52.8 mN m⁻¹, while **C₆AzoOC₄E₄**, which occupies only 30-40% the area per molecule, can lower the surface tension to 35.4 and 31.2 mN m⁻¹ depending on the isomeric form.

When surfactants with constant spacer length, but differing pendant tail lengths are considered the results become very interesting. For intermediate pendant tail lengths, **C₆AzoOC₄E₄** and **C₈AzoOC₄E₄**, the results seem quite intuitive. Both are significantly smaller than **C₈AzoOC₈E₄**, in terms of molecular area, with the area occupied per molecule increasing with the number of methylene groups in the tail (34 Å² and 50 Å² for *trans*-isomers and 49 Å² and 50 Å² for *cis*-isomers respectively). These values are in good agreement with results for diethylene glycol AzoPS reported by Shang *et al.*, where their most similar AzoPS, C₄AzoOC₄E₂, was found to have an area of 21 Å² and 35 Å².¹² Single alkyl chain surfactants, such as n-alkanoic and fatty acids, typically present areas per molecule values of 20 to 60 Å², with values of less than 40 Å² characteristic of a condensed surface monolayer phase and values of over 40 Å² characteristic of an expanded surface monolayer phases.^{40,41} The area per molecule values presented here for **C₆AzoOC₄E₄** and **C₈AzoOC₄E₄** (Table 4.4) are on the high side of this range, implying the presence of expanded monolayer phases. However, as these photosurfactants contain a bulky azobenzene group in the alkyl tail, direct comparisons to the surfactant literature, which almost exclusively refer to non-photoactive, long alkyl chain surfactants, must be done with caution. Regardless, both isomers of **C₆AzoOC₄E₄** and **C₈AzoOC₄E₄** are excellent at lowering the surface tension, but the surface tension is insensitive to illumination conditions.

For **C₂AzoOC₄E₄**, values of 57 Å² and 98 Å² per molecule are seen for *trans*- and *cis*-isomers respectively. It seems sensible that the linear *trans*-form takes up a significantly smaller area than the bent *cis*-form; what is at first unintuitive is that these values are both larger than

the values seen for **C₆AzoOC₄E₄** and **C₈AzoOC₄E₄**. It appears that the extremely short pendant tail of **C₂AzoOC₄E₄** has a striking effect on the interfacial properties, with the increased values for area per molecule implying that **C₂AzoOC₄E₄** packs into a more expanded surface phase than the other two AzoPS of the same spacer length. The rigidity of the 2 carbon pendant tail compared to the more flexible 6 and 8 carbon pendant tails of **C₆AzoOC₄E₄** and **C₈AzoOC₄E₄** means that upon photoisomerisation very pronounced differences in values for surface excess, interfacial area, and saturated surface tension (up to 14.6 mN m⁻¹) are seen.

4.4 Conclusions

The design, synthesis and characterisation of a series of four novel neutral azobenzene photosurfactants has been achieved. This series of surfactants was targeted to investigate the effect of molecular structure and photoisomerisation on the optical and physicochemical properties of the surfactants. All four AzoPS demonstrated excellent photo-switching ability, with exceptional optical *trans*- isomer recoveries of 88-95%. The CMCs of these neutral AzoPS are very low (μmol L⁻¹), compared to typical CMCs for ionic AzoPS (mmol L⁻¹).^{42,43} This means that for a given application very little AzoPS would need to be used.

The results presented here have shown that varying the length of the pendant tail and spacer moiety is an effective method to control the surface activity and interfacial properties of the surfactants. Extremely large differences in surface properties were seen for AzoPS with very short pendant tails and moderate spacers. For example, in aqueous solutions of these AzoPS below the CMC, surface tension can increase by as much as 16.1 mN m⁻¹ under UV illumination. Moreover, saturated surface tension differences up to 14.6 mN m⁻¹ were seen upon photoisomerisation. To the best of my knowledge these results rival the best available in the literature. Shang *et al.* reported on a series of diethylene glycol AzoPS, with differences in saturated surface tension of 14.4 mN m⁻¹ seen for a molecule with a moderate tail and long spacer, C₄AzoOC₈E₂. Their work emphasised the importance of the spacer moiety over the pendant tail. The work in this chapter shows that the role of the tail should not be underestimated, with equivalently high differences in saturated surface tension found for an AzoPS with a very short tail and moderate spacer. In short, it is clear that consideration of surfactant structure is imperative to achieve the desired physicochemical behaviour, with a structure-based approach being imperative for AzoPS to be useful tools in surface tension based industries.

4.5 References

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Chapter 5

The Effect of Molecular Structure on the Self-Assembly Behaviour of Tetraethylene Glycol Azobenzene Photosurfactants

5.1 Introduction

From Chapter 4 it has been established that both the molecular structure and isomeric form of an AzoPS play a key role in determining the physicochemical properties of the surfactant, such as its CMC and surface tension. This chapter will now turn to the impact of molecular structure on the self-assembly behaviour of the AzoPS at concentrations above the CMC, with particular attention paid to the shape and size of self-assembled structures, and the impact of photoisomerisation and increased temperature on the AzoPS system.

The self-assembly of surfactants into organised micellar structures has led to surfactants having extensive applications in detergency,^{1,2} cosmetics,^{1,2} templating of mesoporous materials³⁻⁵ and micellar catalysis.^{6,7} A flexible and reversible method to control surfactant self-assembly, such as light illumination of photosurfactants, could enhance and extend the use of surfactants in commercial applications and industries such as these. It has already been demonstrated in this thesis that incorporating an azobenzene moiety into a surfactant structure is a simple and extremely effective method to moderate the physicochemical properties of the surfactant. As the self-assembly process relies on a similar interplay of hydrophobicity, hydrophilicity and steric factors it would be expected to be responsive to changes in molecular structure and illumination conditions.⁸⁻¹⁰

The effect of the *trans*-to-*cis* isomerisation of an azobenzene moiety on the self-assembled structure formed by the AzoPS is yet to be fully understood. There is evidence that the change in molecular structure (and hydrophilicity) upon photoisomerisation from *cis* to *trans* can result in the complete loss of the aggregate structure, usually when the AzoPS concentration is above the CMC for the *trans*-isomer but below the CMC for the *cis*-isomer.¹¹ For example, Lund *et al.* found from *in situ* SAXS studies that upon photoisomerisation of the cationic photosurfactant, 4-butyl-4'-(3-trimethyl ammoniumpropoxy)phenylazobenzene, AzoTMA, there was an almost instantaneous loss of surfactant micelles.¹¹ Photoisomerisation has also been shown to alter the phase of the self-assembled AzoPS.¹² Shang *et al.* found that the *trans*-isomers of two neutral AzoPS, (diethylene glycol mono(4',4-butyloxybutyl-azobenzene), C₄AzoOC₄E₂, and diethylene glycol mono(4',4-hexyloxybutyl-azobenzene), C₄AzoOC₆E₂) formed bilayer vesicles at concentrations above the CMC, while the *cis*-isomer at the same concentration formed a bicontinuous phase.¹² However, this is one of few studies investigating the effect of AzoPS structure on self-assembly behaviour.

The aim of this chapter is to determine the size, shape and structure of self-assembled neutral azobenzene photosurfactants using SANS, and to study the effect of UV illumination

and temperature on the self-assembled aggregates formed. Thorough knowledge of the AzoPS self-assembly behaviour and associated photo- and temperature-controlled structural changes will allow AzoPS to be used as tools in surfactant-based applications, such as templating and micellar catalysis.

5.2 Experimental

5.2.1 Materials

C₂AzoOC₄E₄, **C₆AzoOC₄E₄**, **C₈AzoOC₄E₄** and **C₈AzoOC₈E₄** were synthesised as described previously in Chapter 4.

5.2.2 Instrumentation

The instrumentation used for small-angle neutron scattering is outlined in the Experimental, Chapter 3.

5.2.2 Methods

5.2.2.1 Small-Angle Neutron Scattering

Samples of each AzoPS (1 mmol L⁻¹) were prepared in D₂O to provide good scattering contrast. Temperature studies were performed using a Jubalo water bath and 10 min equilibration time between each temperature increment. Samples for the *cis*-isomer measurements were irradiated with UV-light ($\lambda_{\text{ex}} = 365$ nm) for 7 min directly before each measurement. UV-Vis absorption spectra were recorded on a NanoDrop 2000c spectrophotometer (ThermoScientific), to ensure that photoisomerisation to the *cis*-PSS had occurred. The scattering profiles were fit using non-linear least-squares analysis to either the Lamellar, Lamellar (HG), Elliptical Cylinder, Cylinder, Flexible Elliptical Cylinder or Flexible Cylinder form factor models using the SasView programme (version 4.0.1). Full mathematical descriptions of the form factor models can be found in the Experimental, Chapter 3. The *q*-scaling analysis and general model fitting procedures have been detailed in Chapter 2.

5.3 Results and Discussion

5.3.1 Using SANS to Probe the Organisation of *trans*-AzoPS above the CMC

SANS was used to elucidate the organisation of the self-assembled structures formed for four different AzoPS in D₂O. SANS is a useful method to determine the shape, structure and dimensions of micellar aggregates at low concentration. Figure 5.1 shows SANS data for the *trans*-isomers of **C₂AzoOC₄E₄**, **C₆AzoOC₄E₄**, **C₈AzoOC₄E₄** and **C₈AzoOC₈E₄** in D₂O at concentrations above their CMCs (1 mmol L⁻¹) at T = 25 °C. It is clear that there are striking differences in the scattering profiles for each AzoPS, implying that the self-assembly process varies from surfactant to surfactant. All *q*-scaling and model fitting described below are summarised in Tables 5.2-5.5.

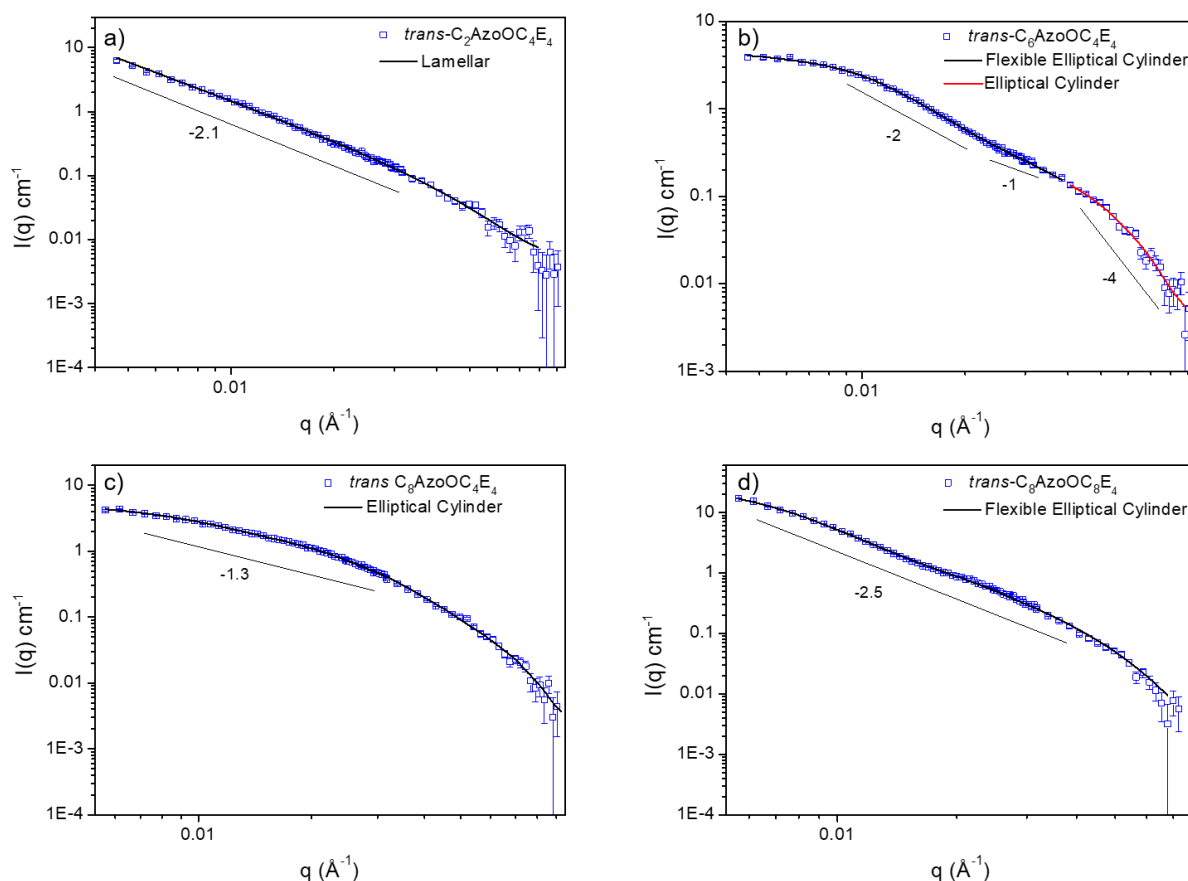


Figure 5.1 SANS data for the *trans*-isomers of (a) **C₂AzoOC₄E₄**, (b) **C₆AzoOC₄E₄**, (c) **C₈AzoOC₄E₄** and (d) **C₈AzoOC₈E₄** in D₂O (1 mmol L⁻¹) at 25 °C. Straight lines serve to guide the eye along the monotonic decays which are interpreted by *q*-scaling analysis. The solid lines overlaying the SANS data correspond to the fits to the form factor models described in-text.

The SANS scattering profiles were initially interpreted using scaling concepts, to provide preliminary information about the AzoPS aggregate shape and fractal dimension, and to inform the choice of form factor. For *trans*-**C₂AzoOC₄E₄** (1 mmol L⁻¹ in D₂O) a decay of *q*

^{2,1} was seen in the low q region (Figure 5.1a, $q < 0.04 \text{ \AA}^{-1}$) indicative of scattering from sheet-like objects (q^{-2}). The lamellar model fits this data well, yielding wet sheets (74% D₂O) with a thickness of 62.2 Å. It should be noted that this lamellar phase could also represent part of a large vesicle, the radius of which is larger than the observation window of this SANS experiment (6-157 nm).

The scattering profile of *trans*-**C₆AzoOC₄E₄** (1 mmol L⁻¹ in D₂O) is shown in Figure 5.1b and displays several changes in slope across the entire q -range, implying the presence of multiple length scales.¹³ This particular scattering profile is characteristic of scattering from wormlike micelles, which are elongated, flexible, self-assembly structures that can entangle into a dynamic network.¹³⁻¹⁶ Wormlike micelles are typically characterised in terms of four main parameters (Figure 5.2) – radius of gyration, R_g , contour length, L_C , Kuhn length, L_K , and cross-sectional cylinder radius, R_{CS} .^{13,14} R_g gives an indication of the size of the micellar aggregate, and for wormlike micelles often lies outside the observation window of SANS experiments.¹³ L_C is the overall length of the wormlike micelle and typically ranges from several nanometres to micrometres.¹³ L_K gives a measure of the distance over which wormlike micelle segments can be considered rigid,¹⁷ and R_{CS} gives the cross-sectional radius of the rigid cylinder, as indicated in Figure 5.2. Each of these parameters can be related to the various length scales seen in the scattering profile. For example, the behaviour at low q (large d) gives an indication of R_g and the overall size of the aggregates,^{13,17} the decay of q^{-2} at slightly higher q corresponds to the self-avoiding random walk of the wormlike micelles, and is the region from which information about L_C is found.^{13,17,18} A mid- q decay of q^{-1} (at $q \approx 0.03 \text{ \AA}^{-1}$ in Figure 5.1b) correlates to scattering from rigid cylinders, and so describes the Kuhn length of the wormlike micelles.^{13,17,18} The sharp decrease in scattering at high q (a decay of q^{-4}) is a result of scattering from sharp interfaces, in this case from the finite cylindrical cross sections of the wormlike micelles.^{13,17,18}

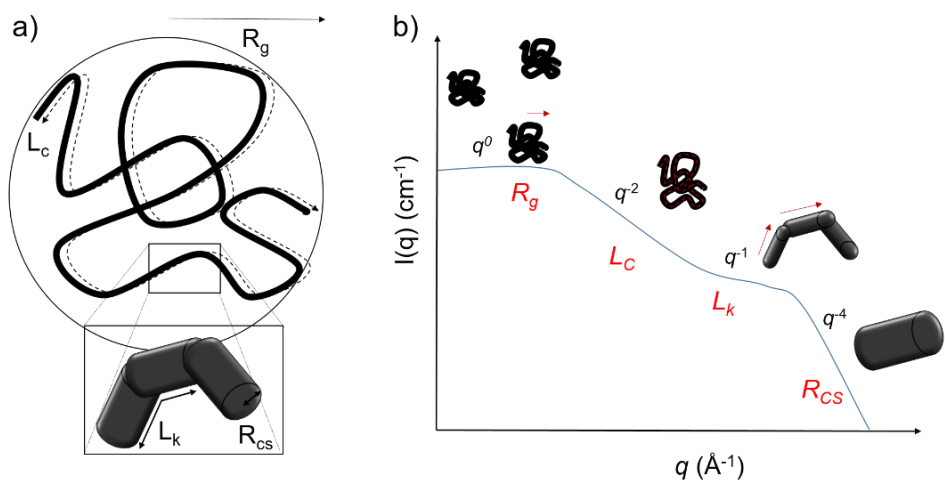


Figure 5.2 (a) Schematic representation of worm-like micelles, with a radius of gyration, R_g , contour length, L_c , Kuhn length, L_k , and cross-sectional cylinder area of R_{cs} . (b) Graphical depiction of a typical scattering profile for wormlike micelles, displaying the q -regions and scalings characteristic to each parameter, R_g , L_c , L_k and R_{cs} .

Ideally wormlike micelles are fit with one form factor model to determine fundamental parameters such as L_c , L_k , and R_{cs} .¹⁸ However, it is not unprecedented for wormlike micelles to be decoupled into two contributions: one describing a semi-flexible chain, giving information about the large scale features of the wormlike micelle, *i.e.* contour length, Kuhn length, and another contribution describing scattering from a cylinder or rigid rod, giving values for cross sectional cylinder radius.^{13,17,18} It has been established in the literature that in the high q -region, scattering intensity is independent of surfactant concentration,¹⁹ as wormlike micelles tend to grow one-dimensionally along their contour length, leaving the cross-sectional cylinder radius unchanged.¹⁷ This means that analysis of the high q -region can be done with single particle scattering functions separate to the semi-flexible chain model used to describe the rest of the dataset at lower q .^{13,18,19}

It was not possible to fit the entire q -range for *trans*-**C₆AzoOC₄E₄** with one model and as described above, two separate models are used to treat the low and high q data.^{13,17,18} Low to mid q data for *trans*-**C₆AzoOC₄E₄** ($q < 0.04 \text{ \AA}^{-1}$) was described well by the flexible elliptical cylinder model. This model provides values for L_c (429.0 $\text{\AA}$) and L_k (333.3 $\text{\AA}$), consistent with the fact that the decays of q^{-2} and q^{-1} , which correspond to these parameters, fall within the q -range fitted. For the higher q -range of $0.04 - 0.09 \text{ \AA}^{-1}$ an elliptical cylinder model was used. This q -range corresponds to the region where the scattering profile decays rapidly due to scattering from the finite cylinder cross-section of the wormlike micelle, and as such, values for R_{sc} ($r_a = 36.0 \text{ \AA}$, $r_b = 43.0 \text{ \AA}$) were obtained from this region. A value of $344.3 \text{ \AA}$ was found for the rigid cylinder length, in very good agreement with the value

attained for L_K . Both the flexible elliptical cylinder and elliptical cylinder model produced similar values for wetness, of 64% and 67% D₂O, respectively.

The scattering profile for *trans*-**C₈AzoOC₄E₄** (1 mmol L⁻¹ in D₂O) displayed a decay of $q^{-1.3}$ in the low q -region (Figure 5.1c) implying that scattering occurs from rod-like objects, with an elliptical cylinder model providing a good fit ($r_a = 33.6$ Å, $r_b = 84.3$ Å, $L = 496.0$ Å, 75% D₂O). The scattering profile of *trans*-**C₈AzoOC₈E₄** (1 mmol L⁻¹ in D₂O) decayed as $q^{-2.5}$ in the low q -region, a value which correlates to rough fractals. A flexible elliptical cylinder model was found to correspond to this data very well, describing dryer aggregates ($r_a = 40.8$ Å, $r_b = 252.0$ Å, $L_K = 460.0$ Å, $L_C = 1246.0$, 64% D₂O). This flexible elliptical cylinder seem very similar to the wormlike micelles found for *trans*-**C₆AzoOC₄E₄** at 25 °C, but the variation in length scales is much less pronounced in the scattering profile for *trans*-**C₈AzoOC₈E₄** than for *trans*-**C₆AzoOC₄E₄** (Figure 5.1b vs. 5.1d). It is likely that the length scales for *trans*-**C₈AzoOC₈E₄** are not as well-separated as those for *trans*-**C₆AzoOC₄E₄**, as the value for the major cylinder radius (252.0 Å) is on the same order of magnitude as the Kuhn length (460.0 Å), meaning that these two length scales will overlap in the mid q -region. As a result, the distinctive regions corresponding to the different wormlike micelle parameters (L_C , L_K , R_{CS}), which were clearly seen in the scattering profile for *trans*-**C₆AzoOC₄E₄**, are not as obvious for *trans*-**C₈AzoOC₈E₄**. The structural parameters obtained here for room temperature measurements will be described in more detail in the next section, in comparison with the scattering profiles for the *trans*-isomers of all four AzoPS at elevated temperatures.

5.3.2 Effect of Temperature on the Self-Assembly Behaviour of AzoPS

Temperature plays a key role in controlling the structure and size of surfactant aggregates, thus the SANS data for AzoPS aggregates in the *trans*-form were measured at one concentration (1 mmol L⁻¹) as a function of temperature (25 - 80 °C for **C₈AzoOC₈E₄** and **C₈AzoOC₄E₄** and due to time constraints only 25 and 40 °C for **C₂AzoOC₄E₄** and **C₆AzoOC₄E₄**). Due to different detector distances being used, some of the higher temperature measurements probe a lower q region than the room temperature measurements, evident from the wider q -range on the scattering profiles.²⁰ All q -scaling and model fitting described below are summarised in Tables 5.2-5.5. A temperature study was not carried out on the *cis*-forms of the AzoPS. The *cis-trans* reverse isomerisation process can proceed thermally and as a result it would be difficult to ensure that the sample remained fully in the *cis*-PSS while at elevated temperatures over the course of a SANS measurement (~60-90 min).

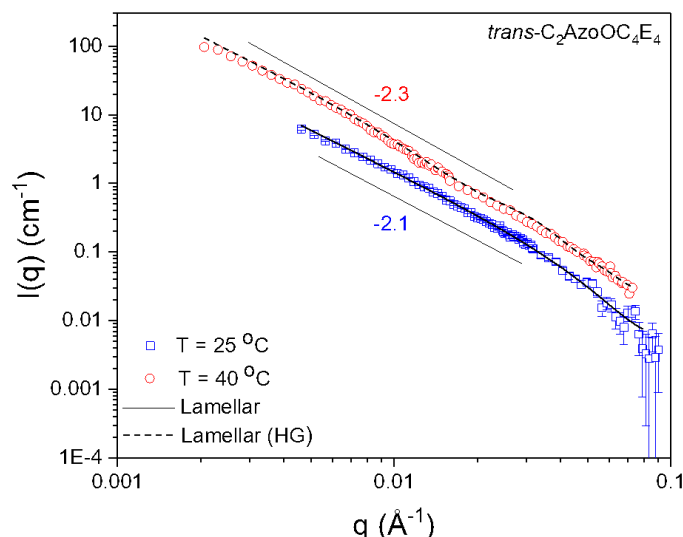


Figure 5.3 SANS data for *trans*-C₂AzoOC₄E₄ at 25 °C (blue) and 40 °C (red). The solid and dashed black lines overlaying the data corresponds to the Lamellar and Lamellar (HG) models, respectively. The straight lines shows decays of -2.3 and -2.1 for comparison.

Figure 5.3 displays the SANS data for *trans*-C₂AzoOC₄E₄ at both 25 and 40 °C. As previously discussed, the scattering profile at 25 °C is described well by the Lamellar model. At 40 °C the low q decay steepens from $q^{-2.1}$ to $q^{-2.3}$, with the most significant deviation from the 25 °C measurement occurring at low q (Figure 5.3). The Lamellar model is no longer adequate to describe the data at 40 °C, but the Lamellar (HG) model fits the scattering profile very well (Figure 5.3). This model assumes the sample is a random lamellar phase of distinct head and tail groups (Figure 5.4). The reason that a model relying on the separate consideration of head and tail groups describes the 40 °C scattering profile best becomes apparent when the values obtained for wetness and layer thickness are examined. At 25 °C a lamellar sheet ($T = 62.2$ Å, 74% D₂O) is obtained, while upon heating to 40 °C a lamellar (HG) sheet of tail thickness 32.3 Å and head thickness 203.0 Å was found. The wetness at 40 °C was 40% D₂O for the tail segment and 98% D₂O for the head segment. Unsurprisingly, solvent permeation increases greatly upon heating, with D₂O molecules partitioning in the hydrophilic tetraethylene glycol head component of the AzoPS over the hydrophobic tail component. This explains the large value for head thickness (203.0 Å) and wetness (98%), with the discrepancy in wetness between head and tail moieties at 40 °C requiring a lamellar model that regards that head and tail components individually.

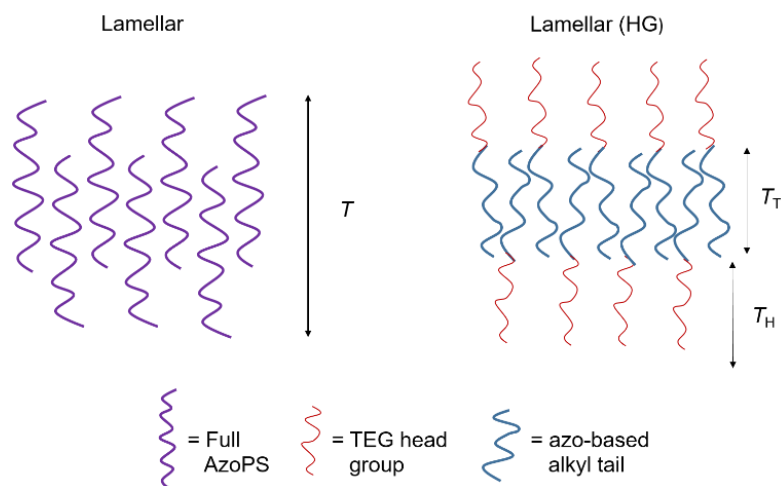


Figure 5.4 Schematic representation of the two lamellar models fitted to *trans*-**C₂AzoC₄E₄** at 25 °C (left, lamellar) and 40 °C (right, lamellar (HG)), respectively. The entire AzoPS molecule is indicated in purple for the lamellar phase, with an overall sheet thickness of T . For clarity, the head/tail components are not shown separately for the lamellar phase, but it is presumed that the polar head groups are oriented outwards towards the solvent. For the lamellar (HG) phase the TEG head group is given in red, with a thickness indicated by T_H and the azobenzene-based alkyl tail is given in blue, with a tail length indicated by T_T .

