The Synthesis and Characterisation of Photoactive Materials and Their Use in Fluidic Transport Systems

Yang Xiao
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The Synthesis and Characterisation of Photoactive Materials and Their Use in Fluidic Transport Systems

Yang Xiao

Supervisors:
Professor David L. Officer and Dr Pawel Wagner

This thesis is presented as part of the requirement for the conferral of the degree:

Doctor of Philosophy

University of Wollongong
Australian Institute for Innovative Materials
Intelligent Polymer Research Institute

October 2019
Abstract

The controlled movement of droplets through another immiscible liquid has the potential to impact on a diverse range of applications, from the study of biological and fluidic chemical transport to microreactor development and localised chemical reactions. Based on the Marangoni effect, control of motion can be realised by creating tension gradients through the external stimuli such as chemical, temperature and light. Among all the manipulation methods, light control is flexible and contactless and can be easily realised by using photoactive materials either in the external environment or in the droplet itself. Reports of the use of photoactive materials in the external environment to create gradients have shown limited control of droplet motion. The use of photoactive materials in the droplet had the potential to be a promising way to realise better control. However, it has scarcely been reported due to the difficulty in finding appropriate photoactive materials for the construction of such motion systems.

This dissertation focused on the synthesis and characterisation of photoactive materials and their application in photocontrolled droplet motion systems. The photoactive materials mostly used in this thesis were based on spiropyran/merocyanine photoisomers. However, throughout the study, other materials like phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide and 2-nitrobenzaldehyde were also found to be applicable, opening a wider field of the research. Depending on the solubility of the photoactive materials, two types of droplet motion systems, that is, organic droplets in water (oil-in-water) and water droplets in organic medium (water-in-oil), were developed.

In order to investigate the potential of acidic merocyanines, a series of merocyaninesulphonic acids were synthesised and characterised, most of which were able to act as photoacids to decrease pH by 0.3 to 1.5 pH units under light illumination. These photoacids were so sensitive to base that they could be easily deprotonated in organic solvents to generate spiropyrans via highly coloured merocyanine intermediates. Based on this, a basic gas sensor was developed to detect gaseous base.
A photoactive organic droplet was developed by dissolving a spiropyran (SPCH$_2$CH$_2$OH) in organic solvents to create an oil-in-water system. The resulting SPCH$_2$CH$_2$OH droplet moved away from 365 nm light and then towards 405 nm light in the presence of the surfactant sodium dodecylbenzenesulphonate. The motion could largely be promoted by acid either in the aqueous phase or in the droplet. With the aid of acid, the total distance could reach 2817 mm and the maximum velocity 14.9 mm/s.

Without the presence of surfactant, the SPCH$_2$CH$_2$OH droplet moved towards 365 nm light with a velocity of 3.3 mm/s and only a distance of 24 mm. In order to improve the performance of motion in DI water, a protonated merocyanine/surfactant salt (MCH$^+$DBS$^-$) was prepared from SPCH$_2$CH$_2$OH and 4-dodecylbenzenesulphonic acid and used to construct the photoactive droplets. The resulting MCH$^+$DBS$^-$ droplet moved towards 365 nm light or 405 nm light in DI water with a speed of up to 15.8 mm/s and a distance of 315 mm.

In order to develop a water-in-oil system for droplet motion, MC$_8$H$^+$SO$_3^-$, a water soluble merocyaninesulphonic acid synthesised at the beginning as a photoacid, was used. The MC$_8$H$^+$SO$_3^-$ aqueous droplet moved towards 405 nm light in fatty alcohols with a velocity up to 7 mm/s and a distance of 52 mm.

Marangoni flows resulting from changes of interfacial tension (IFT) were clearly observed during the conducted experiments and were recorded on movies. It was found that when light irradiation decreased IFT in the illuminated part at the droplet/water interface, the droplet moved towards light. In contrast, when light irradiation increased IFT, the droplet moved away from light. By adjusting the density of droplet or the medium, 3D movement was realised and based on this, the driving force provided by light illumination was measured and calculated, which was on the scale of nN to µN.

These photocontrolled droplet motion systems were used for the controlled transport of encapsulated particles, delivery of chemicals to precisely initiate chemical reactions, as well as the transportation of liquid in tubes, which opened up new ways for light-controlled cargo transport and light-driven pumps in...
microfluidics and have great potential to emulate the biological transport and motion process in nature.
Acknowledgments

I would like to thank my supervisors Professor David L. Officer and Dr Pawel Wagner for their invaluable guidance and support in my PhD study. Special thanks go to Dr Klaudia Wagner for her assistance and encouragement throughout my progress.