The value of 32.3 Å obtained for tail thickness of *trans*-**C₂AzoOC₄E₄** at 40 °C corresponds well to the calculated tail length of the molecule (~32.4 Å). This implies that the tail segments of the AzoPS overlap significantly within the lamellar (HG) phase, as depicted in Figure 5.4. The value of 62.2 Å obtained for lamellar sheet thickness at 25 °C is just under double the calculated tail length of the molecule, excluding the length contribution from the head group. From this it can be concluded that there is also a significant overlap between AzoPS molecules at 25 °C, but without the large degree of head group solvation seen at 40 °C. A full description and the references used for the calculation of the length of the hydrophobic tail are presented in the Appendix, Table A.5.1. The length of the polar head group cannot be estimated as tetraethylene glycol can adopt several conformations in aqueous solution, with an overall length that is likely to depend on temperature.^{21–24} Consequently, only a qualitative discussion about the size of the hydrophilic head-group will be possible. This appears to be conventional for studies which involve the discussion of the size and conformation of neutral ethylene glycol head-groups.²⁵

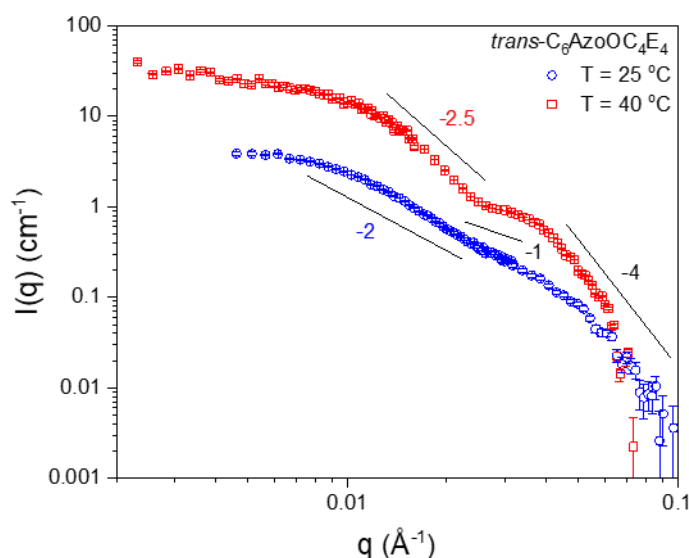


Figure 5.5 SANS data for *trans*-**C₆AzoOC₄E₄** at 25 °C (blue) and 40 °C (red). The intensity at 40 °C has been offset by a factor of 10, for clarity. Straight lines show -1, -2, -2.5 and -4 decays for comparison.

Figure 5.5 presents the SANS data for *trans*-**C₆AzoOC₄E₄**, at both 25 and 40 °C. This AzoPS at 25 °C was described well by decoupling the scattering profile, which was characteristic of wormlike micelles, into contributions from a flexible elliptical cylinder and an elliptical cylinder. At first glance the scattering profile at 40 °C also appears characteristic of wormlike micelles, as there are clear, well-separated length scales, potentially corresponding to the different parameters of the wormlike micelle (L_C , L_K , R_{CS} etc.). In fact, the q^{-1} decay at mid- q , indicating scattering from rigid rods, is significantly more pronounced at 40 °C compared to 25 °C. There is also an increased steepness of decay from q^{-2} to $q^{-2.5}$ in the region which generally describes the self-avoiding random walk of the wormlike micelles.¹³ However, due to these more dramatic slopes and plateaus it was not possible to adequately fit the scattering profile of *trans*-**C₆AzoOC₄E₄** at 40 °C, either with one model or via decoupling into high and low q contributions. Consequently, the structure of *trans*-**C₆AzoOC₄E₄** at 40 °C is as of yet undetermined.

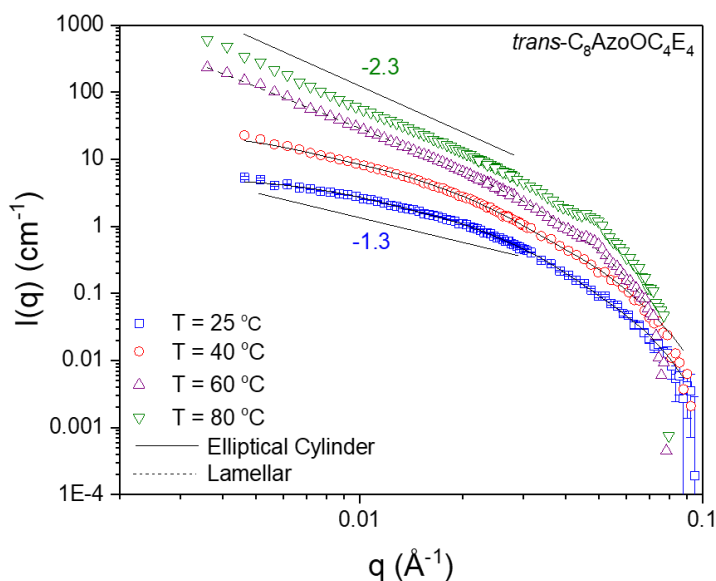


Figure 5.6 SANS data for *trans*-C₈AzoOC₄E₄ at 25 °C (blue), 40 °C (red) 60 °C (purple) and 80 °C (green). The scattering profiles at each temperature have been offset for clarity. The solid and dashed black lines overlaying the data corresponds to the Elliptical Cylinder and Lamellar models, respectively. Straight lines show decays of -1.3, -1.6, -2.2 and -2.3 for comparison.

The scattering profiles for *trans*-C₈AzoOC₄E₄ obtained at 25-80 °C are presented in Figure 5.6. The scattering profile for the room temperature measurement, previously discussed in Section 5.3.1, is described well by an elliptical cylinder model ($r_a = 32.3$ Å, $r_b = 84.3$ Å, $L = 542.0$ Å, 75% D₂O). Upon heating to 40 °C, very little change is seen in the scattering profile with an elliptical cylinder model still describing the data well ($r_a = 32.0$ Å, $r_b = 110.8$ Å, $L = 818.7$ Å, 74% D₂O). Upon heating to 60 °C there is a flattening out of the scattering profile, with a concomitant change in slope to $q^{-2.2}$. A small bump at $q = \sim 0.005$ Å⁻¹ also appeared, which was not observed at lower temperatures. Fitting in this case was done with the Lamellar model ($T = 67.5$ Å, 79% D₂O). The increase in wetness is consistent with the general observation that solvent penetration increases with increased temperature. The scattering profile for *trans*-C₈AzoOC₄E₄ at 80 °C is quite similar to that seen for 60 °C, although the bump at $q = \sim 0.005$ Å⁻¹ is much more pronounced. As a result of this bump, and the slight increase in slope in the low q -region to $q^{-2.3}$, this scattering profile could not be fit with any form factor alone and so remains unassigned. It is quite likely that as the temperature increases inter-particle interactions become more pronounced, manifesting as bumps in the scattering profile. As a result, the form factor model also requires a structure factor contribution to accurately describe the scattering profile. However, it is not currently possible to combine the Lamellar model with a structure factor model in SASview.

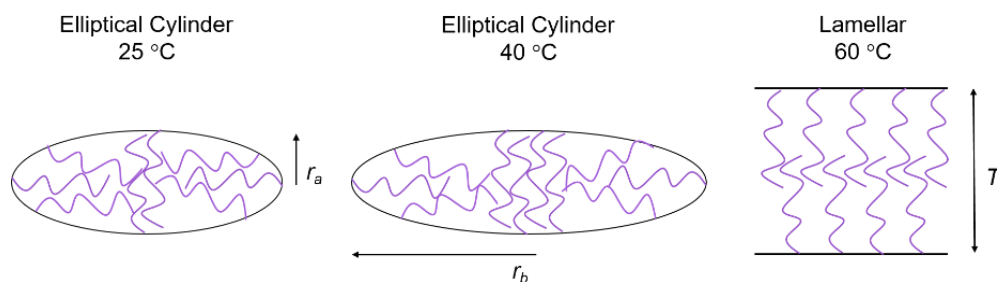


Figure 5.7 Schematic representations of the structures formed by *trans*-**C₈AzoOC₄E₄** at 25-60 °C. At both 25 °C and 40 °C elliptical cylinders are seen, while at 60 °C the AzoPS self-assembles into a lamellar phase. The AzoPS molecule is represented by a purple shape, self-assembled into either an elliptical cylinder or lamellar sheet. For clarity, the head/tail components are not shown separately, but it is presumed that the hydrophilic head groups are oriented outwards towards the solvent, with the hydrophobic azobenzene-based alkyl tail forming the inner core of the structures.

From the above it can be concluded that *trans*-**C₈AzoOC₄E₄** consists of elliptical cylinders at room temperature, the eccentricity and length of which increases with increasing temperature, ultimately forming lamellar sheets at 60 °C. Lamellar sheets can be thought of as very long elliptical cylinders with such a high eccentricity that it is more favourable for the molecules to form opposing layers than maintain the high curvature that would be required to connect the layers (Figure 5.7). The values obtained from SANS correlate well with the calculated length of the tail of the *trans*-**C₈AzoOC₄E₄** molecule (41.6 Å). For the elliptical cylinders the minor axis (32.3 or 32.0 Å, depending on the temperature) would be expected to consist of overlapping AzoPS molecules, while the major axis (84.3 or 110.8 Å) is significantly longer to compensate for the overlap along the minor axis (Figure 5.7). The lamellar sheets observed at 60 °C have a thickness of 67.5 Å, suggesting a large degree of overlap between the AzoPS molecules, much like that found for **C₂AzoOC₄E₄** at 25 °C.

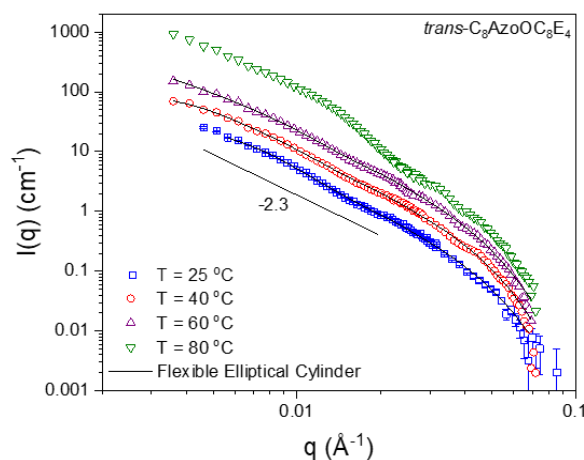


Figure 5.8 SANS data for *trans*-**C₈AzoOC₈E₄** at 25 °C (blue), 40 °C (red) 60 °C (purple) and 80 °C (green). The scattering profiles at each temperature have been offset for clarity. The black lines overlaying the data corresponds to the Flexible Elliptical Cylinder model. A straight lines show a decay of -2.3 for comparison.

The scattering profiles for *trans*-**C₈AzoOC₈E₄** obtained at 25-80 °C are presented in Figure 5.8. It is clear that in comparison to 25 °C, heating to 40 and 60 °C leads to very little change in the scattering profile. For all three temperatures, the data is best fit by the flexible elliptical cylinder model. Upon increasing the temperature to 40 and 60 °C, an increase in all parameters is observed, the values of which can be found in Table 5.2. This increase in aggregate dimensions is in agreement with the increase in wetness, as larger spaces between AzoPS molecules allow a greater degree of solvent permeation. There is a striking difference in the scattering profile of 80 °C compared to the other three, with a sharp change in slope observed in the mid q -region. However, no form factor model could describe this scattering profile well.

Table 5.1 Dimensions and wetness obtained for *trans*-**C₈AzoOC₈E₄** at 25, 40 and 60 °C from the Elliptical Cylinder fit to the scattering profiles. r_a and r_b are the minor and major cylinder radii, respectively, L_C is the contour length, L_K is the Kuhn length and the percentage of D₂O gives the degree of wetness.

Temperature (°C)	r_a (Å)	r_b (Å)	L_C (Å)	L_K (Å)	D ₂ O (%)
25	40.8	252.0	1246.2	406.0	65
40	41.6	262.0	1724.0	626.4	71
60	42.3	262.3	7473.0	747.2.	72

In general, it appears that temperature plays an important role in AzoPS self-assembly, with *trans*-**C₈AzoOC₄E₄** displaying the most striking changes in micellar shape and structure upon heating. For all the AzoPS which could be fitted with form factor models, an increase in solvent penetration was seen upon an increase in temperature, along with an increase in aggregate dimensions (thickness, length, radius, *etc*). In the next section, the impact of photoisomerisation on the self-assembly process for AzoPS will be presented, followed by a general discussion of the SANS results across all temperatures and isomers.

Table 5.2 Structural parameters obtained from SANS data for *trans*-C₂AzoOC₄E4 in D₂O (1.0×10^{-3} mol L⁻¹) at 25 °C and 40 °C and *cis*-C₂AzoOC₄E4 in D₂O (1×10^{-3} mol L⁻¹) at 25 °C: α is the scattering power of the defined q region. T_{sheet} is sheet thickness, obtained from the best fit to the data using the Lamellar Model, L_T and L_H are the head and tail lengths obtained from the best fit to the data using the Lamellar (HG) model in SasView. X_{sol} is the calculated solvent fraction in the aggregates, ϕ_{dry} is the theoretical volume mass of dry material each fit represents and χ^2 is the goodness-of-fit parameter.

Isomer	Temp. (°C)	q^α ($q < 0.04 \text{ \AA}^{-1}$)	Model	T_{sheet} (Å)	L_T (Å)	L_H (Å)	SLD_{agg} ($\times 10^{-6} \text{ \AA}^{-2}$)	Scale	X_{sol}	ϕ_{dry}	χ^2
<i>trans</i>	25	-2.1	Lamellar	62.2	-	-	5.0	0.0065	0.74	0.0017	1.48
<i>trans</i>	40	-2.3	Lamellar (HG)	-	32.3	203	3.3 (tail) 6.2 (head)	0.0032	0.4 (tail) 0.98 (head)	0.0018	1.37
<i>cis</i>	25	-2.5	-	-	-	-	-	-	-	-	-

Table 5.3 Structural parameters obtained from SANS data for *trans*-**C₆AzoOC₄E₄** in D₂O (1×10^{-3} mol L⁻¹) at 25 °C and 40 °C and *cis*-**C₆AzoOC₄E₄** in D₂O (1×10^{-3} mol L⁻¹) at 25 °C: α is the scattering power of the defined q region. L_c , L_k , r_a and r_b are the cylinder contour length, Kuhn length and radii of the short and long cylinder axes respectively, obtained from the best fit to the data using the Elliptical Cylinder Model in SasView. L , r_a and r_b are the cylinder length and radii of the short and long axes respectively, obtained from the best fit to the data using the Elliptical Cylinder Model in SasView. X_{sol} is the calculated solvent fraction in the aggregates, ϕ_{dry} is the theoretical volume mass of dry material each fit represents and χ^2 is the goodness-of-fit parameter.

Isomer	Temp. (°C)	q^α ($q < 0.04 \text{ \AA}^{-1}$)	Model	r_a (Å)	r_b (Å)	L_c (Å)	L_k (Å)	L (Å)	SLD_{agg} ($\times 10^{-6} \text{ \AA}^{-2}$)	Scale	X_{sol}	ϕ_{dry}	χ^2
<i>trans</i>	25	-2.3	Flexible Elliptical Cylinder ($q = 0.0046 - 0.04$)	-	-	429	333.3	-	4.4	*	0.64	*	1.28
			Elliptical Cylinder ($q = 0.04 - 0.09$)	36	43	-	-	334.3	4.6	*	0.67	*	0.94
<i>trans</i>	40	-3	-	-	-	-	-	-	-	-	-	-	-
<i>cis</i>	20	-2.5	Flexible Elliptical Cylinder ($q = 0.0045 - 0.022$)	-	-	-	-	-	-	-	-	-	-
			Elliptical Cylinder ($q = 0.035 - 0.09$)	39.7	39.8	-	-	347.3	3.9	0.004	0.54	0.0018	0.65

*indicates where scale and ϕ_{dry} cannot be reported as being representative of the theoretical volume mass of dry material for the entire sample, due to the q -range being fitted by two different models

Table 5.4 Structural parameters obtained from SANS data for *trans*-**C₈AzoOC₄E₄** in D₂O ($1. \times 10^{-3}$ mol L⁻¹) as a function of temperature and *cis*-**C₈AzoOC₄E₄** in D₂O (1×10^{-3} mol L⁻¹): α is the scattering power of the defined q region. L , r_a and r_b are the cylinder length and radii of the short and long axes respectively, obtained from the best fit to the data using the Elliptical Cylinder Model in SasView and T_{sheet} is sheet thickness, obtained from the best fit to the data using the Lamellar Model in SasView. X_{sol} is the calculated solvent fraction in the aggregates, ϕ_{dry} is the theoretical volume mass of dry material each fit represents and χ^2 is the goodness-of-fit parameter.

Isomer	Temp. (°C)	q^α ($q < 0.04 \text{ \AA}^{-1}$)	Model	r_a (Å)	r_b (Å)	L (Å)	T (Å)	SLD_{agg} ($\times 10^{-6} \text{ \AA}^{-2}$)	Scale	X_{sol}	ϕ_{dry}	χ^2
<i>trans</i>	25	-1.3	Elliptical Cylinder	32.3	84.3	524.2	-	5.0	0.0068	0.75	0.0018	1.48
<i>trans</i>	40	-1.6	Elliptical Cylinder	32	110.8	818.7	-	4.9	0.0064	0.74	0.0017	1.85
<i>trans</i>	60	-2.2	Lamellar	-	-	-	67.5	5.2	0.0085	0.79	0.0017	6.83
<i>trans</i>	80	-2.3	-	-	-	-	-	-	-	-	-	-
<i>cis</i>	25	-2.2	Cylinder ($0.035 \text{ \AA}^{-1} < q < 0.08 \text{ \AA}^{-1}$)	42.2	42.2	257.1	-	3.5	*	0.40	*	1.60

Table 5.5 Structural parameters obtained from SANS data for *trans*-**C₈AzoOC₈E₄** in D₂O (1.0×10^{-3} mol L⁻¹) as a function of temperature and *cis*-**C₈AzoOC₈E₄**: α is the scattering power of the defined q region. L_c , L_k , r_a and r_b are the cylinder counter length, Kuhn length and radii of the short and long axes respectively, obtained from the best fit to the data using the Elliptical Cylinder Model in SasView. X_{sol} is the calculated solvent fraction in the aggregates, ϕ_{dry} is the theoretical volume mass of dry material each fit represents and χ^2 is the goodness-of-fit parameter.

Isomer	Temp. (°C)	q^α ($q < 0.04 \text{ \AA}^{-1}$)	Model	r_a (Å)	r_b (Å)	L_c (Å)	L_K (Å)	SLD_{agg} ($\times 10^{-6} \text{ \AA}^{-2}$)	Scale	X_{sol}	ϕ_{dry}	χ^2
<i>trans</i>	25	-2.5	Flexible Elliptical Cylinder	40.8	252.0	1246.2	406	4.40	0.0050	0.65	0.0017	2.98
<i>trans</i>	40	-2.3	Flexible Elliptical Cylinder	41.6	262.0	1724	626.4	4.74	0.0057	0.71	0.0017	5.5
<i>trans</i>	60	-2.3	Flexible Elliptical Cylinder	42.3	262.3	7473.4	747.2	4.75	0.0058	0.72	0.0017	3.81
<i>trans</i>	80	-2.6	-	-	-	-	-	-	-	-	-	-
<i>cis</i>	25	-4	-	-	-	-	-	-	-	-	-	-

5.3.3 Effect of Photoisomerisation on the Self-Assembly Behaviour of AzoPS

The effect of photoisomerisation on the nanoscale organisation of the four AzoPS was investigated by analysing four *cis*-AzoPS solutions in D₂O (1 mmol L⁻¹) at 25 °C using SANS. The scattering profiles for these measurements, in comparison with the *trans*-from, are shown in Figure 5.9. All *q*-scaling and model fitting described below are summarised in Tables 5.2-5.5. As photoisomerisation leads to a substantial change in both the geometry and hydrophilic-hydrophobic balance of the AzoPS molecule,²⁶ it is expected to have a significant impact on the shape and structure of the self-assembled aggregates. The SANS observation window for the *cis* samples is slightly wider than that of the *trans*, due to different detector distances being used during the measurement process.²⁰

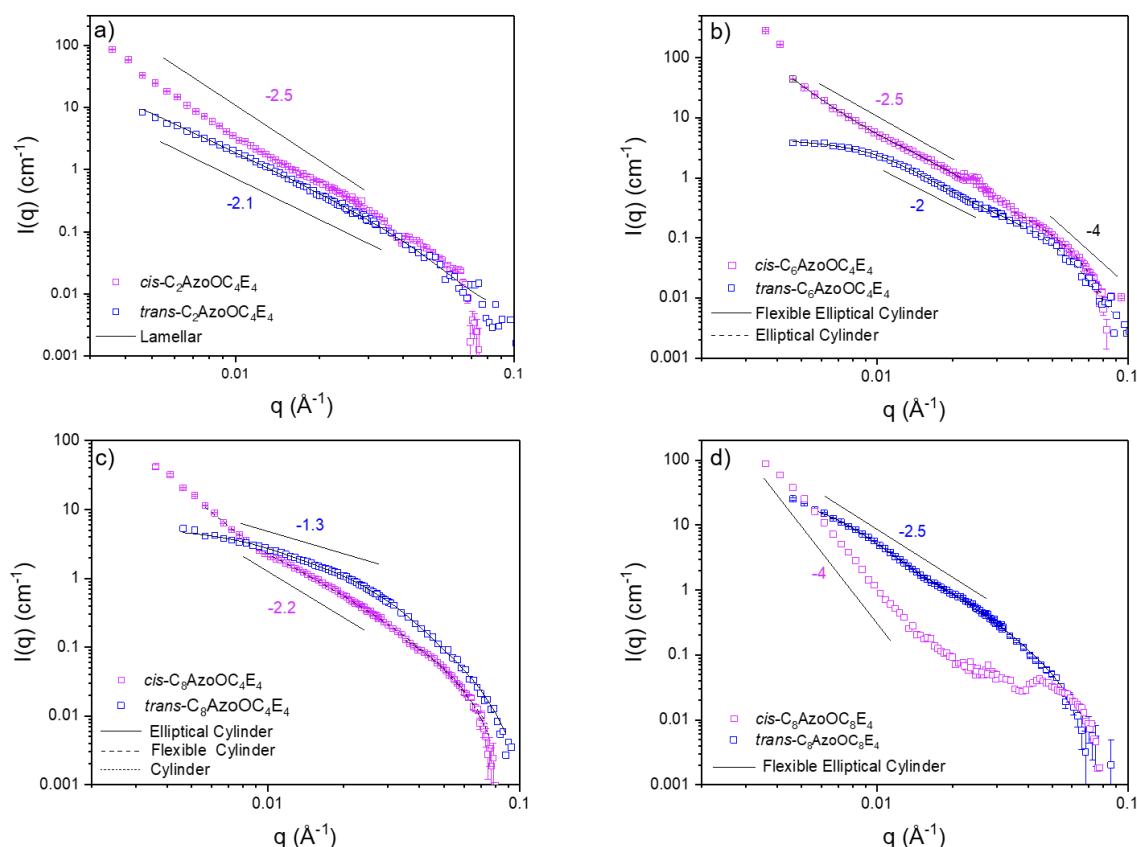


Figure 5.9 SANS data for the *trans*- (blue) and *cis*-isomers (pink) of (a) **C₂AzoOC₄E₄**, (b) **C₆AzoOC₄E₄**, (c) **C₈AzoOC₄E₄** and (d) **C₈AzoOC₈E₄** in D₂O (1 mmol L⁻¹) at 25 °C. In the case of **C₂AzoOC₄E₄** and **C₆AzoOC₄E₄**, the *cis*-isomer is offset by a factor of 2.5 for clarity. Straight lines representing the scattering decay are given for comparison. The black lines overlaying the SANS data correspond to the fits to the form factor models described in-text.

Figure 5.9a displays scattering profiles for *cis*-**C₂AzoOC₄E₄** at 25 °C, with the profile for *trans*-**C₂AzoOC₄E₄** at the same temperature given for comparison. While *trans*-**C₂AzoOC₄E₄** could be described very well by a lamellar model it was not possible to fit *cis*-

C₂AzoOC₄E₄ using any form factor model. The mid q -region for the *cis*- and *trans*-forms appear quite similar in terms of steepness of decay and scattering intensity, with the most striking differences between the two scattering profiles being the bumps at $q = 0.003 - 0.004 \text{ \AA}^{-1}$ and the increased upturn at low q , both observed for the *cis*-form. The decay of $q^{-2.5}$ seen for the *cis*-form would typically be assigned to scatter from a rough fractal, but no fractal model described the data well. It is possible that this $q^{-2.5}$ decay is actually closer to a q^{-2} decay which has been distorted by the increase in scattering intensity at low q . An upturn in intensity at low q and bumps at mid q are often indicative of attractive inter-particle interactions, such as aggregation.^{27–29} Such inter-particle interactions need to be taken into account by multiplying the particle form factor by a structure factor model. However, in SASview, it is not currently possible to combine structure factor with a lamellar model, so it could not be investigated if the observed *cis*-**C₂AzoOC₄E₄** scattering profile observed here is a lamellar structure, similar to the *trans*-form, but with increased structure factor due to inter-sheet interactions. One way in which to determine if this hypothesis is correct would be to monitor the growth of inter-particle interactions within the scattering profile as a function of *cis*-**C₂AzoOC₄E₄** concentration. If the bumps at mid- q were to become more pronounced upon increasing concentration, this would be strong evidence for their origin to be inter-micellar interactions. However, at present, the scattering profile seen for the *cis*-form of **C₂AzoOC₄E₄** cannot be unequivocally assigned.

Figure 5.9b shows the scattering profiles for both *cis*- and *trans*-**C₆AzoOC₄E₄**. In section 5.3.1 *trans*-**C₆AzoOC₄E₄** was found to consist of wormlike micelles and its scattering profile was fitted through decoupling into a flexible elliptical cylinder component and an elliptical cylinder component. The shape and intensity of the curves for *cis*- and *trans*-**C₆AzoOC₄E₄** are quite similar, apart from the upturn at low q and bump at mid q for the *cis*-isomer, implying that this scattering profile may also be a result of wormlike micelles. A flexible elliptical cylinder model ($0.004 < q < 0.02 \text{ \AA}^{-1}$) and elliptical cylinder model ($q > 0.03 \text{ \AA}^{-1}$) were fitted to the *cis*-**C₆AzoOC₄E₄** scattering profile, neglecting the upturn at low q and bump at mid q . As mentioned previously, an increase in scattering intensity at low q and presence of bumps at mid q are indicative of attractive inter-particle interactions, which need to be taken into account by multiplying the particle form factor by a structure factor.^{18,27–29} However, the flexible elliptical cylinder model is valid for dilute solutions only, and does not allow for combination with structure factors.^{17,18} Consequently, values for L_C , L_K , etc. taken from this flexible elliptical cylinder fit are not accurate unless inter-particle interactions are taken into account *via* inclusion of a structure factor.^{13,17,18} As such, none of the parameters

taken from this fit are reported. The fitting of a flexible cylinder model in this case is merely to highlight that it is likely that *cis*-**C₆AzoOC₄E₄** also forms wormlike micelles. Future work will focus on developing a method to account for inter-particle interactions in the scattering profiles of wormlike micelles.

At high q , however, where the scattering decays as q^{-4} due to the finite cylindrical cross section of the wormlike micelle, the scattering intensity can be considered as independent of sample concentration,^{19,17} with inter-micelle interactions also being highly screened on these local length scales.¹³ As a result, it is possible to extract parameters for the rigid cylinder segments of the wormlike micelle from the fit of an elliptical cylinder model to this region. It was found that upon photoisomerisation, the elliptical cylinder ($r_a = 36.0$ Å, $r_b = 43.0$ Å, $L = 334.3$ Å, 74% D₂O) found for *trans*-**C₆AzoOC₄E₄** changed to an almost spherical cylinder ($r_a = 39.7$ Å, $r_b = 39.8$ Å, $L = 347.3$ Å, 61% D₂O) upon photoisomerisation. This can only be considered as a preliminary analysis, however, due to the incomplete fitting of the scattering profile.

Figure 5.9c shows the scattering profile for *cis*-**C₈AzoOC₄E₄** and *trans*-**C₈AzoOC₄E₄** at 25 °C. In the low q region ($q > 0.01$ Å⁻¹), the scattering profiles are quite similar. However, like the two other *cis*-isomers already discussed, there is a significant increase in intensity at low q . This makes fitting the data in this region extremely difficult, with form factor models unable to take the sharp increase in intensity into account. A flexible cylinder model was the only form factor to reasonably describe the scattering profile for the *cis*-isomer, neglecting the upturn at low q ($q < 0.005$ Å⁻¹). This implies, that similarly to *trans*-**C₆AzoOC₄E₄** and *trans*-**C₈AzoOC₈E₄**, *cis*-**C₈AzoOC₄E₄** is quite likely to consist of wormlike micelles. However the values obtained from this flexible cylinder fit did not make good physical sense, in line with the general observation that neglecting inter-particle interactions leads to unreliable physical parameters.^{13,17,30,31} Due to this, the scattering profile was decoupled into two contributions, with a cylinder model used to fit the high q -region, $0.035 < q < 0.08$ Å⁻¹, ($R = 42.2$ Å, $L = 257$ Å, 40% D₂O). These values should be considered as preliminary however, as it cannot be unambiguously stated that *cis*-**C₈AzoOC₄E₄** forms wormlike micelles due to the incomplete fitting of the low q -region. Further studies using additional techniques, such as cryo-TEM, are required to provide insight into the structure of these aggregates.

Figure 5.9d displays the scattering profile for both *cis*-**C₈AzoOC₈E₄** and *trans*-**C₈AzoOC₈E₄** at 25 °C. There is a clear loss of scattering intensity upon photoisomerisation, with a concomitant decrease in the slope of the scattering decay at low q from $q^{-2.5}$ to q^{-4} . This

q^{-4} decay is indicative of scattering from the sharp interfaces of smooth fractals. It should be noted that unlike the other AzoPS which achieve a solution of 84-90% *cis*-isomers in the PSS state upon photoisomerisation, **C₈AzoOC₈E₄** consists of only 61% *cis*-isomers upon irradiation with UV light. It is likely then that some sort of mixed fractal phase is formed for *cis*-**C₈AzoOC₈E₄**, with neither *cis*- nor *trans*-**C₈AzoOC₈E₄** being present in a significant enough proportion to dominate a particular phase. At the present moment, the scattering profile for *cis*-**C₈AzoOC₈E₄** cannot be assigned.

In general, the scattering profiles of the *cis*-isomers were more difficult to fit than those of the *trans*-isomers, with fittings to form factors either being not possible (**C₂AzoOC₄E₄**, **C₈AzoOC₈E₄**) or needing further refinement (**C₆AzoOC₄E₄**, **C₈AzoOC₄E₄**). This is attributed to photoisomeration to a solution of 100% *cis*-isomers not being possible. It seems that the more mixed the sample in terms of *cis*- and *trans*-isomers, the more difficult it is to assign the scattering profiles of the self-assembled aggregates. This demonstrates that the photophysical properties of the individual AzoPS have a significant impact on the large-scale self-assembly behaviour.

5.3.4 General Discussion on the Self-Assembly Behaviour of AzoPS

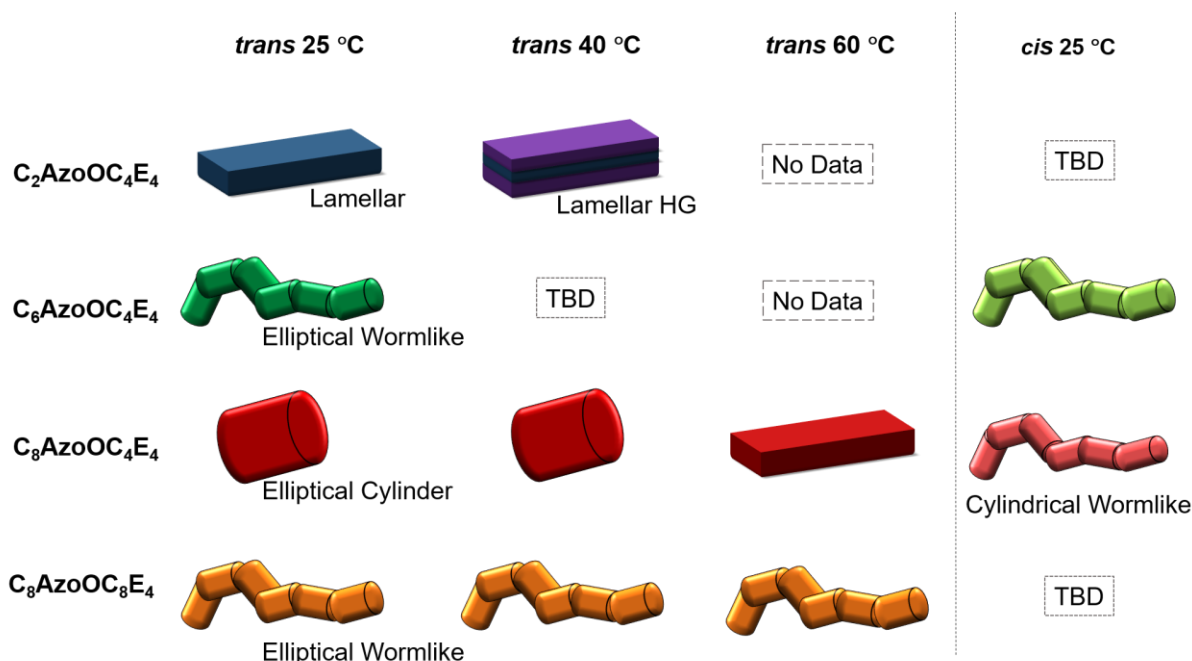


Figure 5.10 Pictorial summary of the self-assembled structures adopted by each AzoPS as a function of both temperature and isomeric form, as determined using SANS. TBD indicates where the scattering profiles have yet to be determined.

It is clear that the self-assembly process varies with changes in the molecular structure of the AzoPS. Figure 5.10 summarises of the self-assembled structures formed for each

AzoPS, as a function of both isomeric form and temperature. For AzoPS of the same spacer length, but increasing tail lengths (**C₂AzoOC₄E₄**, **C₆AzoOC₄E₄**, **C₈AzoOC₄E₄**) there is a transition from lamellar to cylindrical phases. Lamellar phases are typically seen for surfactants where the tail length is similar in length to the head group, in this case with **C₂AzoOC₄E₄** (tail = 32.3 Å) presenting a lamellar phase.³² Upon increasing the tail length to 38.5 Å (**C₆AzoOC₄E₄**), it is more favourable for the system to form elliptical wormlike micelles, albeit quite rigid ones ($L_C = 429.0$ Å, $L_K = 333.3$ Å). A further increase in tail length to 41.6 Å (**C₈AzoOC₄E₄**) leads to elliptical cylinders, with a length similar to the contour length of the **C₆AzoOC₄E₄** elliptical wormlike micelles (496.0 Å).

For **C₈AzoOC₈E₄**, an AzoPS of the same pendant tail length but differing spacer length to **C₈AzoOC₄E₄**, elliptical wormlike micelles are seen once again, this time with longer radii than any of the previous (40.8 Å and 252.0 Å). This is in agreement with the increased tail length of this AzoPS (47.8 Å). The difference between forming elliptical wormlike micelles vs. elliptical cylinders is very slight, varying with a small change in the number of carbon atoms in the tail or spacer. This is highlighted by the fact that wormlike micelles are formed by **C₆AzoOC₄E₄** and **C₈AzoOC₈E₄** in the *trans*-form, but not by *trans*-**C₈AzoOC₄E₄**, while the *cis*-form of **C₈AzoOC₄E₄** does form wormlike micelles. Evidently, the formation of wormlike micelles is highly dependent on the interplay of hydrophobicity and molecular structure. In general, it was more favourable for the *trans*-AzoPS to self-assemble into elliptical cylinder/wormlike phases, while the *cis*-AzoPS consisted of circular cylinders/wormlike phases. Clearly, the change in molecular shape from linear to bent upon photoisomerisation alters the packing behaviour within the self-assembled structure, with a subsequent impact on the geometry (circular vs. elliptical) of the structure formed.

For all four AzoPS, a different scattering profile was seen for the *cis*-form than the *trans*-form, meaning that these AzoPS form ‘smart’ micelles, which change their shape and structure in response to light illumination. The most striking difference between *cis*- and *trans*-forms was observed for **C₂AzoOC₄E₄** and **C₈AzoOCE₄**, the scattering profiles of which could not be fit for the *cis*-form of either surfactant. The formation of wormlike micelles (*trans*-**C₆AzoOC₄E₄**, *trans*-**C₈AzoOC₈E₄**) is interesting, in particular for **C₈AzoOC₈E₄**, where the wormlike micelle structure appears to be completely lost upon photoisomerisation. Smart wormlike micelles, which respond to stimuli such as pH, temperature and light, are a promising area of study,^{13,16} and have been used in many applications, such as the oil industry, biomedicine, rheology control and cleaning processes.^{16,33–35} However, most light-responsive wormlike micelles to date are complex formulations of binary or ternary

systems.³⁶⁻³⁹ To the best of my knowledge, there is only one report in the literature of a single component light-responsive wormlike micelle system, namely a gemini azobenzene photosurfactant, sodium-2,20-(diazene-1,2-diylbis(4,1-phenylene))-didodecanoate.⁴⁰ Photoisomerisation in the case of this gemini AzoPS, could switch ‘on’ or ‘off’ the wormlike micelle structure, with this structural change varying macroscopic properties of the system such as viscosity and elasticity. In the present work, **C₈AzoOC₈E₄**, switches between ‘on’ and ‘off’ states for the wormlike micelle structure upon photoisomerisation, with **C₆AzoOC₄E₄** also having obvious differences between the scattering profiles of *cis*- and *trans*-forms. It will be interesting to probe the rheological and viscoelastic behaviour of these AzoPS, to ascertain if these light-responsive structural changes have further effects on the macroscopic AzoPS properties.

5.4 Conclusions and Outlook

It is evident that molecular structure plays a key role in the self-assembly process for azobenzene photosurfactants, with increasing tail length leading to an increase in the curvature of the self-assembled system (*i.e* from lamellar to cylindrical/wormlike phases), and the *trans*-forms forming more distorted elliptical phases than the *cis*-forms. Each of the four AzoPS presented in this chapter demonstrate different self-assembly behaviour, with scattering profiles which changed as a function of both temperature and isomeric form. The change in scattering behaviour between *cis*- and *trans*-forms is very intriguing as it presents the possibility to use AzoPS as photoresponsive switches, with the *trans*- and *cis*-forms representing ‘on’ and ‘off’ states for the system. This means these AzoPS have the potential to be used in photo-responsive applications such as template synthesis, micellar catalysis and rheology control.^{1,2,4-7}

Temperature studies were not performed on the *cis*-isomers due to the possibility of reverse isomerisation to the more thermodynamically stable *trans*-form along a thermal pathway. However, should an experimental set up which allows *in situ* UV illumination of the sample during the SANS measurement be developed, it could become possible to measure the scattering from the self-assembled structures of the *cis*-PSS at a variety of temperatures. *in situ* illumination of the AzoPS sample would also allow the transition between the *trans* and *cis* self-assembled structures to be monitored in real-time. In an ideal world this could be combined with *in situ* UV-Vis measurements to ascertain the quantity of *cis*-isomers in solution and relate this to the changes in the scattering profile. In the future, work will also

focus on extending the temperature range to include more elevated temperatures for the *trans*-forms of **C₂AzoOC₄E₄** and **C₆AzoOC₄E₄**.

In future work, cryo-TEM will be employed to allow the self-assembled structures of the AzoPS to be visualised. This would be particularly useful for **C₂AzoOC₄E₄** to establish if the lamellar sheets formed are instead large vesicles, and for **C₆AzoOC₄E₄** and **C₈AzoOC₈E₄**, to directly visualise the wormlike micelles. Cryo-TEM will also allow the degree of branching (if any) within the wormlike micelles to be determined, which is difficult to determine from SANS. Similarly, cryo-TEM could provide some insights into the self-assembled structures adopted by the *cis*-AzoPS solutions and inform future form factor choices. Future work will also involve concentration studies, to monitor the growth of inter-particle interactions upon increased AzoPS concentration. This will provide a basis for refining the lamellar and flexible elliptical cylinder form factor models to include structure factor contributions. Studies at higher concentrations will undoubtedly rely on SAXS in complement to SANS studies. SAXS will allow any long range order within the system, such as LLC phases, to be revealed. AzoPS systems which form LLC phases would theoretically have the ability to form photo-deformable templates, opening up an avenue to create mesoporous materials with a well-defined and tunable internal porosity.

In short, a fascinating variety of self-assembly behaviour was observed here for these four AzoPS systems. This work highlights the sensitivity of the self-assembly process to minor changes in temperature, molecular shape and hydrophilicity within the system. The array of different *trans*-isomer structures found, from wormlike micelles to lamellar sheets, and loss of such structures upon photoisomerisation, means that these AzoPS systems have a promising future, with potential developments in many directions.

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Chapter Six

Probing Aggregation-Induced Emission in Micellar Media

6.1 Introduction

Most π -conjugated organic dyes show a tendency to aggregate through π - π stacking interactions at high concentrations or in condensed media leading to quenching of their fluorescence.^{1–4} However, in 2001, Tang and co-workers pioneered a new family of π -conjugated chromophores based on the silole or tetraphenylethene motif, for whom aggregation “switches-on” fluorescence from the dormant fluorophore.^{1,5,6} Since this initial report, additional structures exhibiting aggregation-induced emission have been identified and have attracted considerable attention for solid-state light-emitting displays, solar energy conversion and optical storage.^{7–9} The AIE phenomenon is believed to be due to the restriction of intramolecular rotations (RIR) about the core upon aggregation, which switches off competing non-radiative mechanisms for energy dissipation, leading to enhanced rates of radiative relaxation.⁸ However, no solid experimental evidence exists to support this claim to date.

Experimental confirmation of the RIR mechanism can only be obtained through detailed investigation of the “switch-on” of AIE as a function of the intermolecular packing distance of the AIEgen and correlation of this response to the molecular structure. Micellar systems prepared from well-characterised surfactants (*e.g.* sodium dodecyl sulfate, SDS) could provide a suitably benign host environment to investigate this phenomenon. Guan *et al.* recently reported an AIE-active surfactant (TPE-SDS, Figure 6.1) based on SDS with a TPE core.¹⁰ The formation of pure micelles of TPE-SDS in water resulted in AIE, enabling direct visualisation of the micellisation process for the first time. Surface tension, conductivity and fluorescence intensity measurements confirmed micelle formation, with a CMC of $\sim 30 \mu\text{mol L}^{-1}$. Preliminary studies on the effect of intermolecular packing of TPE-SDS on the AIE response were performed in oil-in-water microemulsion droplets (MEDs) of varying size.¹⁰ As expected, as the MED size increased the fluorescence intensity decreased, due to a presumed increase of the intermolecular packing distance. Theoretical calculations supported the RIR mechanism to some extent, but relied on several approximations regarding the local intramolecular environment. We hypothesised that an improved understanding of the intermolecular packing environment, and thus the AIE mechanism, could be obtained through “dilution” of the AIE-surfactant in micelles of anionic SDS surfactants, coupled with an analysis of the internal micellar environment using SANS.

The aim of this chapter is to undertake a structure-activity study to determine if SANS can be used to determine the packing behaviour of TPE-SDS molecules in mixed surfactant micelles, and to relate this packing to the occurrence of AIE. SANS studies will be carried out

to determine the size, shape and internal organisation of mixed micelle aggregates of SDS with increasing TPE-SDS mole fraction. Analogous samples prepared using d_{25} -SDS will allow the specific aggregation state of the TPE-SDS molecules within the micelles to be isolated *via* contrast-matching of the host SDS micelle with the D_2O solvent, in the hope of determining the true effect of intermolecular packing on the AIE response. The results of this SANS study will then be correlated with the photoluminescence behaviour of the mixed SDS/TPE-SDS solutions and compared to the photoluminescence of the pure AIEgen at the same concentration. The goal is to develop a combined SANS/photoluminescence spectroscopy method based on the analysis of mixed micelles with varying degrees of AIE activity, in order to elucidate the minimum distance required for AIE to occur. It is hoped that this approach will lead the way in providing firm experimental evidence for the RIR mechanism.

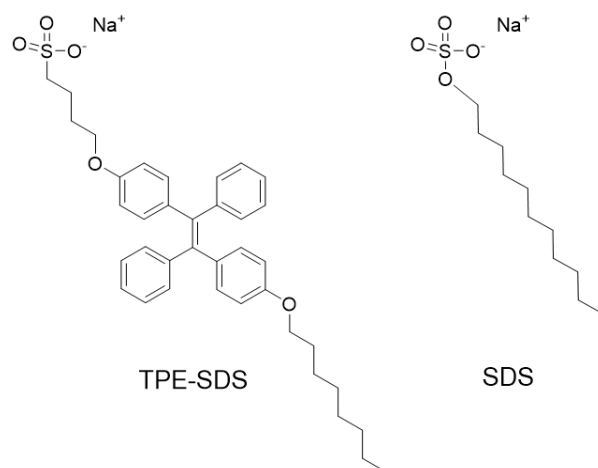


Figure 6.1 Molecular structure of two of the surfactants used in this chapter. Left: TPE-SDS, the AIE-active surfactant designed by Guan *et al.*¹⁰ Right: SDS, an archetypal anionic surfactant.

6.2 Experimental

6.2.1 Materials

Sodium dodecyl sulfate (SDS, $\geq 99\%$) was purchased from Sigma Aldrich. Deuterated sodium dodecyl sulfate (d_{25} -SDS, $> 98\%$) was purchased from Santa Cruz Biotechnology. Tetraphenylethylene sodium dodecyl sulfate (TPE-SDS) was a generous gift from Professor Ben Zhong Tang of The Hong Kong University of Science and Technology. All reagents were used as received.

6.2.2 Instrumentation

The instrumentation used for UV-Vis absorption spectroscopy, photoluminescence spectroscopy, (cryo)-transmission electron microscopy and small-angle neutron scattering is outlined in the Experimental, Chapter 3.

6.2.3 Methods

SANS: Mixed SDS/TPE-SDS and d_{25} -SDS/TPE-SDS solutions were prepared in D₂O to provide good scattering contrast (total volume 0.4 mL). The mole percent of TPE-SDS within the mixed solution was varied between 10 and 70. Samples of pure TPE-SDS, SDS and d_{25} -SDS of analogous concentration were prepared in D₂O as controls. The scattering functions were fitted using non-linear least-squares analysis to the Lamellar form factor models using the SasView programme (Version 4.0.1).

cryo-TEM: Samples of TPE-SDS (3.0 mmol L⁻¹) and SDS-AIE X ($X = 10, 70$) were prepared in D₂O (total volume = 0.05 mL). A MultiA holey carbon coated grid was used as the TEM substrate. The measurements were performed by Dr. Marie-Sousai Appavou at the Juelich Centre for Neutron Science, Munich. The preparation method involved depositing a 10 μ L drop of sample on the grid, blotting by hand after several minutes, leaving the sample in the cryo-plunge chamber at 20 °C and 80% relative humidity for 30 seconds, blotting again with the cryo-plunge device, before finally plunging the grid in liquid ethane.

TEM: Samples of TPE-SDS (3.0 mmol L⁻¹) and SDS-AIE- X ($X = 10, 20$) were made up in D₂O (total volume 0.05 mL). A MultiA holey carbon coated grid was used as the substrate. The measurements were performed by Dr. Marie-Sousai Appavou at the Juelich Centre for Neutron Science, Munich. The preparation involved depositing a 10 μ L drop of sample on the grid, blotting after several minutes and leaving to dry in air before insertion into the specimen holder and introduction into the instrument.

UV-Vis Absorption Spectroscopy: SDS-AIE- X solutions of analogous mole fraction to the SANS solutions were prepared in Millipore water (total volume = 1 mL). These samples were diluted by a factor of 25 relative to the SANS samples. Measurements were carried out in quartz cells (10 mm path length), with Millipore water used as a reference.

Photoluminescence Spectroscopy: TPE-SDS and SDS-AIE- X solutions were prepared in Millipore water (total volume = 0.5 mL) of analogous mole fraction and concentration to the SANS solutions. In all cases, $\lambda_{\text{ex}} = 320$ nm, slit width = 2.2 nm. Measurements were carried out in quartz cells (3 mm path length).

6.3 Results

6.3.1 A SANS Study into the Packing of SDS-TPE in Mixed (d_{25})-SDS/TPE-SDS Solutions

A SANS study was carried out to probe the self-assembly and packing behaviour of pure TPE-SDS, and mixtures of SDS/TPE-SDS. The goal is to study the self-assembly of TPE-SDS using SANS for the first time and to see if TPE-SDS and SDS form mixed micelles in which it is possible to tune the amount of TPE-SDS by varying its molar percent. Two sets of samples were created for the mixed surfactant systems, one using hydrogenated SDS to study the shape and structure of the overall aggregates, with analogous solutions prepared using d_{25} -SDS to allow the specific aggregation state of the TPE-SDS molecules to be isolated *via* contrast-matching. A note on nomenclature in advance of the results: the mixed SDS/TPE-SDS and d_{25} -SDS/TPE-SDS solutions are referred to as “(d_{25})-SDS-AIE- X ”, where the presence of ‘ d_{25} ’ indicates d_{25} -SDS and its absence indicates SDS, AIE refers to the AIEgen, TPE-SDS, and X corresponds to the mole percent of the AIEgen in the sample. For example, d_{25} -SDS-AIE-10 refers to a solution of 10 mole percent TPE-SDS and 90 mole percent d_{25} -SDS, in D_2O . Samples of the pure AIE-gen, TPE-SDS, are denoted as TPE-SDS- X where X in this case corresponds to the same concentration of TPE-SDS as in the analogous mixed surfactant solutions. A further description of the samples is available in the Appendix (Table A.6.1). For all the SDS-AIE- X and d_{25} -SDS-AIE- X solutions measured by SANS, the concentrations of both surfactants were above the CMC for the mixed surfactant solution, CMC_{mixed} , calculated using Equation 6.1.,^{11,12}

$$\frac{1}{CMC_{mixed}} = \frac{1}{CMC_{TPE-SDS}} + \frac{1}{CMC_{SDS}} \quad (6.1)$$

where the CMC of TPE-SDS¹⁰ is 0.03 mmol L^{-1} and that of SDS/ d_{25} -SDS is 8.2 mmol L^{-1} .¹³ In the following section, the self-assembly behaviour of TPE-SDS alone will first be presented followed by the results of the mixed SDS/TPE-SDS SANS study.

Samples of the pure AIEgen, TPE-SDS, were measured in D_2O , at concentrations above the CMC (0.03 mmol L^{-1}) at 25°C . The concentrations were chosen to correspond to two of the mixed SDS-AIE samples, specifically SDS-AIE-10 (1.5 mmol L^{-1} TPE-SDS) and SDS-AIE-20 (3.0 mmol L^{-1} TPE-SDS). The scattering profiles for TPE-SDS-10 and TPE-SDS-20 are shown in Figure 6.2, with the associated structural parameters determined from the form factor fits to the data presented in Table 6.1. Different detector distances were used for each of these measurements, resulting in different q -ranges for the samples.¹⁴ At low q ($q < 0.04 \text{ \AA}^{-1}$) the data decay as $q^{-2.1}$ in both scattering profiles, indicative of scattering from sheet-like objects.^{15,16} As no plateau was observed in the low q region, an estimate for the overall size of

these structures could not be obtained.^{17,18} The scattering intensity is higher for TPE-SDS-20 (3.0 mmol L⁻¹) than TPE-SDS-10 (1.5 mmol L⁻¹), as expected from a more concentrated sample. The scattering curve for TPE-SDS-20 is also shifted to higher q relative to TPE-SDS-10, a strong indication of the formation of smaller aggregate structures.

A Lamellar model was used to fit both the scattering profile of TPE-SDS-10, (Thickness, T , = 48.0 Å, 77% D₂O) and TPE-SDS-20 (T = 36.1 Å, 63% D₂O), the respective structural parameters of which can be found in Table 6.1. The smaller value for sheet thickness obtained for the higher concentration sample is in good agreement with the decreased wetness and high q shift of the TPE-SDS-20 scattering profile. Based on the work of Guan *et al.*, the length of the TPE-SDS molecule is taken to be 29.7 Å.¹⁰ This implies that for TPE-SDS-10, the alkyl tails of the surfactant are almost fully extended within the lamellar sheet, while for TPE-SDS-20 there is a much larger degree of overlap of the surfactant tails. The fluorescence intensity for TPE-SDS-20 would therefore be expected to be higher than that of TPE-SDS-10 as a result of the tighter packing of the TPE-SDS molecules, indicated by the thinner and dryer sheets, which should enhance the RIR mechanism. This will be further discussed in Section 6.3.2.

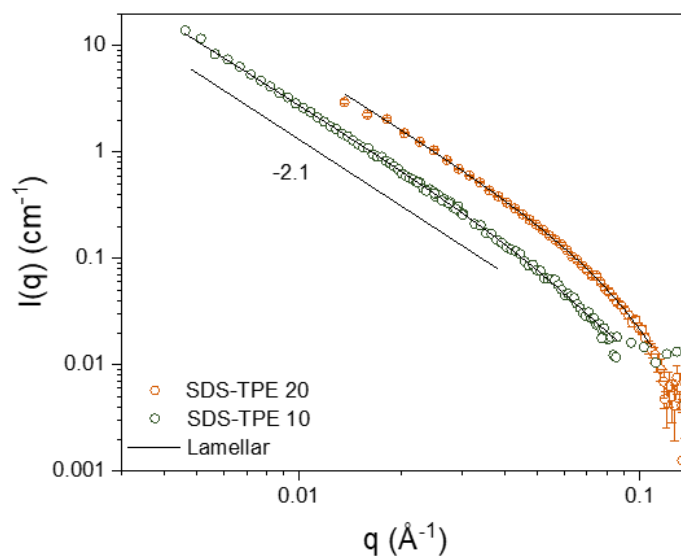


Figure 6.2 SANS data for pure TPE-SDS aggregates, at concentrations equivalent to those of SDS-AIE 10 (1.5 mmol L⁻¹, orange) and SDS-AIE 20 (3.0 mmol L⁻¹, green). The solid black lines correspond to a fit to the Lamellar model, and a decay of -2.1 is shown for comparison.

Table 6.1 Structural parameters obtained from the SANS data for TPE-SDS-10 and TPE-SDS-20 in D₂O (1.5 and 3.0 mmol L⁻¹, respectively) at 25 °C: α is the scattering power of the defined q region, T is the sheet thickness, obtained from the best fit to the data using the Lamellar Model in SasView. X_{sol} is the calculated solvent fraction in the aggregates, ϕ_{dry} is the theoretical volume mass of dry material each fit represents and χ^2 is the goodness-of-fit parameter.

Conc. (mmol L ⁻¹)	q^α ($q < 0.04 \text{ \AA}^{-1}$)	Model	T (Å)	SLD_{agg} ($\times 10^{-6} \text{ \AA}^{-2}$)	Scale	X_{sol}	ϕ_{dry}	χ^2
1.5	-2.1	Lamellar	48.0	5.18	0.0074	0.77	0.0016	1.19
3	-2.3	Lamellar	36.0	4.40	0.0085	0.63	0.0032	1.62

It has been established in the literature that TPE-SDS self-assembles into spherical micelles.¹⁰ Therefore, the lamellar sheets seen here could represent the walls of such circular structures, *i.e.* vesicles, with a diameter larger than the observation window of these SANS experiments (125 nm for TPE-SDS-10 and 48 nm for TPE-SDS-20). To investigate this further, cryo-TEM was used to image TPE-SDS-20 (3.0 mmol L⁻¹ in D₂O). Figure 6.3 shows a cryo-TEM image for this sample, displaying spherical aggregates 25-50 nm in diameter. These TEM images are very similar to those reported by Guan *et al.*, who found circular structures of varying diameters (10-20 nm) for TPE-SDS at lower concentrations (0.08 mmol L⁻¹). Higher concentrations than those used by Guan *et al.* were required for these experiments to obtain sufficient scattering intensity in SANS. Other similar TPE-based amphiphiles synthesised by Ding *et al.*, were also found to self-assemble into spherical aggregates (20-40 nm in diameter) using TEM.¹⁹ This indicates that the lamellar sheets found here using SANS are likely only to be a snapshot of a larger vesicle structure.

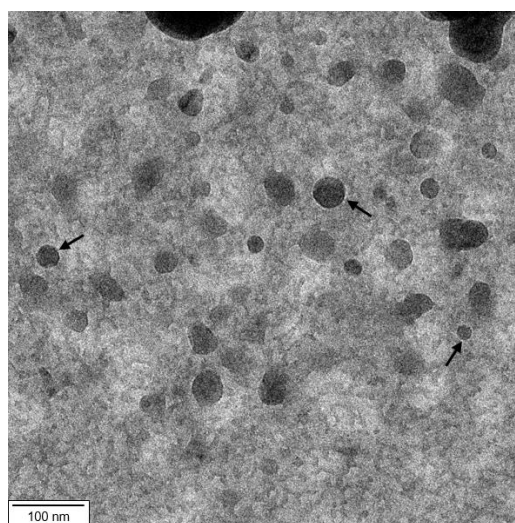


Figure 6.3 Cryo-TEM image of TPE-SDS (3.0 mmol L⁻¹ in D₂O) showing circular TPE-SDS structures, 25-50 nm in diameter. The large dark structures at the top of the image indicate the presence of ice. The scale bar represents 100 nm. Cryo-TEM measurements were performed by Dr Marie-Sousai Appavou.

It has been well-established in the literature that SDS forms ellipsoidal micelles within the concentration range and temperature used here.^{20,21} The scattering profiles of the SDS and d_{25} -SDS control samples are given in the Appendix, Figure A.6.1, and are in agreement with these literature findings. To see if it is possible to vary the intermolecular packing distances of TPE-SDS within its self-assembled aggregates, mixed TPE-SDS/SDS solutions were prepared, which were made more or less ‘dilute’ in terms of the AIEgen by varying the mole percent of TPE-SDS within the solutions. The results of this mixed TPE-SDS/SDS SANS study will be outlined next, followed by the AIE behaviour as probed using photoluminescence spectroscopy.

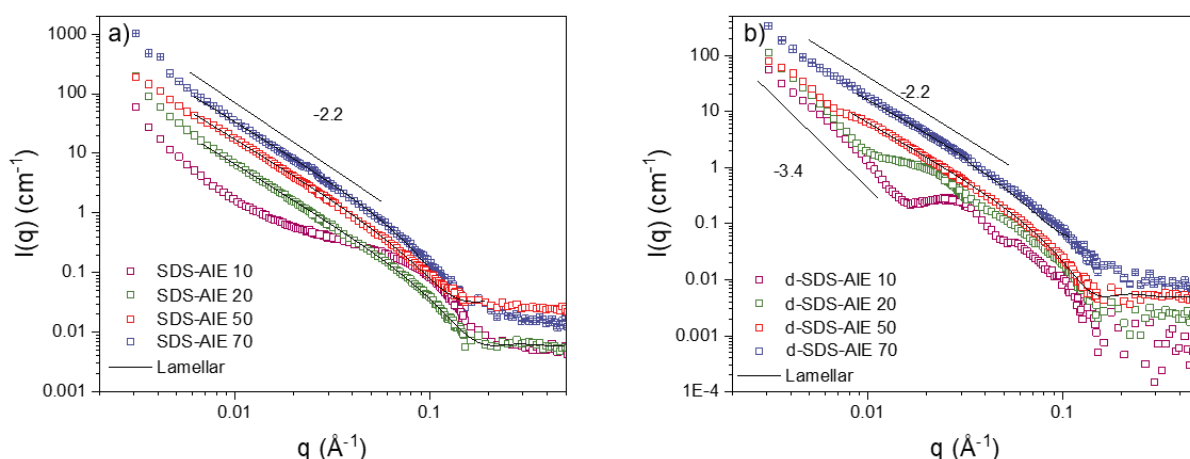


Figure 6.4 SANS data for mixed TPE-SDS/(d_{25})-SDS micelles, (d_{25})-SDS-AIE- X , where X is the mole percent of TPE-SDS. (a) The scattering profiles of SDS-AIE- X where $X = 10$ (purple), $X = 20$ (green), $X = 50$ (red) and $X = 70$ (blue). (b) Scattering profiles for d_{25} -SDS-AIE- X where $X = 10$ (purple), $X = 20$ (green), $X = 50$ (red) and $X = 70$ (blue). The scattering profiles have been offset by factors of 2.5 for clarity. The solid black lines correspond to a fit to the Lamellar model. Straight lines show decays of -2.2 and -3.4 for comparison.

Figure 6.4 shows the SANS data obtained for (d_{25})-SDS-AIE- X ($X = 10$ -70) in D_2O at 25 °C. For the hydrogenated samples, SDS-AIE- X (Figure 6.4a), when X is 20-70, the scattering profiles resemble those of TPE-SDS alone (Figure 6.2), with the same decay of about q^{-2} observed in the low q region. All three of these scattering profiles were fitted with the Lamellar model, the respective structural parameters of which can be found in Table 6.2. In all cases, there was an upturn at low q ($q < 0.06 \text{ Å}^{-1}$), which could not be accounted for by the Lamellar model alone. This is likely to be due to inter-particle interactions. In order to fully fit the scattering profile, the Lamellar form factor model will need to be combined with a structure factor model. Unfortunately, this has not yet been achieved, but future work will focus on combining structure and form factor models to comprehensively account for this.

The sheet thickness determined from the fit to the data increases as the mole percent of TPE-SDS increases ($T = 29.5, 36.8$ and 38.9 Å for $X = 20, 50$ and 70 , respectively), while the

sheet wetness decreases (%D₂O = 16.5, 9.3 and 2.3%, for $X = 20, 50$ and 70 , respectively). This is a reasonable trend given that the differing lengths of the two surfactant molecules ($16.7 \text{ \AA}$ for SDS²² vs. $29.7 \text{ \AA}$ for TPE-SDS¹⁰) and also implies that mixed micelles do indeed form. The sheet thickness and dryness for SDS-AIE-20 ($T = 29.5 \text{ \AA}$) is lower than that found for pure TPE-SDS at the same concentration (AIE-20, $T = 36.0 \text{ \AA}$). This further supports the conclusion that mixed micelles are formed. Cryo-TEM indicates that much like pure TPE-SDS, these lamellar sheets are actually vesicles (Figure 6.5), although with different dimensions to those of pure TPE-SDS. Cryo-TEM images were obtained for SDS-AIE-70, displaying spherical structures, $\sim 400 \text{ \AA}$ in diameter. The thickness of this vesicle, as determined from the fit of the Lamellar model, is $38.9 \text{ \AA}$, indicating that the vesicle interior is $\sim 320 \text{ \AA}$ in diameter.

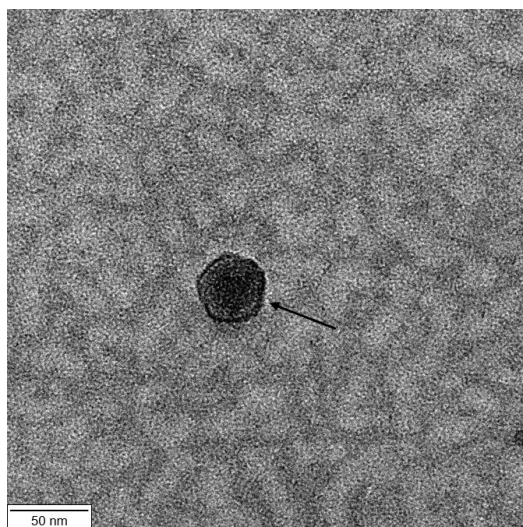


Figure 6.5 Cryo-TEM image of TPE-SDS-70 showing a spherical structure with distinct layers, approximately $400 \text{ \AA}$ in diameter. The scale bar represents 50 nm . Cryo-TEM measurements were performed by Dr Marie-Sousai Appavou.

The scattering profile of SDS-AIE-10 is quite distinct from the other samples, with a much steeper decay of $q^{-2.6}$ at low q ($q < 0.01 \text{ \AA}^{-1}$). There is an upturn in the mid q region ($q = 0.025 \text{ \AA}^{-1}$), before the scattering profile ultimately decays at the same rate as the other samples at high q ($q > 0.1 \text{ \AA}^{-1}$). The scattering profile resembles neither that of pure TPE-SDS nor pure SDS and at present, no form factor has been found to adequately fit this data. One option to try and improve the fitting of these scattering profiles, some of which show indications of inter-particle interactions, would be to subtract the structure factor contribution and then fit a form factor to the resulting scattering profile. This could be done by measuring the scattering from a very dilute sample (form factor only) and from a very concentrated sample (structure factor and form factor). The structure factor contribution could then be determined from the difference between the two curves.

The samples containing deuterated SDS, d_{25} -SDS-AIE- X , are shown in Figure 6.4b. These samples are expected to reveal the aggregation state of TPE-SDS only, as d_{25} -SDS has been contrast-matched to the solvent *via* deuteration. For the samples with a high proportion of AIEgen ($X = 50$ and 70) the scattering profiles are very similar that of TPE-SDS alone. Similar to the hydrogenated samples, both of these scattering profiles were fitted with the Lamellar model, the respective structural parameters of which are available in Table 6.3. Again, the thickness of the lamellar sheet increases as the proportion of TPE-SDS increases, with a corresponding decrease in wetness. ($T = 37.9 \text{ \AA}$, $\%D_2O = 8.9$ for $X = 50$ and $T = 44.6 \text{ \AA}$, $\%D_2O = 2.9$ for $X = 70$) The increase in thickness upon increasing X is proportional to the increase in thickness seen for the analogous hydrogenated samples. The larger values obtained here for the deuterated SDS samples reflect the increased length of the TPE-SDS molecule, compared to the d_{25} -SDS molecule, which has been contrast-matched in this case. For both $X = 50$ and 70 the thickness of the lamellar sheet is less than twice the length of the TPE-SDS molecules ($29.7 \text{ \AA} \times 2 = 59.4 \text{ \AA}$). This, coupled with the aggregates being very dry (8.9 and 2.9 $\%D_2O$), suggests that there is a significant degree of overlap of TPE-SDS molecules within the $X = 50$ and 70 self-assembled aggregates.

Table 6.2 Structural parameters obtained from SANS data for SDS-AIE-20-70 in D_2O at $25^\circ C$. α is the scattering power of the q region. T is the lamellar sheet thickness obtained from the best fit to the data using the Lamellar Model in SasView. X_{sol} is the calculated solvent fraction in the aggregates, ϕ_{dry} is the theoretical volume mass of dry material each fit represents and χ^2 is the goodness-of-fit parameter

Sample	$q^{-\alpha}$ ($q < 0.04 \text{ \AA}^{-1}$)	Model	T ($\text{\AA}$)	SLD ($\times 10^{-6} \text{ \AA}^{-2}$)	Scale	X_{sol}	ϕ_{dry}	χ^2
SDS-AIE-20	-2.2	Lamellar	29.5	1.61	0.00161	16.5	0.0013	4.98
SDS-AIE-50	-2.1	Lamellar	36.8	1.10	0.00110	9.3	0.0011	5.61
SDS-AIE-70	-2.2	Lamellar	38.9	1.60	0.00127	2.3	0.0012	4.82

Table 6.3 Structural parameters obtained from SANS data for d_{25} -SDS-AIE-50-70 in D_2O at $25^\circ C$. α is the scattering power of the q region. T is the Lamellar sheet thickness obtained from the best fit to the data using the Lamellar Model in SasView. X_{sol} is the calculated solvent fraction in the aggregates, ϕ_{dry} is the theoretical volume mass of dry material each fit represents and χ^2 is the goodness-of-fit parameter.

Sample	$q^{-\alpha}$ ($q < 0.04 \text{ \AA}^{-1}$)	Model	T ($\text{\AA}$)	SLD ($\times 10^{-6} \text{ \AA}^{-2}$)	Scale	X_{sol}	ϕ_{dry}	χ^2
d_{25} -SDS-AIE-50	-2.1	Lamellar	37.9	3.13	0.00225	8.9	0.0020	4.19
d_{25} -SDS-AIE-70	-2.2	Lamellar	44.5	2.24	0.00198	2.9	0.0019	3.17

The scattering behaviour changes for d_{25} -SDS-AIE-10 and -20. The scattering profiles for these samples are not characteristic of a lamellar phase, but rather a steep decay of $q^{-3.4}$ is

observed in the low q region, along with pronounced bumps in the mid q region. Unfortunately, similar to SDS-TPE-10, no form factor can be found to accurately describe these scattering profiles at present. One route to unravelling this scattering profile would be to remove the $q^{-3.4}$ dependency at low q by subtracting a power law (of -3.4 in this case) and fitting the resulting curve.²³ This will be the focus of future work. However, room temperature TEM images (Figure 6.6) can provide some insight into the self-assembly behaviour. It appears that for $X = 10$, an unstructured emulsion-like phase is formed (Figure 6.6a), which becomes increasingly structured upon increasing the AIE mole percent to $X = 20$ (Figure 6.6b). The behaviour of the AIEgen dominates at higher X , ultimately forming lamellar/vesicle aggregates which can be assigned from SANS ($X = 50, 70$). While the origin of the self-assembly behaviour at low X is as yet uncertain, there are reports of similar TEM results in the literature for other comparable SDS and TPE-based molecules. Bhowmick *et al.* found that for solutions of SDS mixed with an emissive rhodamine-based sensor, an agglomeration with no particular shape, similar to Figure 6.6, was found at low SDS concentrations, while spherical core-shell microstructures, similar to Figure 6.5, were observed at higher SDS concentrations.²⁴ Mixed TPE solutions can form quite complicated structures, based on an interplay of π - π stacking, Van der Waals interactions and hydrogen bonding. Anuradha *et al.* found that achiral TPE molecules, with alkyl chains protruding from each of the four aryl groups of the TPE core, could form chiral superstructures.²⁵ Using SEM and TEM, Salimimarand *et al.* observed the formation of flower-like fractals and spheres comprised of sharp ribbons for two different TPE-based molecules decorated with alkyl chains.²⁶ The sharp decay of $q^{-3.4}$, indicative of scattering from rough fractals, which is observed here for d_{25} -SDS AIE- X at low X could correspond to one of these such structures, although at present simple form factor models cannot be assigned, and the TEM images show a distinct lack of structure. The goal of unravelling the self-assembly behaviour of SDS-AIE X using more refined SANS analysis in conjunction with electron microscopy makes for exciting future work.

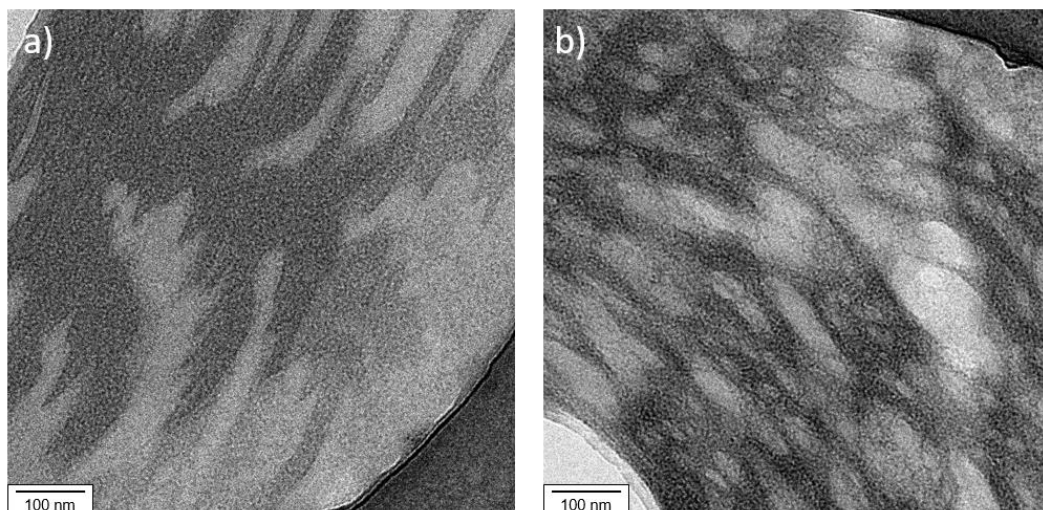


Figure 6.6 TEM images of (a) SDS-AIE-10 and (b) SDS-AIE-20 in D_2O , taken at 25 °C. An unstructured emulsion-like phase can be seen for SDS-AIE-10. Upon increasing the proportion of AIEgen to 20 mole percent, a slightly more structured network is observed. The scale bars represent 100 nm. TEM measurements were performed by Dr Marie-Sousai Appavou.

The SANS results imply that TPE-SDS and SDS self-assemble into mixed micelles, rather than forming two different populations. For the deuterated samples, where only the aggregation state of TPE-SDS is observed, for $X = 10$ and 20 the scattering profile does not resemble the vesicles of TPE-SDS or the ellipsoids of SDS, implying that an alternative, mixed phase is formed. For $X = 50$ and 70 lamellar vesicles are formed, similar to the behaviour of TPE-SDS by itself, but these vesicles have different dimensions than TPE-SDS alone. Moreover, the thickness of the lamellar sheet increases as the concentration of TPE-SDS within the mixed system also increases, contrary to the behaviour seen for TPE-SDS alone. The lamellar sheets observed for the mixed system are also much drier than those found for pure TPE-SDS. This is supported by the general observation that mixed micelles usually form upon mixing of different surfactants, as favoured by entropy.^{11,12} The presence of two discrete micelle populations is typically only seen for surfactants with a significant degree of immiscibility, such as a mixture of fluorocarbon and hydrocarbon surfactants.^{11,12}

6.3.2 Photoluminescence Behaviour of TPE-SDS in Mixed Surfactant Solutions

The photoluminescence behaviour of the SDS-AIE- X solutions was probed in order to gain an insight into the emission properties of TPE-SDS upon incorporation into mixed micelles. The samples used above for SANS were investigated by means of UV-Vis absorption spectroscopy and photoluminescence spectroscopy. The samples for UV-Vis absorption measurements were diluted by a factor of 25 to reduce the absorption to a reasonable value, while maintaining the same molar ratios. In all cases, the concentration of TPE-SDS is still

above its CMC, and the combined surfactant concentration is above the mixed CMC, for these diluted samples. The UV-Vis absorption spectra (Figure 6.7) for SDS-AIE-X showed the same absorption maxima (252 and 320 nm) as those of the pure TPE-SDS samples, in excellent agreement with the findings of Guan *et al.* for this molecule.¹⁰

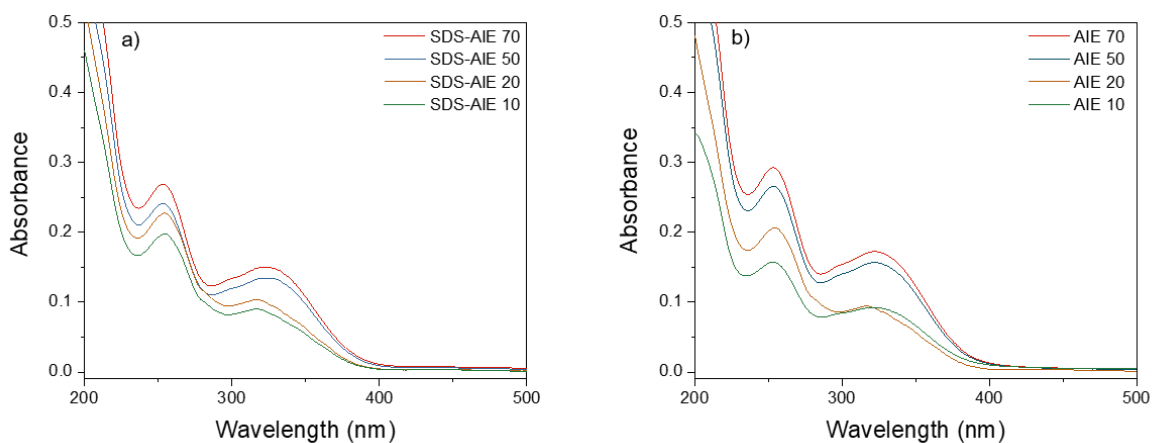


Figure 6.7 UV-Vis absorption spectra of (a) SDS-AIE-10 (green), -20 (orange), -50 (blue) and -70 (red), and (b) TPE SDS alone at analogous concentrations, where TPE-SDS at the same concentration as SDS-AIE-10-70 is designated AIE-10 (green), -20 (orange), -50 (blue), and -70 (red), respectively. Characteristic TPE-SDS absorption maxima at 252 and 319 nm are seen in both cases.

In order to see if TPE-SDS was emissive in mixed SDS/TPE-SDS solutions, the steady-state emission spectra of SDS-AIE-X ($X = 10-70$) and pure TPE-SDS at analogous concentrations were measured (Figure 6.8). The same excitation wavelength (320 nm) and slit widths (2.2 nm) were used in all cases. For all samples, an emission maximum at 490 nm is observed, which is characteristic for TPE-SDS.¹⁰ It is apparent that TPE-SDS not only remains emissive when in the mixed surfactant solution, but also displays slightly enhanced emission for $X = 50$ and 70 compared to pure TPE-SDS at analogous concentrations. For both TPE-SDS and SDS-AIE-X solutions there is an increase in the fluorescence intensity with increasing TPE-SDS concentration, with both insets clearly displaying a linear relationship between these two parameters. All of the emission spectra in Figure 6.8 have a shoulder between about 380 and 425 nm. As these samples are very concentrated, as required to obtain sufficient scattering intensity in SANS, it was hypothesised that this small shoulder is a result of scattering from aggregates in solution. To investigate this further, photoluminescence measurements were run on the same samples, but that had been diluted by a factor of 25 (Appendix A.6.2). For these dilute samples, the same emission behaviour was observed as for the concentrated samples in Figure 6.8 ($\lambda_{\text{max}} = 490$ nm, a linear increase in fluorescence intensity with increasing TPE-concentration), but the shoulder between 380 and 425 nm was not observed.

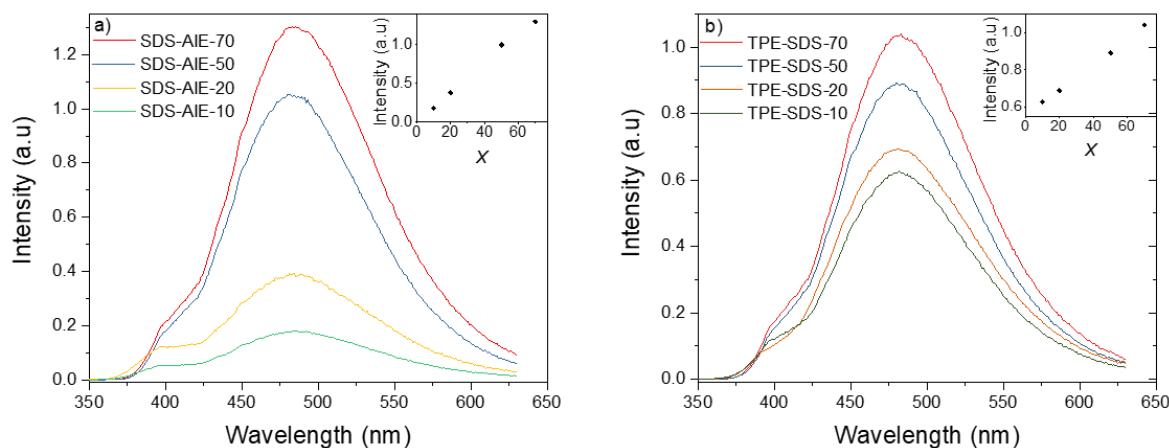


Figure 6.7 AIE activity of TPE-SDS in mixed SDS-AIE- X solutions and in solutions of pure TPE-SDS at analogous concentrations (1.5, 3.0, 5.4 and 6.6 mmol L⁻¹ for each of $X = 10, 20, 50, 70$, respectively). Emission spectra for (a) SDS-AIE- X and (b) pure TPE-SDS for $X = 10$ (green), 20 (orange), 50 (blue) and 70 (red). Inset: Intensity at emission maximum as a function of X . $\lambda_{\text{ex}} = 320$ nm, slit width = 2.2 nm.

This result is important for several reasons. Firstly, it builds on the SANS evidence that TPE-SDS and SDS do indeed form mixed micelles. If TPE-SDS was self-assembling into its own population of micelles, the fluorescence intensity for the mixed micelles would be expected to be the same as that for TPE-SDS alone at the same concentration. Secondly, this result indicates that not only can mixed micelles be formed, but they can be made more or less ‘dilute’ in terms of AIEgen with a fluorescence intensity which is tunable through variation of the TPE-SDS mole fraction. Interestingly, while the fluorescence intensity for SDS-AIE-70 and -50 is slightly higher than that observed for pure TPE-SDS-70 and -50, there is a significant drop in intensity for SDS-AIE-20 and SDS-AIE-10. These results are in good agreement with the RIR mechanism and the SANS and TEM data. Unstructured phases with distinctive scattering profiles were observed for SDS-AIE-10 and -20, in conjunction with decreased emission intensity, while SDS-AIE-70 and -50 were found to form lamellar sheets, likely vesicles, in conjunction with enhanced emission intensity. Furthermore, the increased fluorescence intensity of TPE-SDS in TPE-SDS-20 vs. TPE-SDS-10 is likely to be a result of the tighter packing of TPE-SDS molecules within the thinner and dryer lamellar sheet, anticipated from the SANS data. In the future, it will be interesting to also measure the scattering profiles of TPE-SDS-50 and TPE-SDS-70 as these samples continue to show enhanced fluorescence intensity. These results support the hypothesis that the aggregation environment of the TPE-SDS molecules is a key factor in determining the emission behaviour.

6.3.3 The Impact of the Self-Assembly Behaviour on Photoluminescence

The emission behaviour indicates that as the local environment of TPE-SDS within the mixed SDS-AIE- X system varies, as apparent from the SANS and TEM data, the AIE activity changes correspondingly, with a linear relationship observed between fluorescence intensity and TPE-SDS mole fraction. Both SANS and photoluminescence spectroscopy data point to the formation of mixed surfactant structures, in which the concentration of TPE-SDS can be modulated by varying the mole fraction. Interestingly, the fluorescence intensity was enhanced for TPE-SDS in SDS-AIE- X solutions compared TPE-SDS alone, for $X = 50$ and 70 . This implies that in mixed micelle solutions at high mole percent, the TPE-SDS molecules are packed very efficiently, such that non-radiative deactivation pathways (rotations, vibrations *etc.*) are likely suppressed. On the other hand, the fluorescence intensity when $X = 20$ and 10 is decreased compared to TPE-SDS alone at the same concentration. This indicates that most likely due to a reduction in the number of neighbouring bulky TPE moieties to impart rigidity in the unstructured network observed by TEM, the fluorescence intensity drops within the mixed surfactant systems.

Although the self-assembly structures for the low TPE-SDS mole fractions ($X = 10, 20$) cannot as yet be assigned, TEM measurements indicate the formation of an unstructured phase which becomes gradually more networked upon increasing the TPE-SDS mole percent from $X = 10$ to 20 . Similarly, the SANS data show unusual scattering profiles for these samples, in particular for the deuterated samples, which resemble neither pure TPE-SDS nor SDS. However, both samples are emissive, with maxima observed at 490 nm , the intensity of which fits the same linear trend line of fluorescence intensity vs. TPE-SDS mole fraction as the samples whose self-assembly behaviour could be assigned ($X = 50, 70$). Therefore, it is interesting that the scattering behaviour of the lower and higher concentrated samples should be so distinctive. Furthermore, as the proportion of TPE-SDS within the mixed surfactant system increases, the self-assembly behaviour of the AIEgen begins to dominate, with the scattering profile becoming increasingly similar to that of pure TPE-SDS as X increases from 50 to 70 . These high X scattering profiles were fit by a Lamellar model, likely indicative of a larger vesicle structure, which is supported by cryo-TEM. The fluorescence intensity corresponding to these samples is higher than that of TPE-SDS alone, implying that the TPE-SDS molecules must be packed together very efficiently within this vesicle.

6.4 Conclusions and Outlook

In this work, TPE-SDS was analysed using SANS for the first time. It was found that the circular structures reported in the literature¹⁰ are actually vesicles, visualised using TEM. The thickness of the outer shell of these vesicles was within the observation window of our SANS experiments, and therefore could be determined through fitting of the Lamellar model. These preliminary results were consistent with the RIR mechanism, as increased fluorescence intensity was observed for the TPE-SDS-20, which had a lamellar thickness of 36.0 Å and wetness of 63% D₂O, compared to the presumably more loosely packed TPE-SDS-10, which had a lamellar thickness of 48.0 Å and wetness of 77% D₂O. It was also found through combination of SANS and photoluminescence spectroscopy that TPE-SDS and SDS can form mixed micelles, with a fluorescence intensity which depends linearly on the mole fraction of TPE-SDS. In future work, further proof of mixed micelle formation will be provided by experimentally determining the CMC of the mixed micelle system using DLS and ST. Mixed micelles will display one mixed CMC, rather than two distinct CMCs.

Preliminary SANS analysis and TEM images reveal that at high TPE-SDS mole fractions, the mixed surfactant system forms lamellar phases, which are likely to be the walls of vesicles. However, to detect the entire vesicle structure within the observation window of SANS, a much lower q range would need to be probed. Ultra-small angle neutron scattering (USANS) could be used to explore such smaller q regions, and hence, larger length-scales, such as vesicle diameter.²⁷ Future work will also focus on reducing the TPE-SDS mole fraction further to find a point at which either no fluorescence occurs, or a deviation from the linear trend of fluorescence intensity vs. TPE-SDS concentration is observed within the mixed surfactant system. Any such deviation from linearity would be an indication that TPE-SDS self-assembles into a separate population, or, exists as free monomers in solution.

The work in this chapter provides preliminary evidence that SANS can be used in conjunction with photoluminescence spectroscopy to determine the self-assembled structures formed by, and AIE activity of, a mixed SDS/TPE-SDS surfactant system, although a more comprehensive analysis is needed to fully unravel the scattering profiles and elucidate the aggregated state of TPE-SDS within the mixed micelle. In order to separate concentration effects from enhanced packing effects, future work will also focus on using the results found here to develop a similar SANS/photoluminescence study but with samples in which same amount of TPE-SDS is used in each case, and only the quantity of (d_{25})-SDS varied. In short, this is a very promising start along the path to providing firm experimental evidence for the RIR mechanism.

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Chapter 7

A Tail of Two Surfactants: Conclusions and Outlook

This thesis investigated the structure-property relationships of two classes of photoactive surfactants, namely, azobenzene photosurfactants and an AIE-active surfactant, TPE-SDS. The goal was to probe and understand the effect of molecular structure on the physicochemical properties and self-assembly behaviour of the azobenzene photosurfactants, and in the case of the AIE-active surfactant, begin to understand how the structure and self-assembly behaviour of the surfactant impacted the observed photoluminescence.

The first part of this thesis focused on azobenzene photosurfactants, a class of molecules which show potential as light-responsive switches in a number of surface tension and self-assembly related applications. In **Chapter 4**, the design, synthesis and characterisation of a series of four novel neutral azobenzene photosurfactants was achieved. This series of surfactants was targeted to investigate the effect of molecular structure and photoisomerisation on the optical and physicochemical properties of the surfactants, by varying the number of carbons in the pendant tail and spacer moieties within the overall composite tail. All four AzoPS demonstrated excellent photo-switching abilities. It was found that varying the length of the pendant tail and spacer moiety of the AzoPS is an effective method to control the surface activity and interfacial properties of the surfactant. Extremely large differences in surface tension were observed for the AzoPS with a very short pendant tail and moderate spacer, **C₂AzoOC₄E₄**, with differences in saturated surface tension values between isomers of 14.8 mN m⁻¹, rivalling the best results currently in the literature.

Chapter 5 investigated the self-assembly behaviour of the family of neutral AzoPS synthesised in **Chapter 4**. The self-assembly behaviour was probed using SANS, with each AzoPS investigated as function of temperature and isomeric form. It is clear that the self-assembled structure formed varies as the molecular structure of the AzoPS is altered. Lamellar sheets, wormlike micelles and elliptical cylinders were found to form above the CMC upon increasing the pendant tail length of the AzoPS, while an increase in the spacer length of the AzoPS resulted in a change from elliptical cylinders to wormlike micelles. The formation of wormlike micelles is particularly interesting as, to the best of my knowledge, there is only one report in the literature of another single component light-responsive wormlike micelle system. For all four AzoPS, a different scattering profile was observed for the *cis*-form than the *trans*-form, with the most striking difference between *cis*- and *trans*-isomers observed for **C₈AzoOC₈E₄**, which could switch between ‘on’ and ‘off’ states for the wormlike micelle structure upon photoisomerisation. The work in this chapter highlights the sensitivity of the self-assembly process to small changes in temperature, molecular shape and hydrophilicity.

Future work on these AzoPS systems to investigate the self-assembly behaviour at higher concentrations using SAXS has already begun. It is hoped that these AzoPS will demonstrate LLC phase-forming abilities, with initial results in this regard showing promise. The results of this study may open up the possibility to use these AzoPS in reversible soft-templating applications, which will be the primary goal of future work. The SANS fitting procedures and models used in **Chapter 5** will also be revised and refined, with a view to fully accounting for concentration effects *via* the inclusion of structure factors models with certain form factor models. Focus will also be directed towards developing an experimental set up which allows for *in situ* UV illumination of the AzoPS sample during the SANS measurement, making it possible to measure the scattering from the self-assembled structures of the *cis*-PSS at a variety of temperatures. This would also allow the transition between the *trans* and *cis* self-assembled structures to be monitored in real-time.

In **Chapter 6**, pure TPE-SDS and TPE-SDS/SDS mixed micelles were analysed using SANS for the first time. It was found through a combination of SANS and photoluminescence spectroscopy measurements that TPE-SDS and SDS can form mixed micelles, with a fluorescence intensity which depends linearly on the mole fraction of TPE-SDS present in the mixed micelle. Preliminary SANS analysis reveals that at high TPE-SDS mole fractions, the mixed surfactant system forms lamellar phases. These are likely to be the walls of vesicles, similar to those observed for pure TPE-SDS. This conclusion is supported by the cryo-TEM images obtained for SDS-AIE-70.

It was shown that SANS can be used in conjunction with photoluminescence spectroscopy to probe the self-assembled structures formed by, and AIE activity of, a mixed SDS/TPE-SDS surfactant system. However, a more comprehensive analysis of the SANS data is needed to fully unravel the scattering profiles at low mole percent, and to elucidate the aggregated state of TPE-SDS within the mixed micelle. This will be the primary focus of future work. Future work will also look to separating the effect of increased TPE-SDS concentration from enhanced TPE-SDS packing effects, on the AIE activity of the mixed micelles. This will be achieved by creating mixed micelles in which same amount of TPE-SDS is present in each case, and only the quantity of SDS varied. The resulting micelles will be probed by both SANS and photoluminescence spectroscopy.

This thesis exemplified the versatility and utility of surfactants, and also highlighted the usefulness of light as a clean, remote and instantaneous stimulus. In **Chapters 4** and **5** the incorporation of a photoresponsive azobenzene moiety in the surfactant tail allowed the behaviour of the resulting photosurfactant to be manipulated dynamically with light. In general,

it is the interplay of hydrophobicity and hydrophilicity that imparts surfactants with surface tension lowering and self-assembly properties. It has been shown that manipulating the hydrophobic-hydrophilic balance of the photosurfactant molecule by altering the conformation through photoisomerisation is a straightforward yet extremely effective method of controlling the surface tension and self-assembly behaviour. In **Chapter 6**, the natural tendency of surfactants to self-assemble above a certain critical concentration was taken advantage of to probe the phenomenon of aggregation-induced emission. Through combination of a non-photoactive and an AIE-active surfactant, mixed micelles were created in which the emission behaviour could be tuned by varying the mixed micelle composition.

In all, it is clear that surfactants are incredibly useful tools. Their properties can be used in their own right *i.e.* to lower surface tension, to form self-assembled structures, as required by many industries and applications, or, they can be used as a means of generating an environment in which to study fundamental photophysical processes such as aggregation-induced emission in mixed micelles. In either case, the molecular structure of the surfactant is the key parameter which determines the surfactant's behaviour and properties.

Appendix

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Appendix to Chapter 4

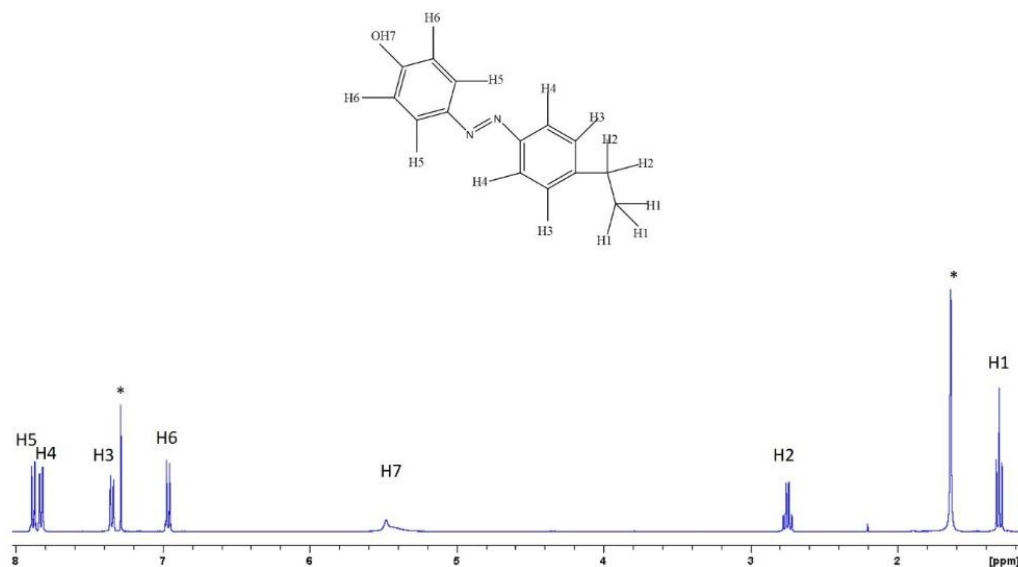


Figure A.4.1 Characterisation of azobenzene photosurfactant **C₂AzoOH** by ¹H NMR spectroscopy. The asterisk at 7.25 ppm indicates the CDCl₃ solvent peak and at 2.6 ppm indicates acetone solvent peak. The assigned molecular structure is given for comparison with the spectrum.

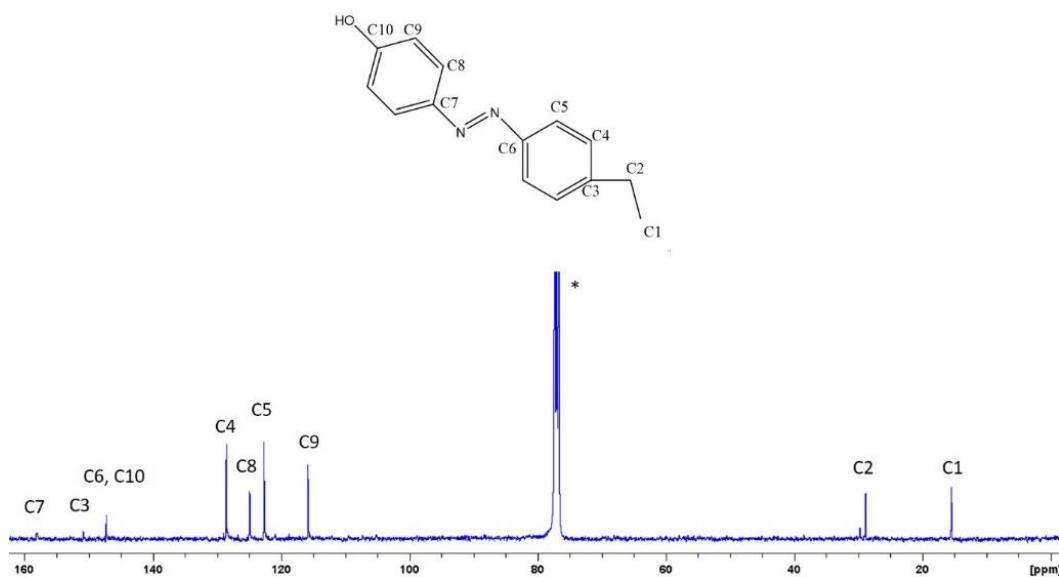


Figure A.4.2 Characterisation of azobenzene photosurfactant **C₂AzoOH** by ¹³C NMR spectroscopy. The asterisk indicates the CDCl₃ solvent peak. The assigned molecular structure is given for comparison with the spectrum.

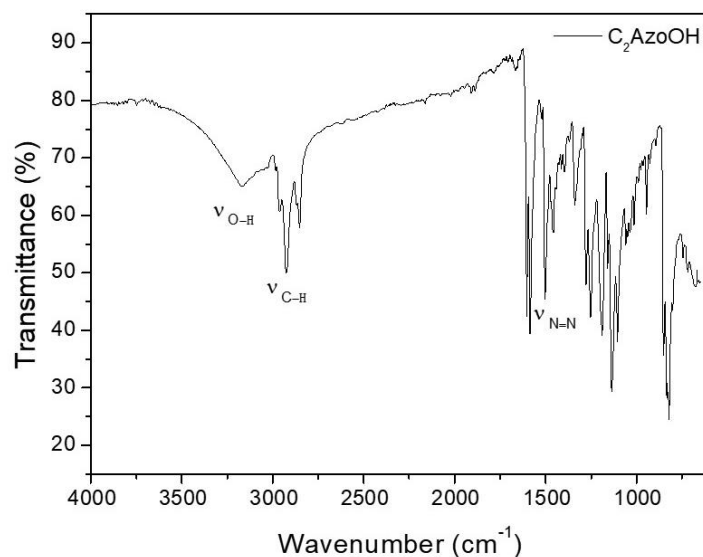


Figure A.4.3 Characterisation of azobenzene photosurfactant **C₂AzoOH** by FTIR spectroscopy.

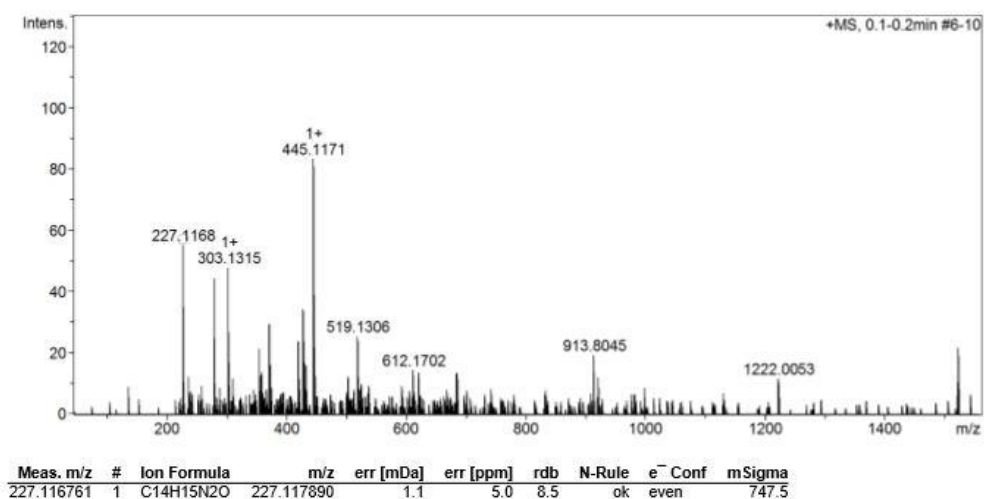


Figure A.4.4 Characterisation of azobenzene photosurfactant **C₂AzoOH** by mass spectrometry.

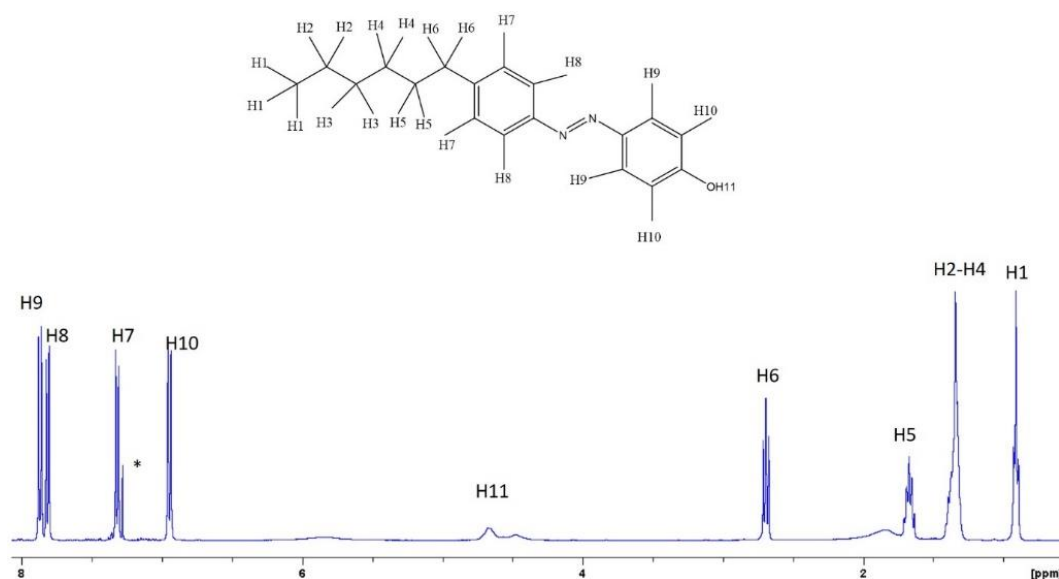


Figure A.4.5 Characterisation of azobenzene photosurfactant **C₆AzoOH** by ¹H NMR spectroscopy. The asterisk at 7.25 ppm indicates the CDCl₃ solvent peak. The assigned molecular structure is given for comparison with the spectrum.

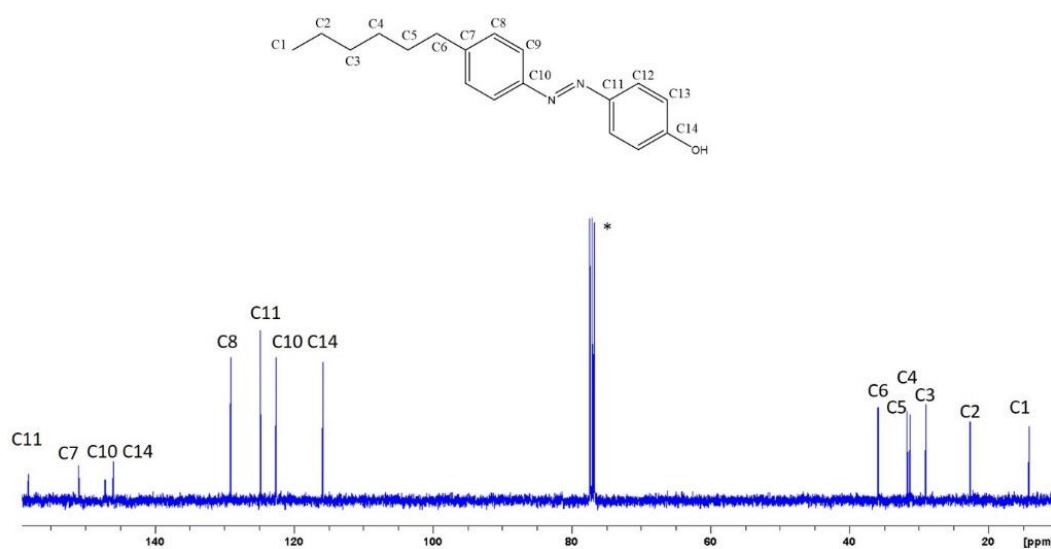


Figure A.4.6 Characterisation of azobenzene photosurfactant **C₆AzoOH** by ¹³C NMR spectroscopy. The asterisk indicates the CDCl₃ solvent peak. The assigned molecular structure is given for comparison with the spectrum.

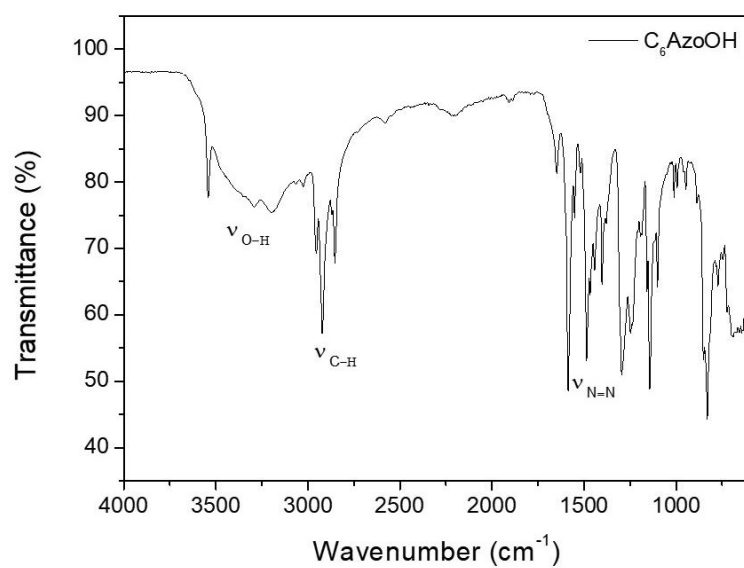


Figure A.4.7 Characterisation of azobenzene photosurfactant **C₆AzoOH** by FTIR spectroscopy

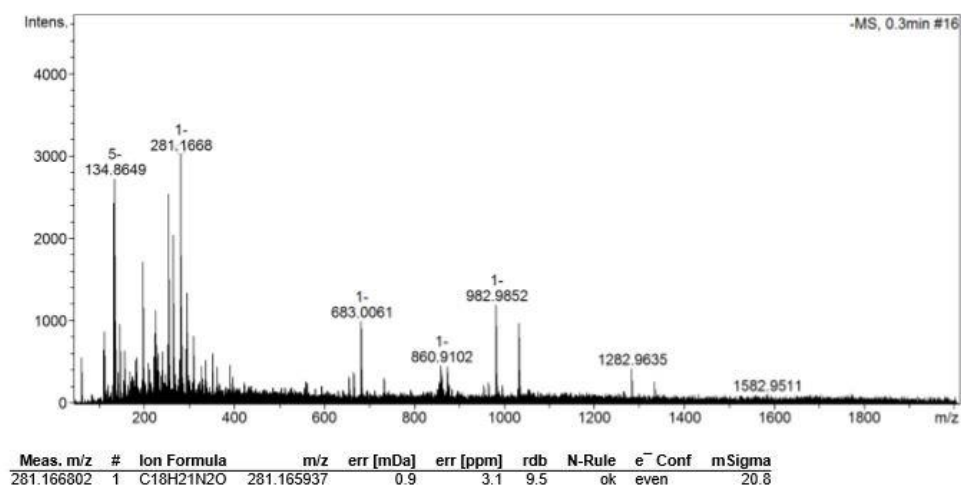


Figure A.4.8 Characterisation of azobenzene photosurfactant **C₆AzoOH** by mass spectrometry.

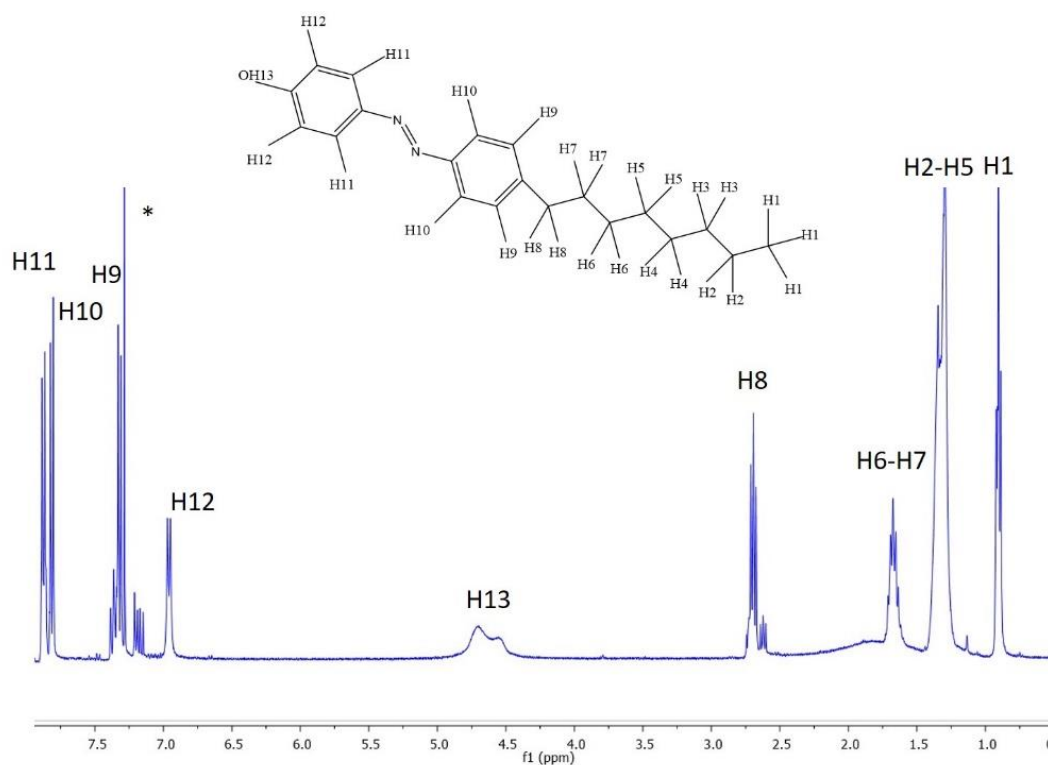


Figure A.4.9 Characterisation of azobenzene photosurfactant **C₈AzoOH** by ^1H NMR spectroscopy. The asterisk at 7.25 ppm indicates the CDCl_3 solvent peak. The assigned molecular structure is given for comparison with the spectrum.

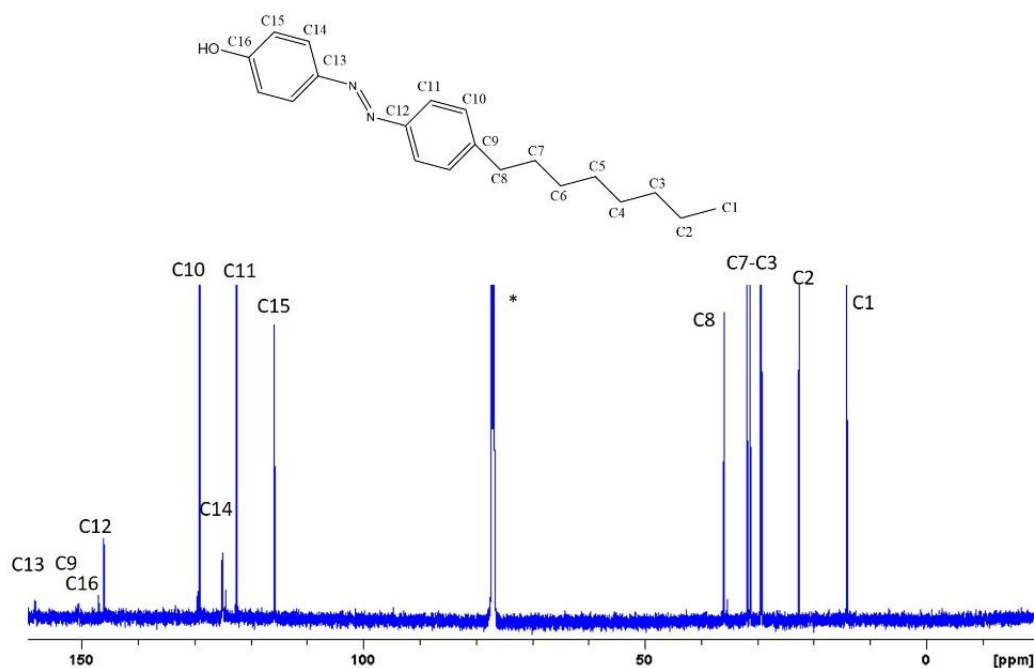


Figure A.4.10 Characterisation of azobenzene photosurfactant **C₈AzoOH** by ^{13}C NMR spectroscopy. The asterisk indicates the CDCl_3 solvent peak. The assigned molecular structure is given for comparison with the spectrum.

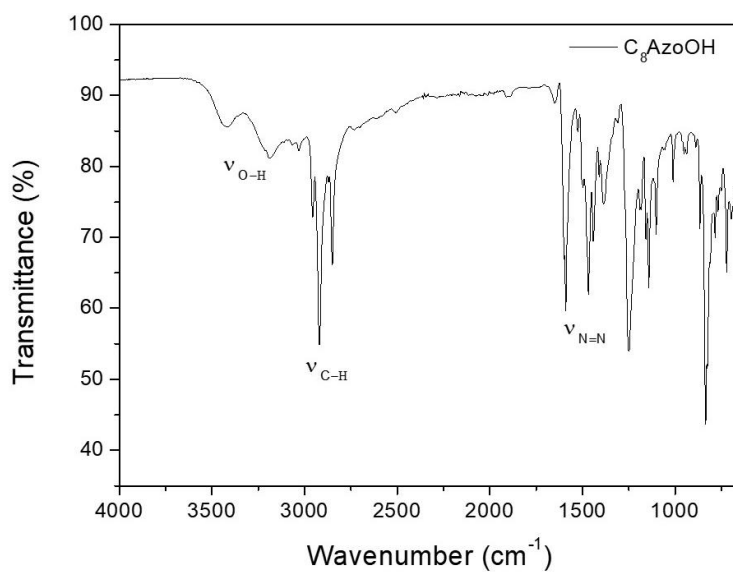


Figure A.4.11 Characterisation of azobenzene photosurfactant **C₈AzoOH** by FTIR spectroscopy

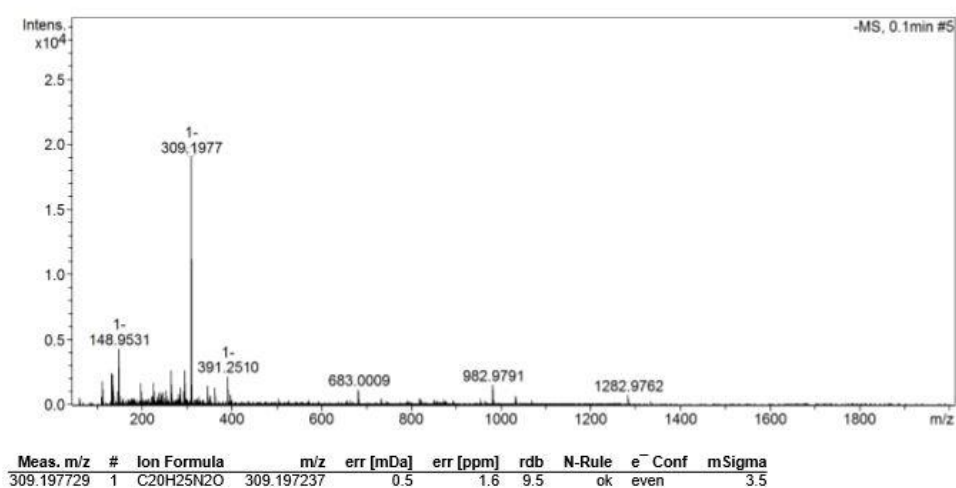


Figure A.4.12 Characterisation of azobenzene photosurfactant **C₈AzoOH** by mass spectrometry.

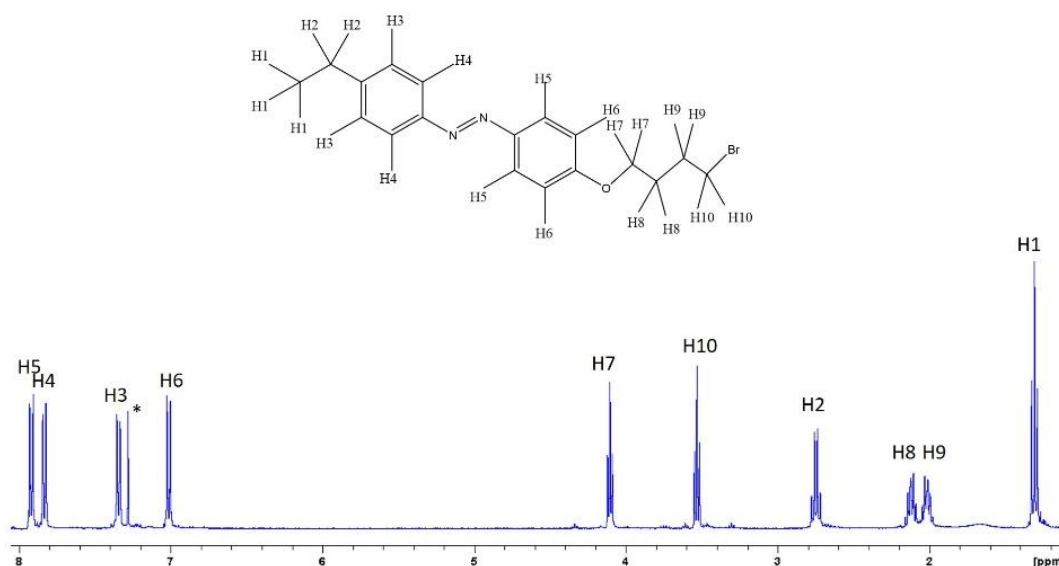


Figure A.4.13 Characterisation of azobenzene photosurfactant **C₂AzoOC₄Br** by ¹H NMR spectroscopy. The asterisk at 7.25 ppm indicates the CDCl₃ solvent peak. The assigned molecular structure is given for comparison with the spectrum.

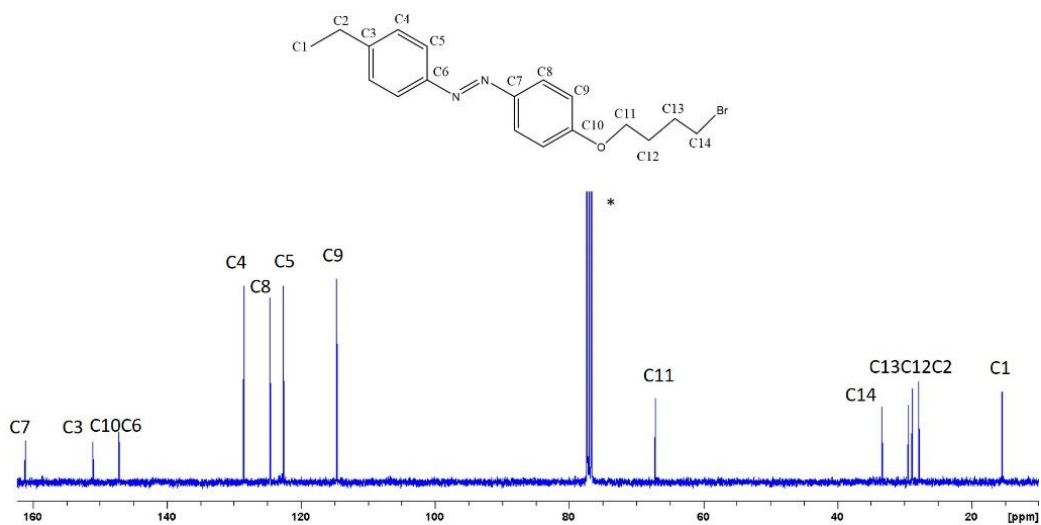


Figure A.4.14 Characterisation of azobenzene photosurfactant **C₂AzoOC₄Br** by ¹³C NMR spectroscopy. The asterisk indicates the CDCl₃ solvent peak. The assigned molecular structure is given for comparison with the spectrum

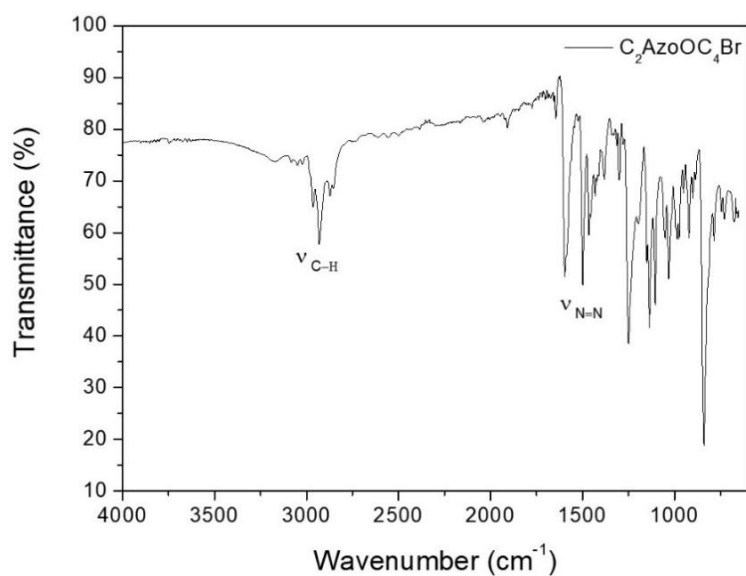


Figure A.4.15 Characterisation of azobenzene photosurfactant **C₂AzoOC₄Br** by FTIR spectroscopy.

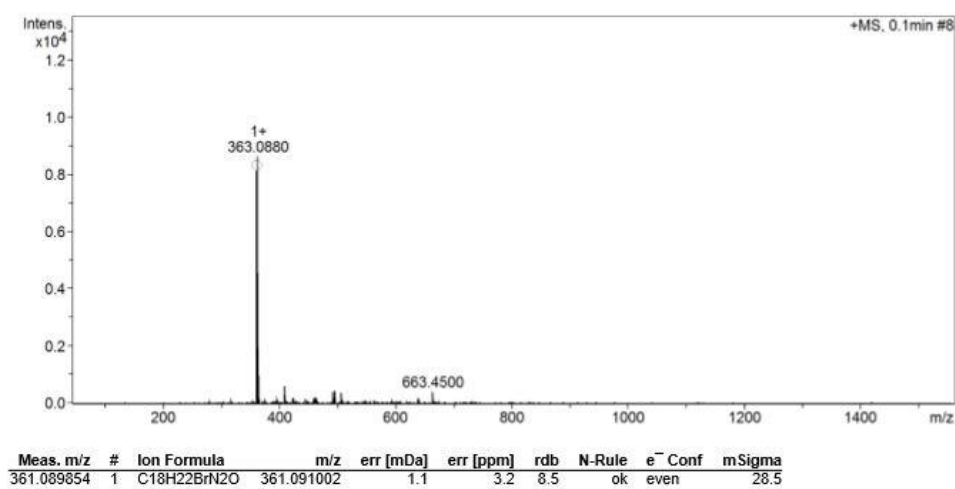


Figure A.4.16 Characterisation of azobenzene photosurfactant **C₂AzoOC₄Br** by mass spectrometry.

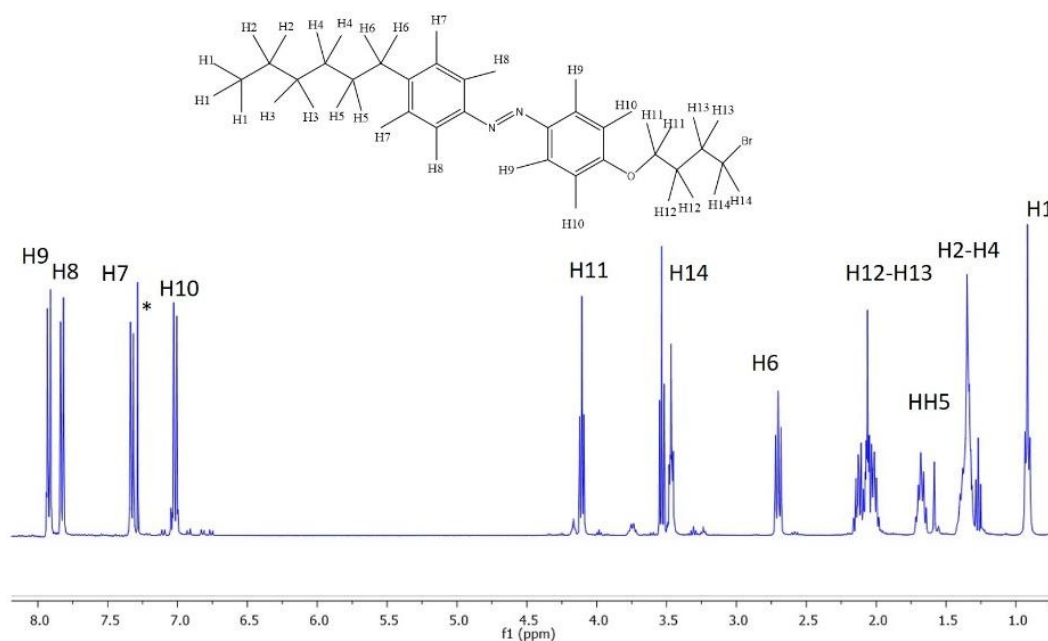


Figure A.4.17 Characterisation of azobenzene photosurfactant **C₆AzoOC₄Br** by ¹H NMR spectroscopy. The asterisk at 7.25 ppm indicates the CDCl₃ solvent peak. The assigned molecular structure is given for comparison with the spectrum.

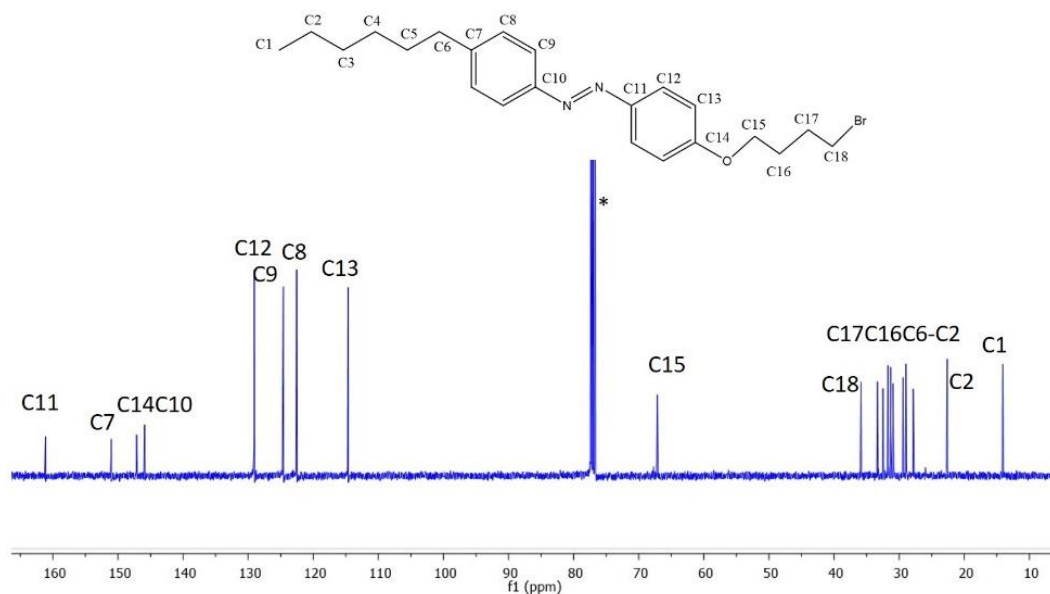


Figure A.4.18 Characterisation of azobenzene photosurfactant **C₆AzoOC₄Br** by ¹³C NMR spectroscopy. The asterisk indicates the CDCl₃ solvent peak. The assigned molecular structure is given for comparison with the spectrum.

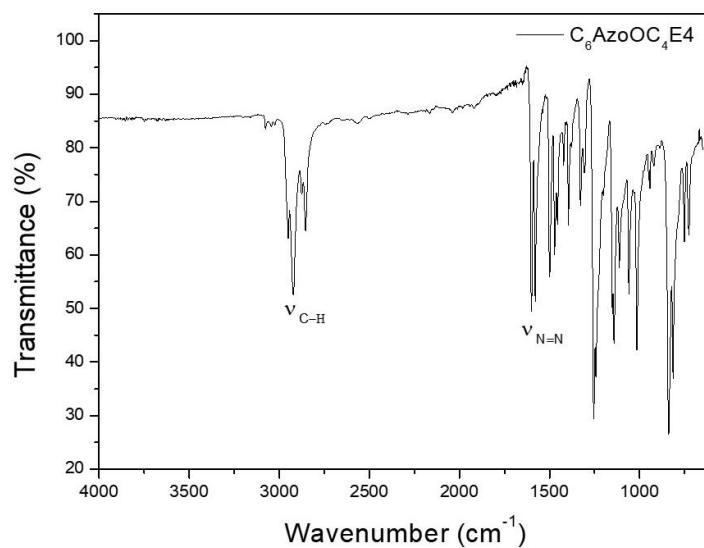


Figure A.4.19 Characterisation of azobenzene photosurfactant **C₆AzoOC₄Br** by FTIR spectroscopy.

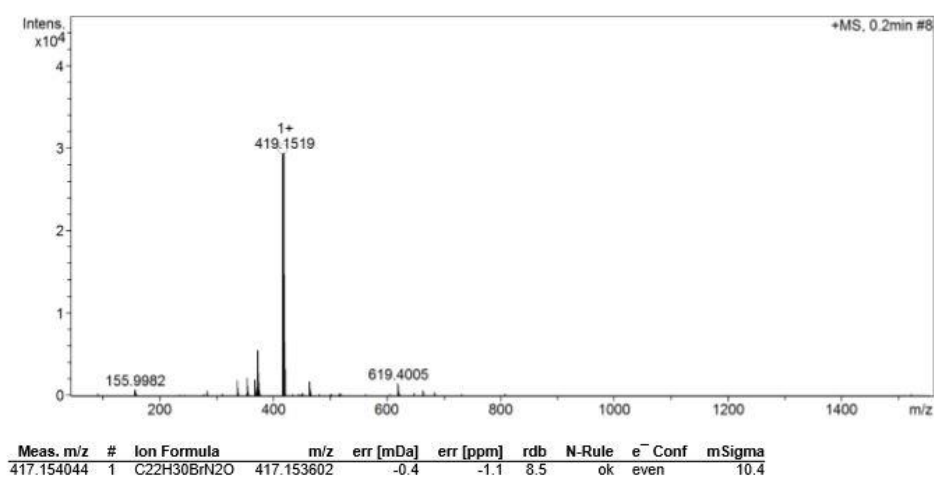


Figure A.4.20 Characterisation of azobenzene photosurfactant **C₆AzoOC₄Br** by mass spectrometry.#

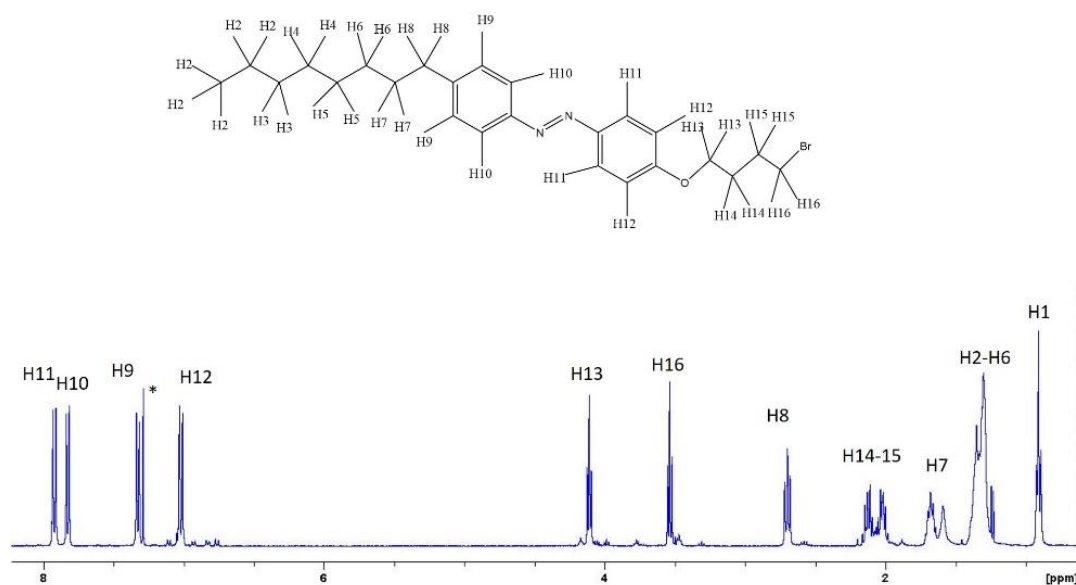


Figure A.4.21 Characterisation of azobenzene photosurfactant **C₈AzoOC₄Br** by ¹H NMR spectroscopy. The asterisk at 7.25 ppm indicates the CDCl₃ solvent peak. The assigned molecular structure is given for comparison with the spectrum.

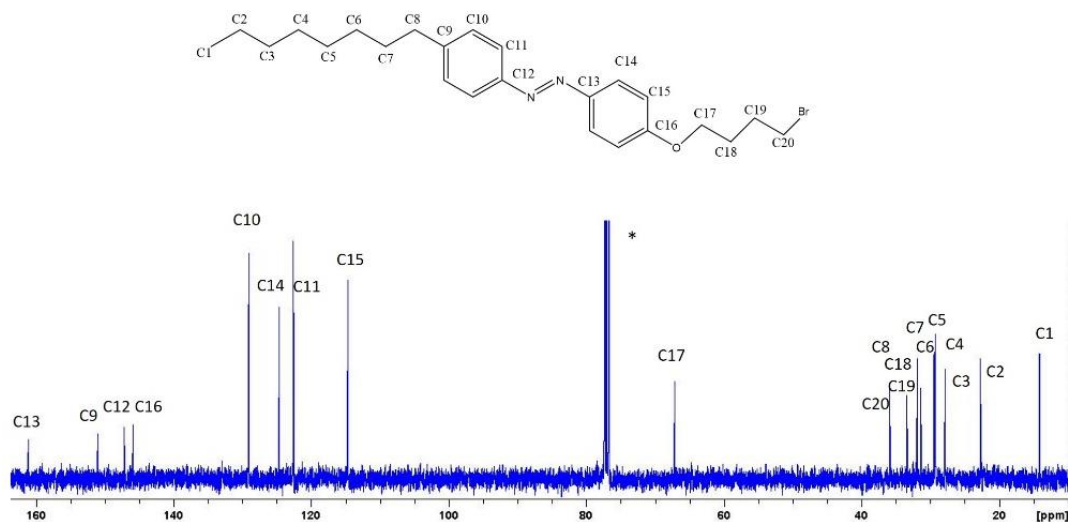


Figure A.4.22 Characterisation of azobenzene photosurfactant **C₈AzoOC₄Br** by ¹³C NMR spectroscopy. The asterisk indicates the CDCl₃ solvent peak. The assigned molecular structure is given for comparison with the spectrum

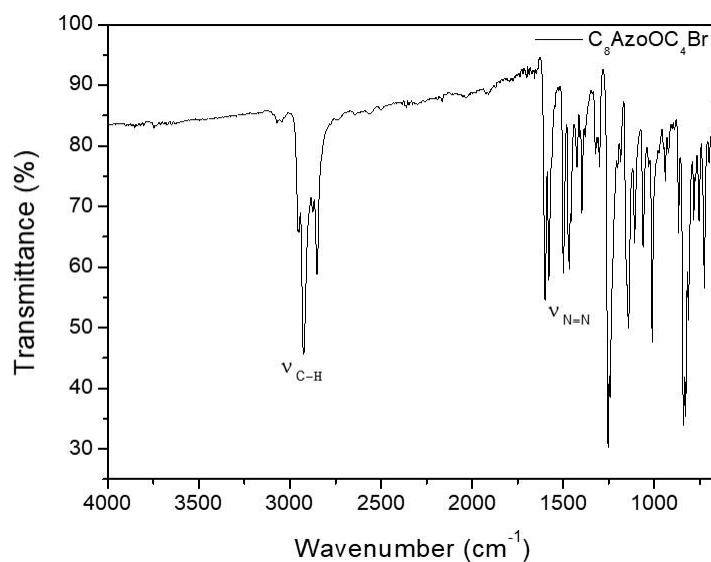


Figure A.4.23 Characterisation of azobenzene photosurfactant **C₈AzoOC₄Br** by FTIR spectroscopy.

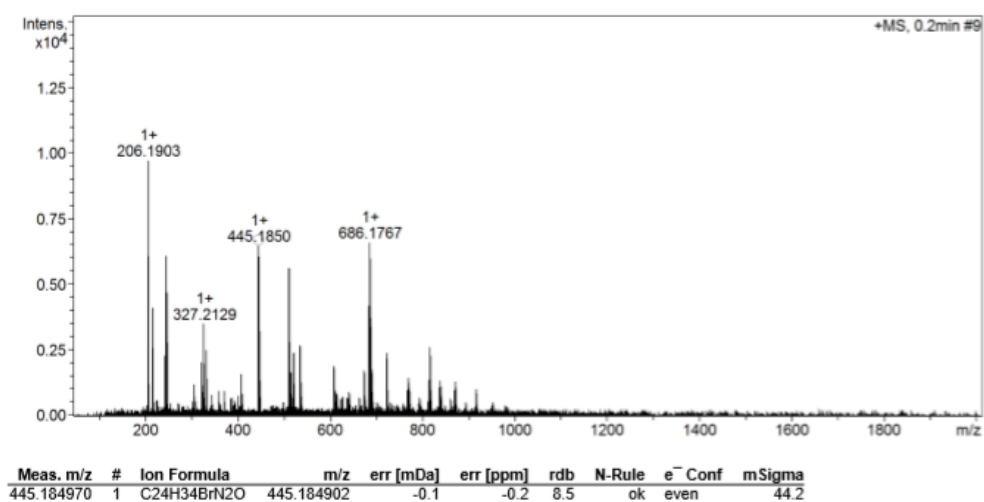


Figure A.4.24 Characterisation of azobenzene photosurfactant **C₈AzoOC₄Br** by mass spectrometry.

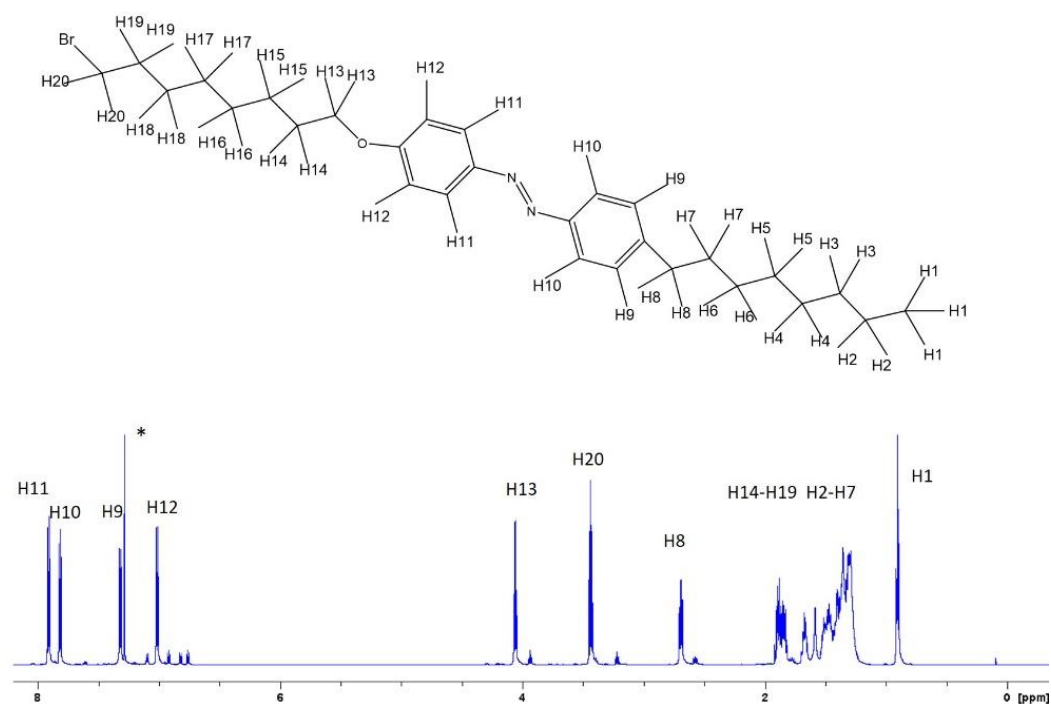


Figure A.4.25 Characterisation of azobenzene photosurfactant **C₈AzoOC₈Br** by ¹H NMR spectroscopy. The asterisk at 7.25 ppm indicates the CDCl₃ solvent peak. The assigned molecular structure is given for comparison with the spectrum.

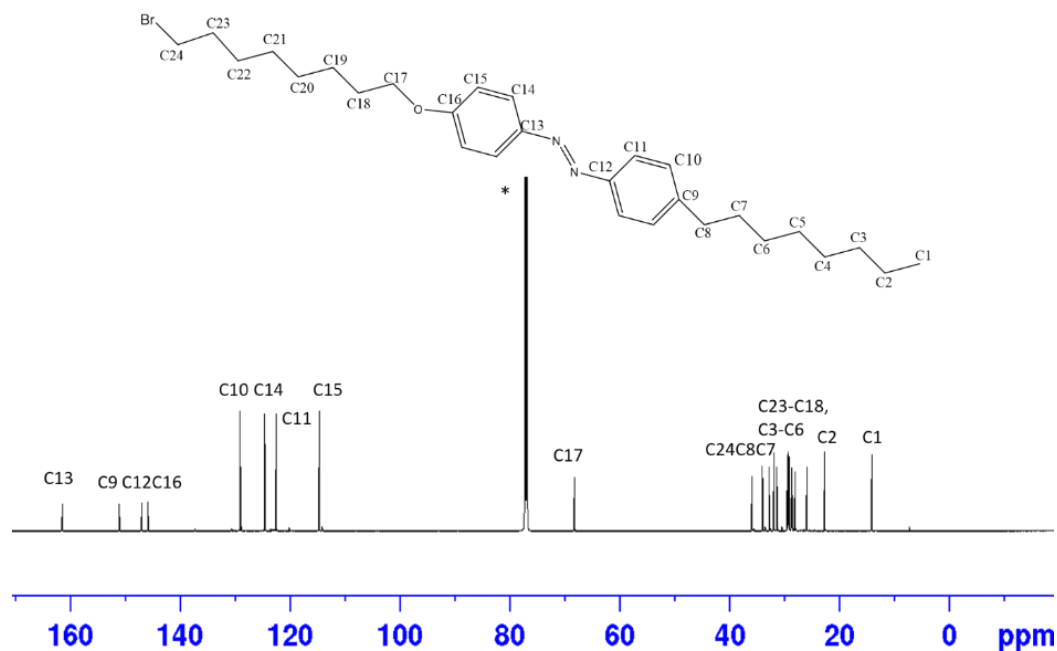


Figure A.4.26 Characterisation of azobenzene photosurfactant **C₈AzoOC₈Br** by ¹³C NMR spectroscopy. The asterisk indicates the CDCl₃ solvent peak. The assigned molecular structure is given for comparison with the spectrum.

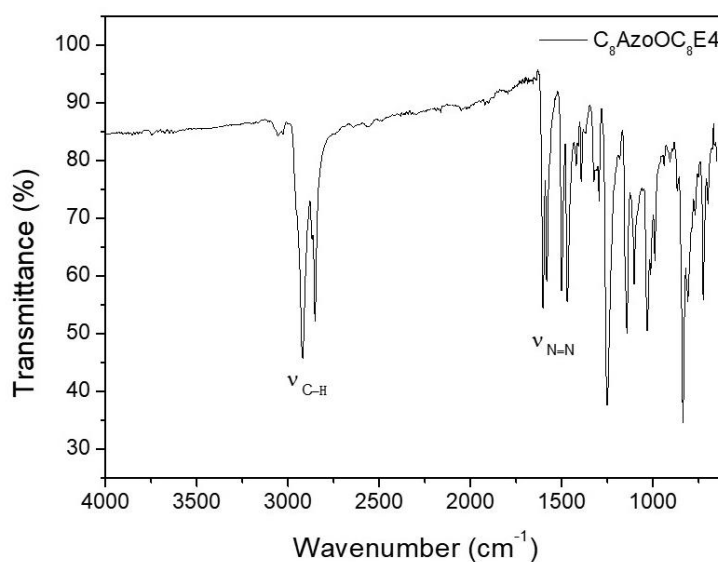


Figure A.4.27 Characterisation of azobenzene photosurfactant **C₈AzoOC₈Br** by FTIR spectroscopy.

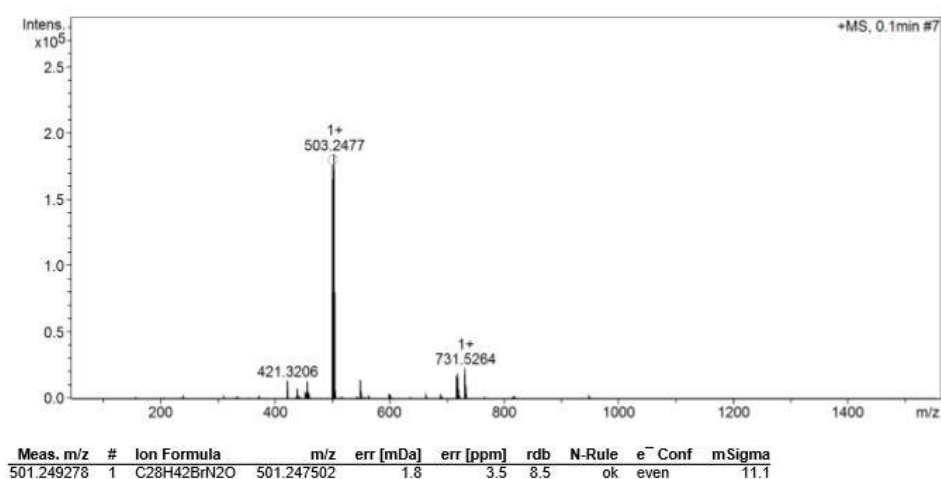


Figure A.4.28 Characterisation of azobenzene photosurfactant **C₈AzoOC₈Br** by mass spectrometry.

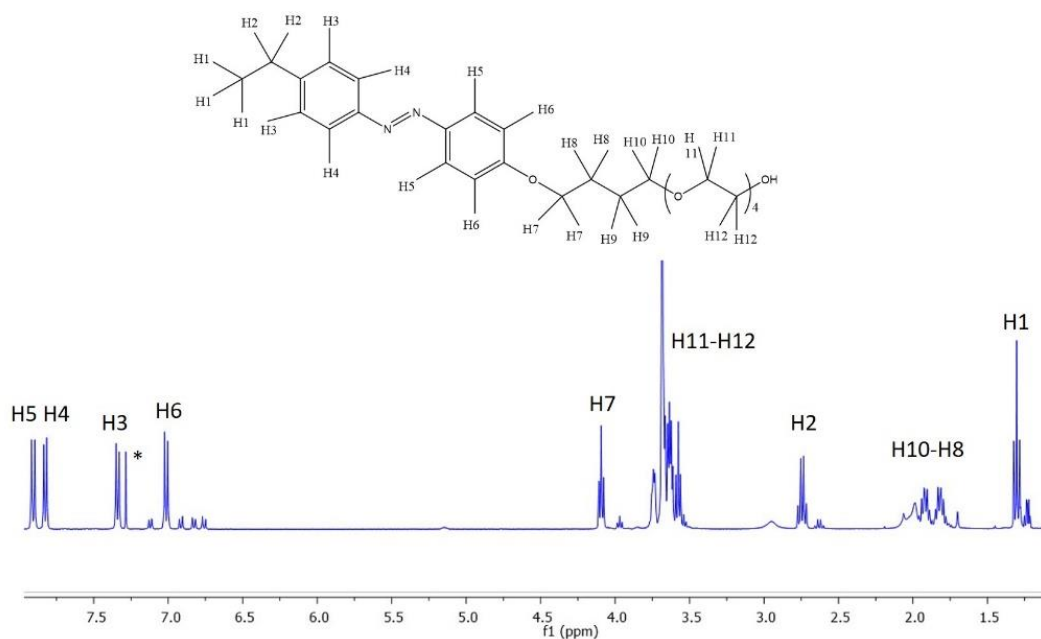


Figure A.4.29 Characterisation of azobenzene photosurfactant **C₂AzoOC₄E₄** by ¹H NMR spectroscopy. The asterisk at 7.25 ppm indicates the CDCl₃ solvent peak. The assigned molecular structure is given for comparison with the spectrum.

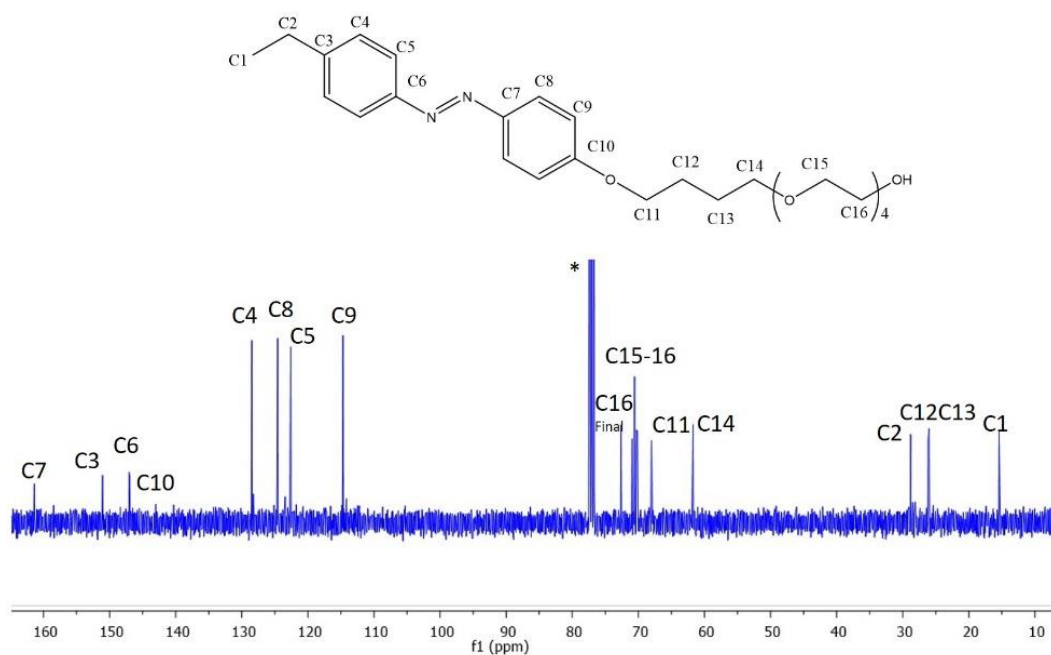


Figure A.4.30 Characterisation of azobenzene photosurfactant **C₂AzoOC₄E₄** by ¹³C NMR spectroscopy. The asterisk indicates the CDCl₃ solvent peak. The assigned molecular structure is given for comparison with the spectrum.

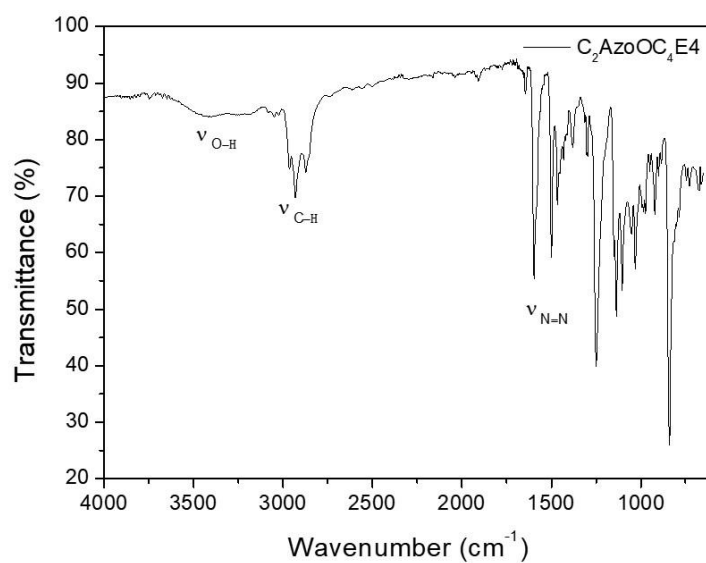


Figure A.4.31 Characterisation of azobenzene photosurfactant **C₂AzoOC₄E₄** by FTIR spectroscopy

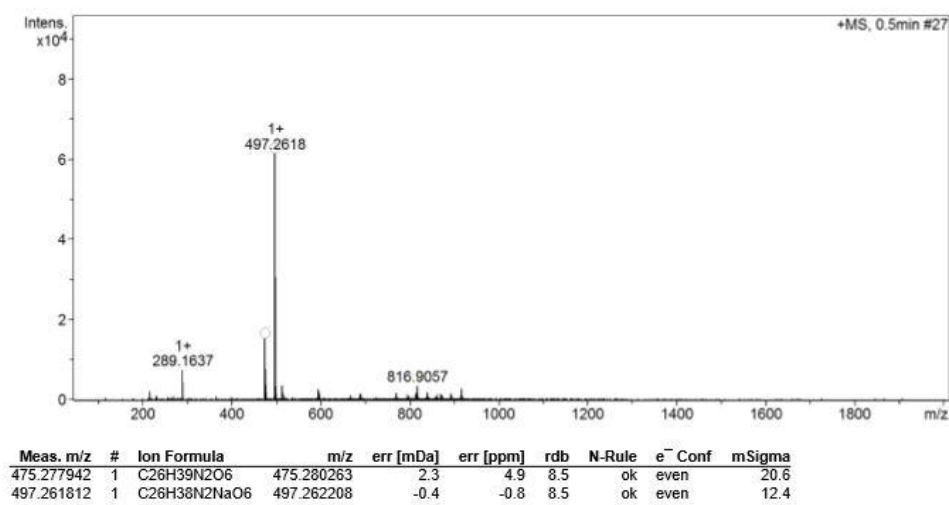


Figure A.4.32 Characterisation of azobenzene photosurfactant **C₂AzoOC₄E₄** by mass spectrometry.

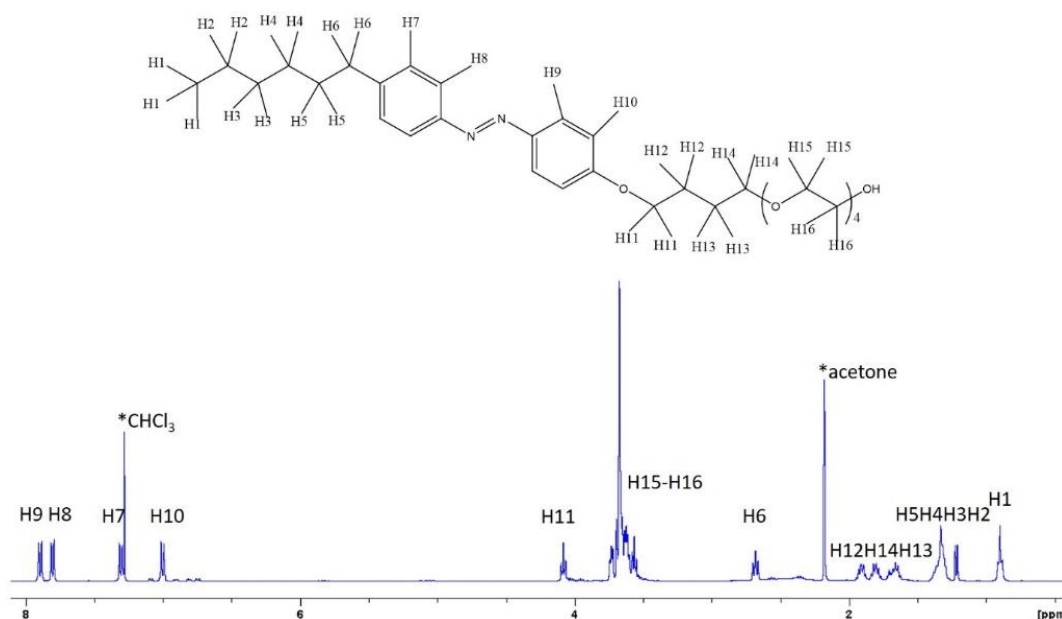


Figure A.4.33 Characterisation of azobenzene photosurfactant **C₆AzoOC₄E₄** by ¹H NMR spectroscopy. The asterisk at 7.25 ppm indicates the CDCl₃ solvent peak and at 2.26 ppm indicates the acetone solvent peak. The assigned molecular structure is given for comparison with the spectrum.

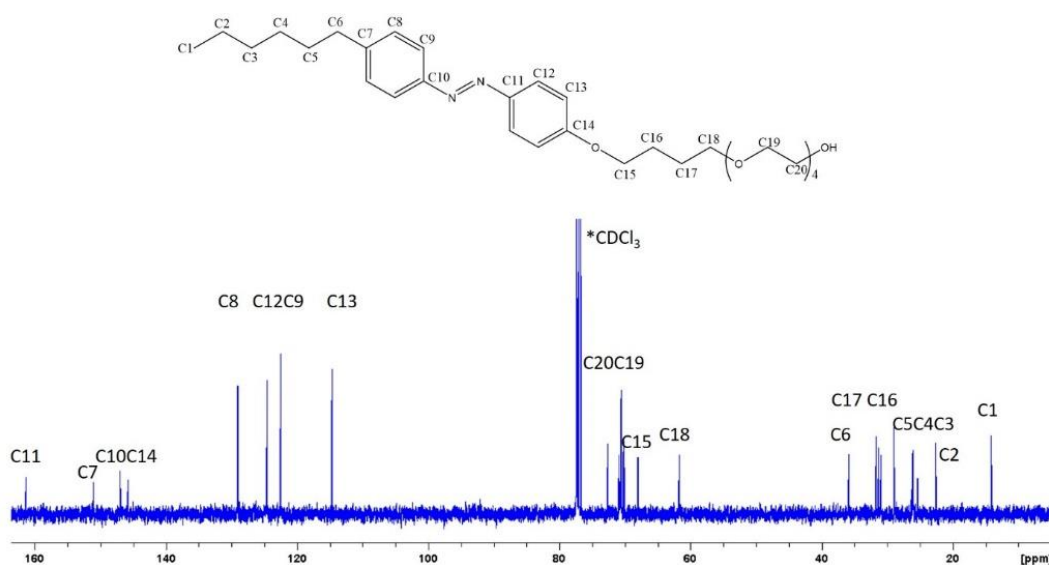


Figure A.4.34 Characterisation of azobenzene photosurfactant **C₆AzoOC₄E₄** by ¹³C NMR spectroscopy. The asterisk indicates the CDCl₃ solvent peak. The assigned molecular structure is given for comparison with the spectrum

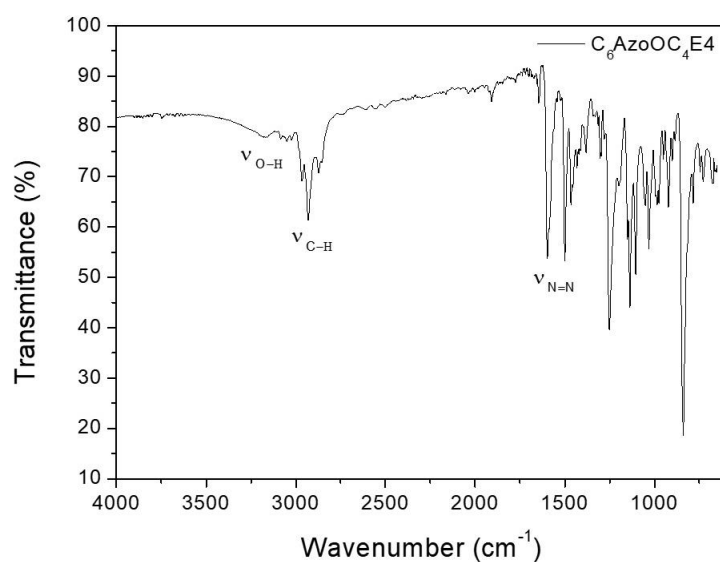


Figure A.4.35 Characterisation of azobenzene photosurfactant **C₆AzoOC₄E₄** by FTIR spectroscopy

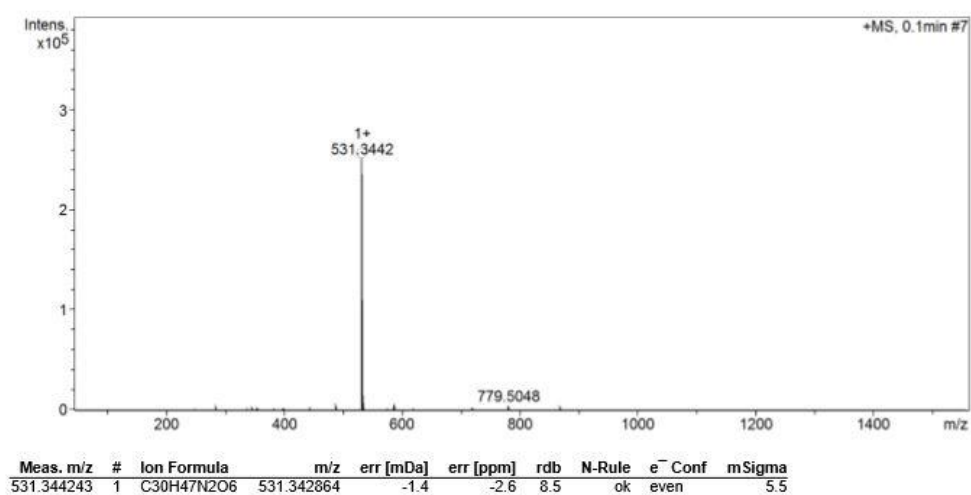


Figure A.4.36 Characterisation of azobenzene photosurfactant **C₆AzoOC₄E₄** by mass spectrometry.

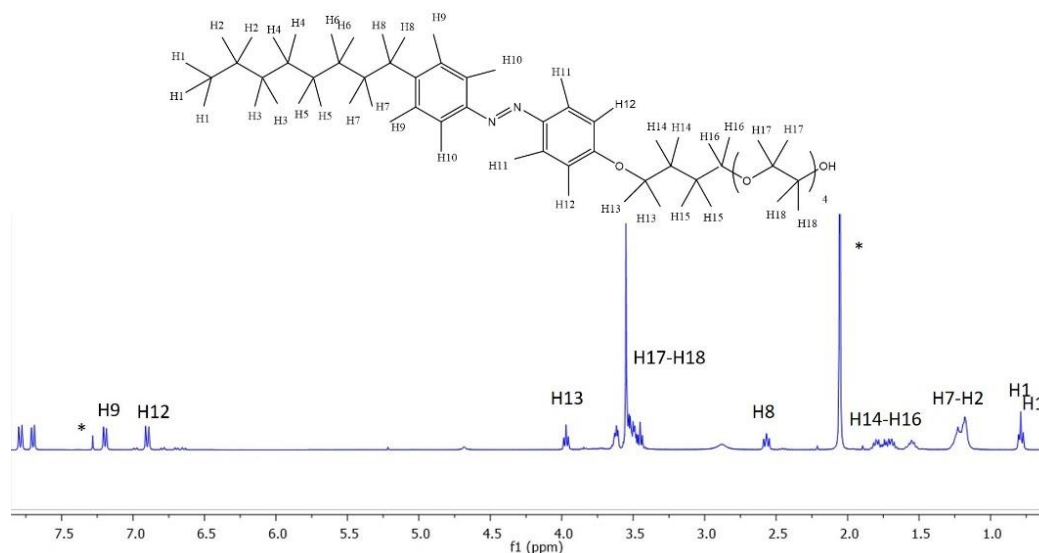


Figure A.4.37 Characterisation of azobenzene photosurfactant **C₈AzoOC₄E₄** by ¹H NMR spectroscopy. The asterisk at 7.25 ppm indicates the CDCl₃ solvent peak and at 2.26 ppm indicates the acetone solvent peak. The assigned molecular structure is given for comparison with the spectrum.

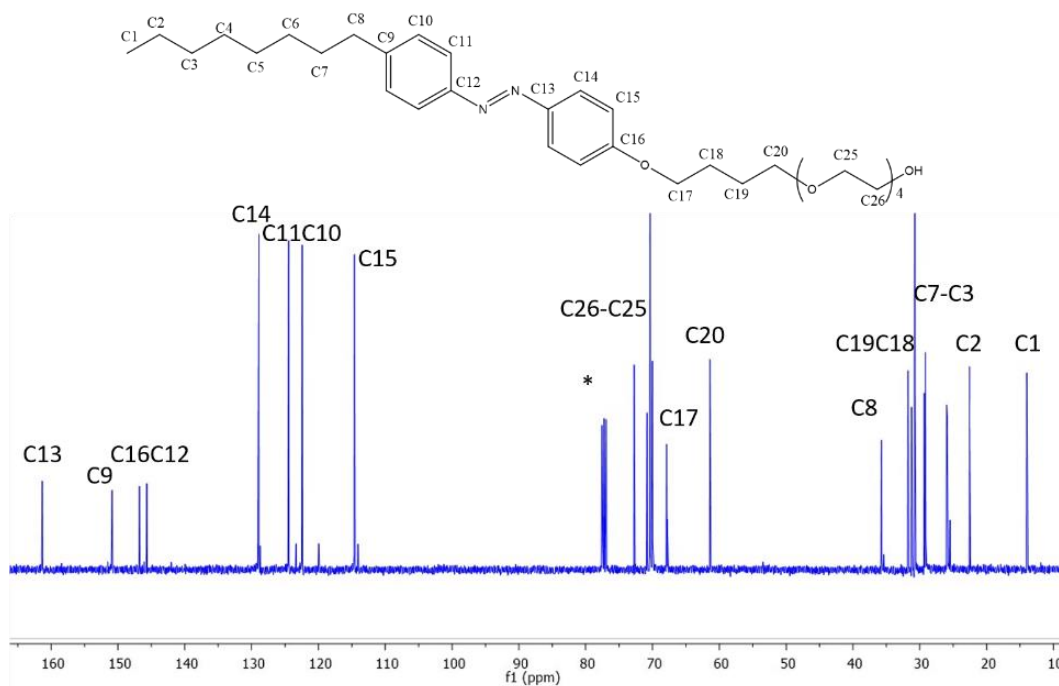


Figure A.4.38 Characterisation of azobenzene photosurfactant **C₈AzoOC₄E₄** by ¹³C NMR spectroscopy. The asterisk indicates the CDCl₃ solvent peak. The assigned molecular structure is given for comparison with the spectrum

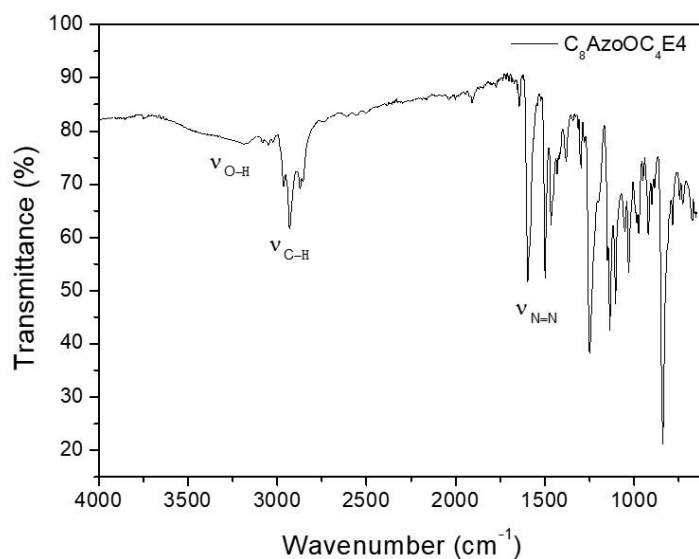


Figure A.4.39 Characterisation of azobenzene photosurfactant **C₈AzoOC₄E₄** by FTIR spectroscopy

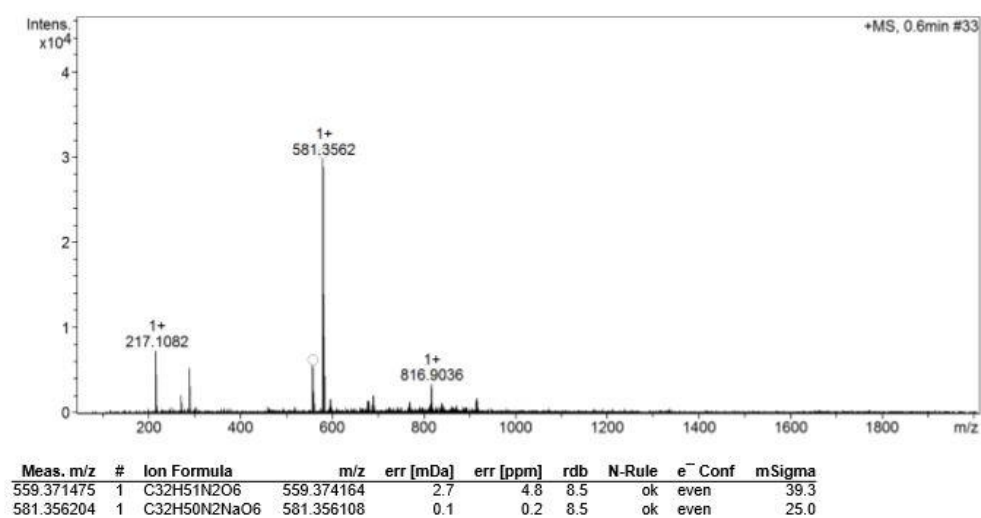


Figure A.4.40 Characterisation of azobenzene photosurfactant **C₈AzoOC₄E₄** by mass spectrometry.

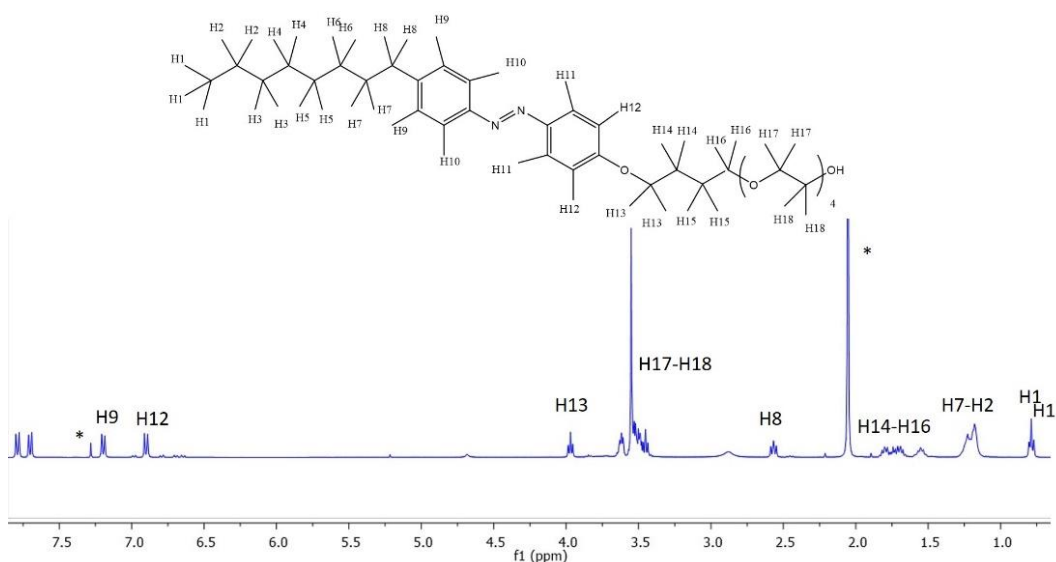


Figure A.4.41 Characterisation of azobenzene photosurfactant **C₈AzoOC₈E₄** by ¹H NMR spectroscopy. The asterisk at 7.25 ppm indicates the CDCl₃ solvent peak and at 2.26 ppm indicates the acetone solvent peak. The assigned molecular structure is given for comparison with the spectrum.

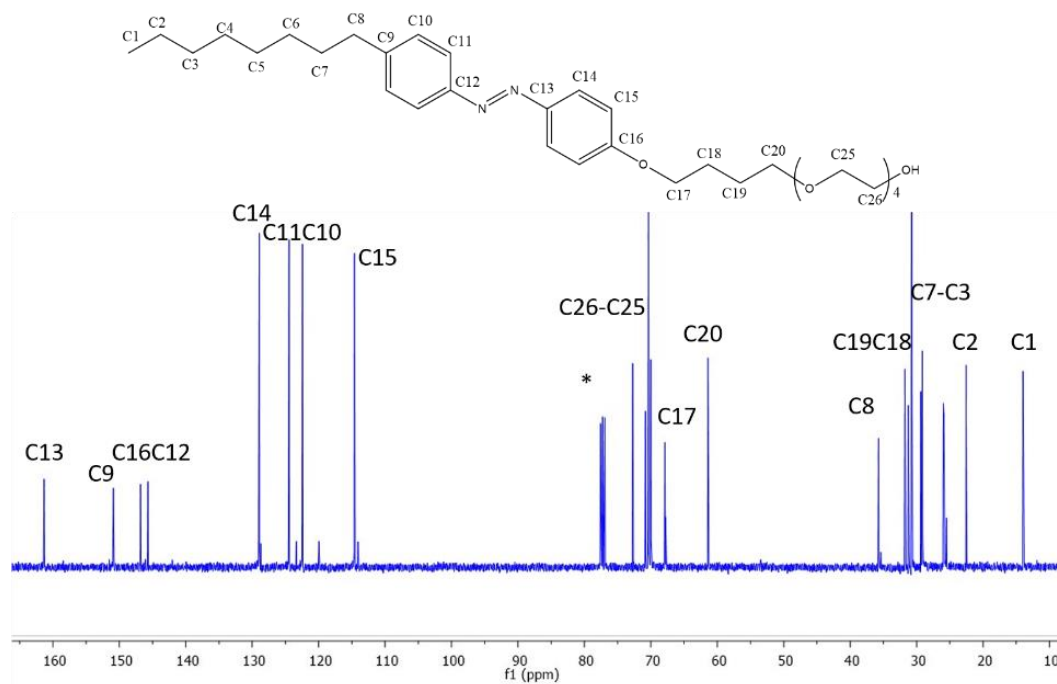


Figure A.4.42 Characterisation of azobenzene photosurfactant **C₈AzoOC₈E₄** by ¹³C NMR spectroscopy. The asterisk indicates the CDCl₃ solvent peak. The assigned molecular structure is given for comparison with the spectrum

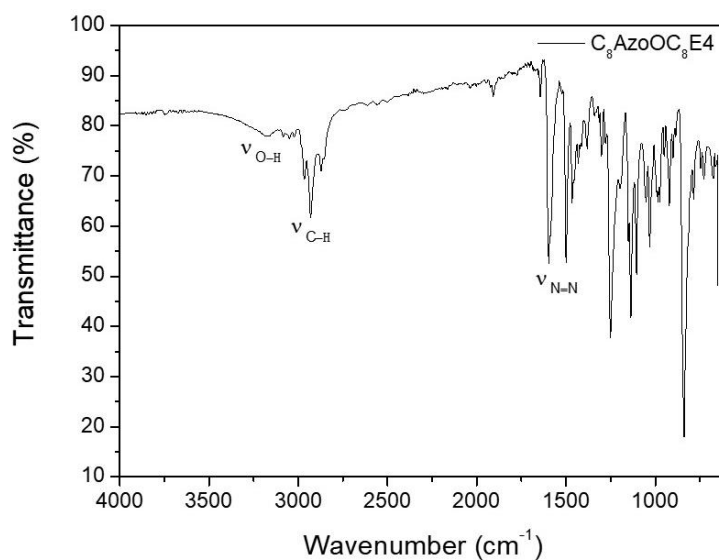


Figure A.4.43 Characterisation of azobenzene photosurfactant **C₈AzoOC₈E₄** by FTIR spectroscopy

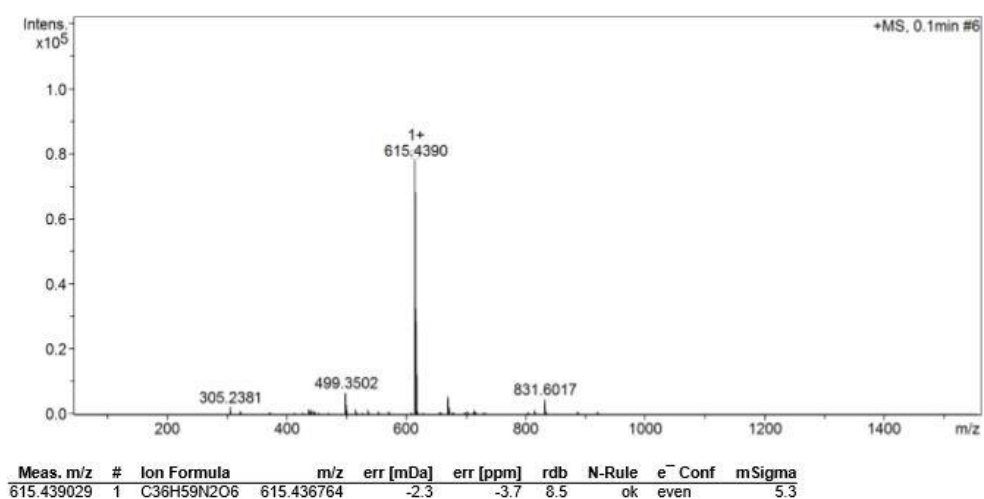


Figure A.4.44 Characterisation of azobenzene photosurfactant **C₈AzoOC₈E₄** by mass spectrometry.

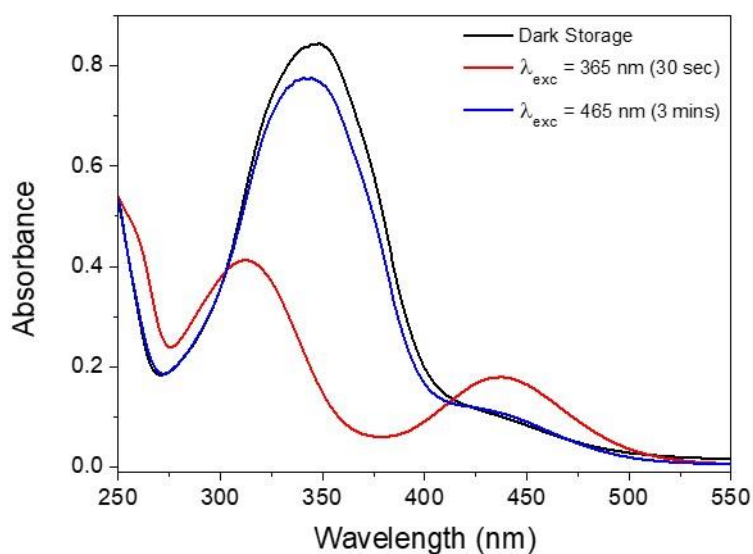


Figure A.4.45 UV-Vis absorption spectra of $C_2AzoOC_4E_4$ in water (0.065 mM) at 20°C. The spectra correspond to the *trans*-form (dark storage, black line), the majority *cis*-photostationary state (after UV irradiation for 30 seconds, red line), and the majority *trans*-photostationary state (blue light illumination, blue line).

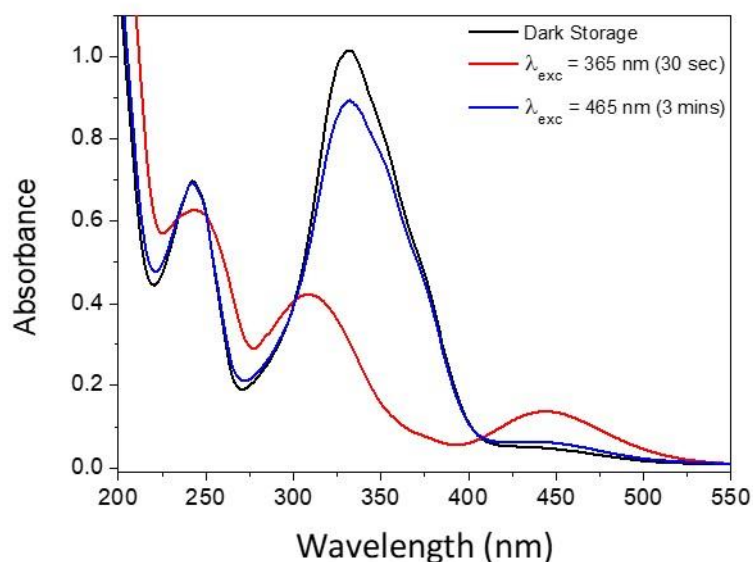


Figure A.4.46 UV-Vis absorption spectra of $C_6AzoOC_4E_4$ in water (0.065 mM) at 20°C. The spectra correspond to the *trans*-form (dark storage, black line), the majority *cis*-photostationary state (after UV irradiation for 30 seconds, red line), and the majority *trans*-photostationary state (blue light illumination, blue line).

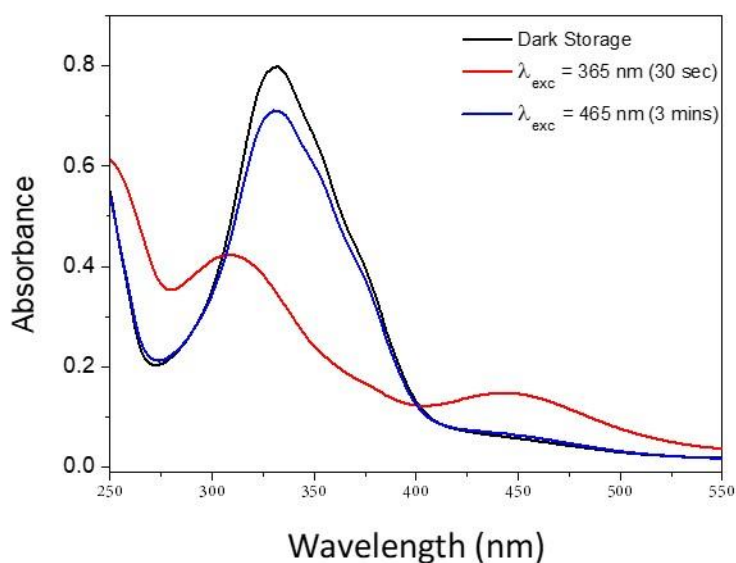


Figure A.4.47 UV-Vis absorption spectra of **C₈AzoOC₈E₄** in water (0.065 mM) at 20°C. The spectra correspond to the *trans*-form (dark storage, black line), the majority *cis*-photostationary state (after UV irradiation for 30 seconds, red line), and the majority *trans*-photostationary state (blue light illumination, blue line).

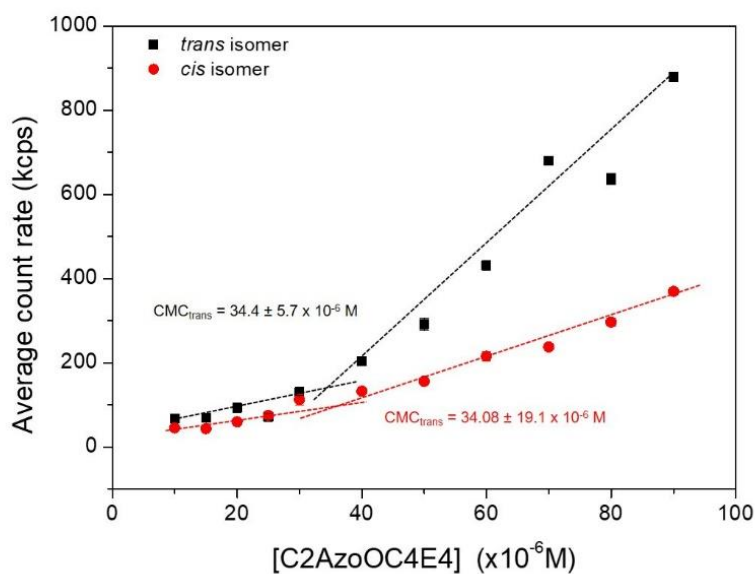


Figure A.4.48 Effect of AzoPS concentration on the intensity of scattered light for an aqueous solution of **C₂AzoOC₄E₄** for both *trans*- and *cis*-isomers at 25 °C. The CMC values are obtained from the intersection between the two linear trend-lines. The error bars show the standard deviation of the mean average count rate obtained over 3 measurements.

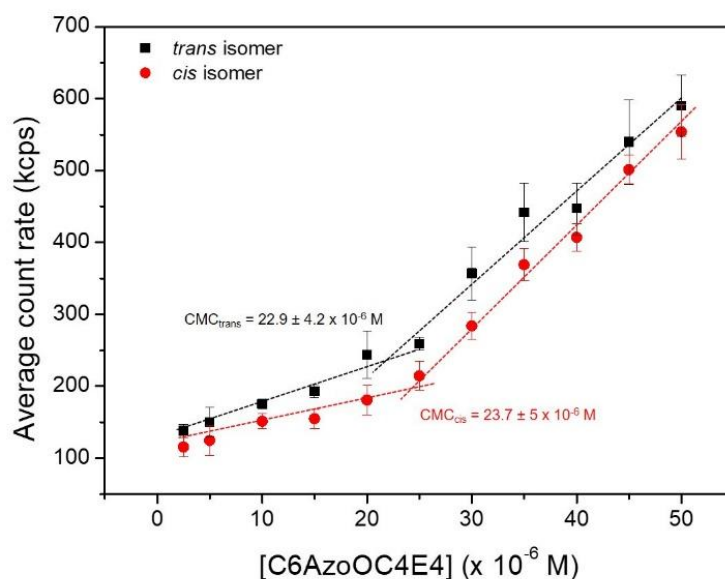


Figure A.4.49 Effect of AzoPS concentration on the intensity of scattered light for an aqueous solution of $C_6AzoOC_4E_4$, for both *trans*- and *cis*-isomers at 25 °C. The CMC values are obtained from the intersection between the two linear trend-lines. The error bars show the standard deviation of the mean average count rate obtained over 3 measurements.

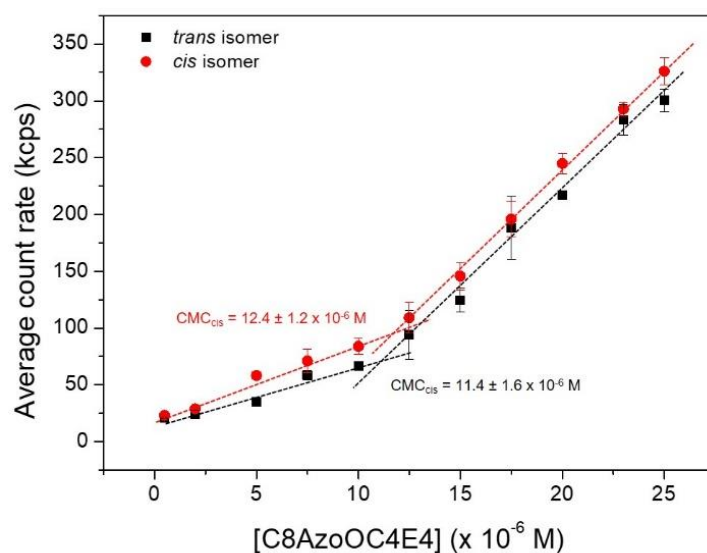


Figure A.4.50 Effect of AzoPS concentration on the intensity of scattered light for an aqueous solution of $C_8AzoOC_4E_4$ for both *trans*- and *cis*-isomers at 25 °C. The CMC values are obtained from the intersection between the two linear trend-lines. The error bars show the standard deviation of the mean average count rate obtained over 3 measurements.

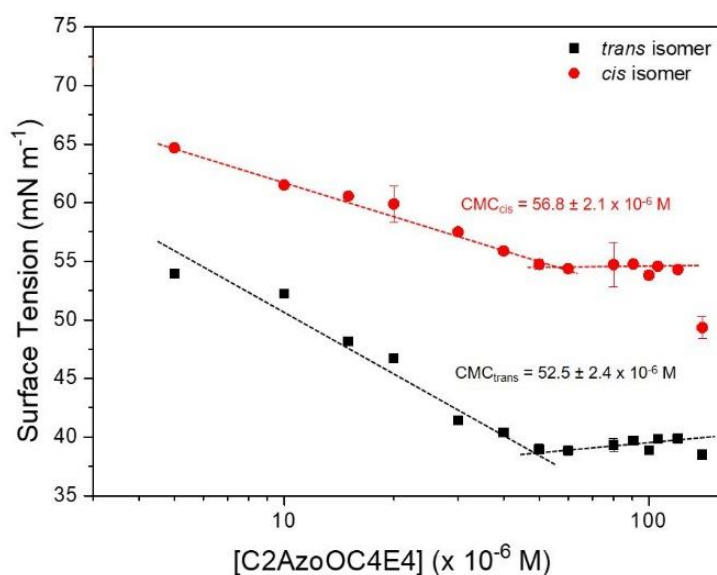


Figure A.4.51 displays the surface tension as a function of concentration for the *trans*- and *cis*-forms of **C₂AzoOC₄E₄** at 25°C. The CMC values are obtained from the intersection between the two linear trend-lines. The error bars show the standard deviation of the mean surface tension obtained over 3 measurements.

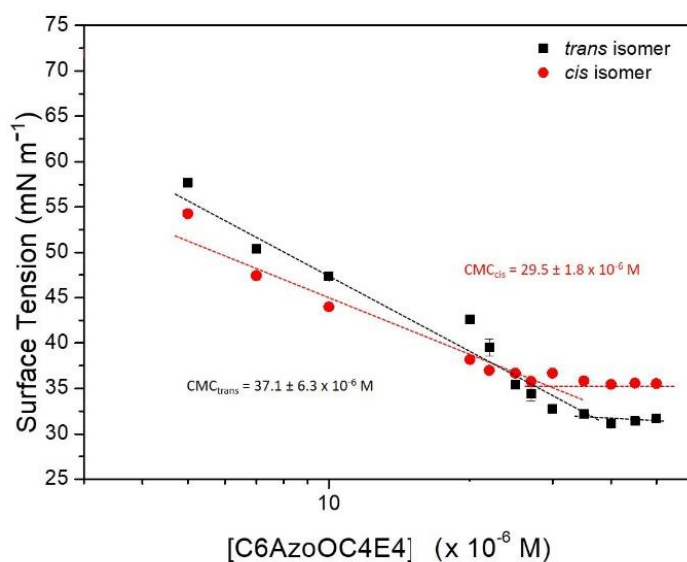


Figure A.4.52 displays the surface tension as a function of concentration for the *trans*- and *cis*-forms of **C₆AzoOC₄E₄** at 25°C. The CMC values are obtained from the intersection between the two linear trend-lines. The error bars show the standard deviation of the mean surface tension obtained over 3 measurements.

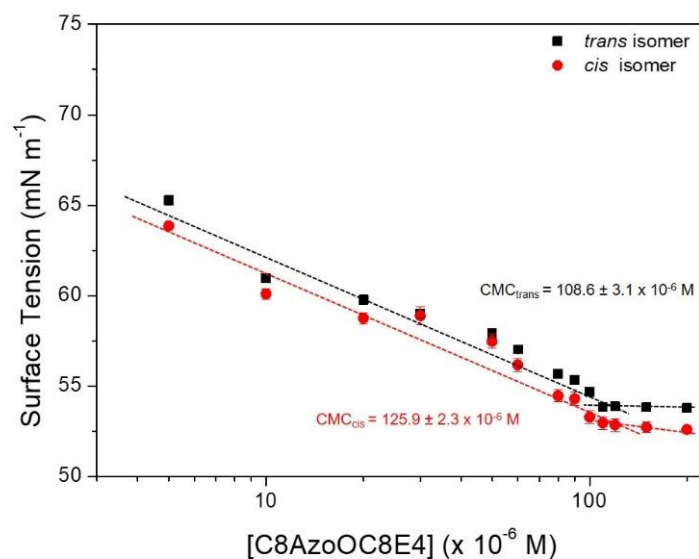


Figure A.4.53 displays the surface tension as a function of concentration for the *trans*- and *cis*-forms of C₈AzoOC₄E₄ at 25°C. The CMC values are obtained from the intersection between the two linear trendlines. The error bars show the standard deviation of the mean surface tension obtained over 3 measurements.

Appendix to Chapter 5

Table A.5.1 Values used for the calculation of the lengths of the azobenzene-based tail of each AzoPS.¹

Component	Length (Å)
<i>trans</i> -azobenzene	21.9
-CH ₂ -	1.54
-CH ₃	1.54
-O-	1.2

- (1) Xing, L.; Mattice, W. L. *Langmuir* **1996**, 12 (6), 3024.

Appendix to Chapter 6

Table A.6.1 Mole percent and concentration of both TPE-SDS and SDS in each of the four mixed surfactant solutions, SDS-AIE- X ($X = 10 - 70$). Samples of analogous concentrations were made using d_{25} -SDS and labelled d_{25} -SDS-AIE- X ($X = 10 - 70$).

Sample	Mole Percent TPE-SDS	Mole Percent (d_{25})-SDS	Concentration TPE-SDS (mmol L^{-1})	Concentration (d_{25})-SDS (mmol L^{-1})
(d_{25})-SDS-AIE-10	10	90	1.5	14.0
(d_{25})-SDS-AIE-20	20	80	2.8	11.0
(d_{25})-SDS-AIE-50	50	50	5.4	5.4
(d_{25})-SDS-AIE-70	70	30	6.6	2.8

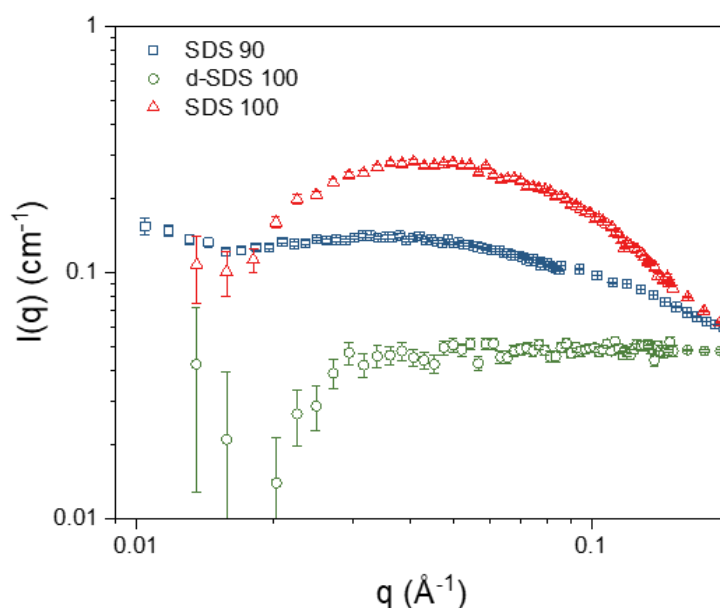


Figure A.6.1 SANS scattering profiles for SDS and d-SDS. SDS 90 (red, 14 mmol L^{-1}) is SDS at the same concentration as SDS in SDS-AIE-10. SDS 100 is 100% SDS (blue, 17 mmol L^{-1}), with d-SDS being its deuterated counterpart (green, 17 mmol L^{-1}). These scattering profiles are characteristic of ellipsoidal micelles,¹ with interparticle interactions also observed for SDS 100 (pronounced hump).¹⁻³ As expected, d-SDS has very little scattering intensity, due to being contrast matched with the solvent.

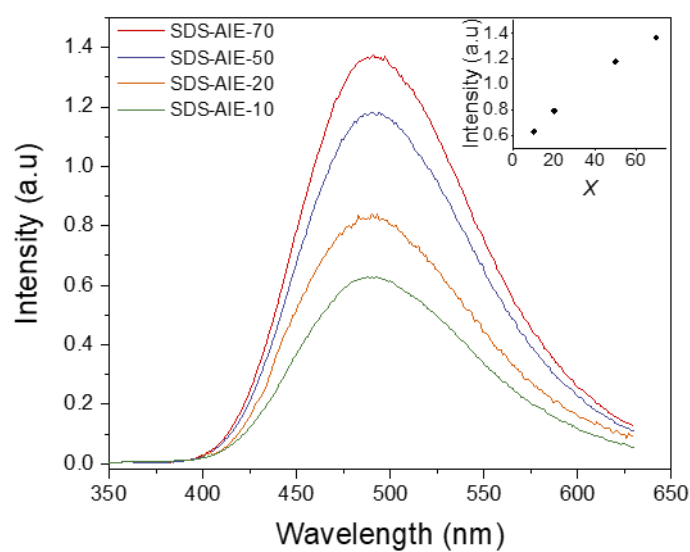


Figure A.6.2 Emission spectra for SDS-AIE- X , where $X = 70$ (red), 50 (blue), 20 (orange), 10 (green). These samples were diluted by a factor of 25 relative to the SANS samples. $\lambda_{\text{ex}} = 320$ nm, slit widths = 2.6 nm