Many thanks to the staff and students of IPRI and ACES. My research would have been impossible without the aid and support from them. I would especially like to thank Professor Geoffrey Spinks for the fruitful discussions in theoretical calculations, Dr Sanjeev Gambhir for his help in graphite particles preparation, Dr Simone Ciampi for his advice on organic synthesis, Dr Paul Molino for his support in biological application, Dr Patricia Hayes for her help in the instruments training, and Ms Sara Zarghami and other colleagues for their assistance in the laboratory.

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Last but not least, I wish to express my heartfelt thanks to my parents, my brother and my girlfriend for their extended support and encouragement all the time.
Publications and Presentations

Publications


Manuscripts in preparation


Conference Presentations (Poster)


I, Yang Xiao, declare that this thesis submitted in fulfilment of the requirements for the conferral of the degree of Doctor of Philosophy from the University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. This document has not been submitted for qualifications at any other academic institution.

Yang Xiao

October 2019
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<table>
<thead>
<tr>
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<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>Degree celsius</td>
</tr>
<tr>
<td>$^{13}$C NMR</td>
<td>Carbon-13 nuclear magnetic resonance</td>
</tr>
<tr>
<td>$^1$H NMR</td>
<td>Proton nuclear magnetic resonance</td>
</tr>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three-dimensional</td>
</tr>
<tr>
<td>Abs</td>
<td>Absorption</td>
</tr>
<tr>
<td>BAPO</td>
<td>Phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide</td>
</tr>
<tr>
<td>BPB</td>
<td>Bromophenol blue</td>
</tr>
<tr>
<td>cm</td>
<td>Centimetre</td>
</tr>
<tr>
<td>CMC</td>
<td>Critical micelle concentration</td>
</tr>
<tr>
<td>conc</td>
<td>Concentrated</td>
</tr>
<tr>
<td>COSY</td>
<td>Two-dimensional correlation spectroscopy</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyltrimethylammonium bromide</td>
</tr>
<tr>
<td>DBSA</td>
<td>4-Dodecylbenzenesulphonic acid</td>
</tr>
<tr>
<td>DCE</td>
<td>1,2-Dichloroethane</td>
</tr>
<tr>
<td>DCM</td>
<td>Dichloromethane</td>
</tr>
<tr>
<td>DI water</td>
<td>Deionised water</td>
</tr>
<tr>
<td>DMN</td>
<td>2-[4-(Dimethylamino)benzylidene]malononitrile</td>
</tr>
<tr>
<td>DMSO</td>
<td>Dimethyl sulphoxide</td>
</tr>
<tr>
<td>$E$</td>
<td>Entgegen (German) – opposite</td>
</tr>
<tr>
<td>equiv</td>
<td>Equivalent</td>
</tr>
<tr>
<td>ESI-MS</td>
<td>Electrospray ionization mass spectrometry</td>
</tr>
<tr>
<td>$F_b$</td>
<td>Buoyancy force</td>
</tr>
<tr>
<td>$F_i$</td>
<td>Irradiation force</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier transform infrared</td>
</tr>
<tr>
<td>$F_v$</td>
<td>Viscous force</td>
</tr>
<tr>
<td>$G$</td>
<td>Gravity</td>
</tr>
<tr>
<td>$g$</td>
<td>Gravitational acceleration</td>
</tr>
<tr>
<td>$h$</td>
<td>Hour</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>HDA</td>
<td>2-Hexyldecanoic acid</td>
</tr>
<tr>
<td>HMBC</td>
<td>Two-dimensional heteronuclear multiple-bond correlation spectroscopy</td>
</tr>
<tr>
<td>HSQC</td>
<td>Two-dimensional heteronuclear single-quantum correlation spectroscopy</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>IFT, $\gamma$</td>
<td>Interfacial tension</td>
</tr>
<tr>
<td>$\Delta \gamma$</td>
<td>Interfacial tension change</td>
</tr>
<tr>
<td>$\nabla \gamma$</td>
<td>Interfacial tension gradient</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>$L$</td>
<td>Liter</td>
</tr>
<tr>
<td>$M$</td>
<td>Molar</td>
</tr>
<tr>
<td>MALDI</td>
<td>Matrix assisted laser desorption ionisation</td>
</tr>
<tr>
<td>MC</td>
<td>Merocyanine</td>
</tr>
<tr>
<td>$\text{MCH}^+$</td>
<td>Protonated merocyanine</td>
</tr>
<tr>
<td>$\text{MCH}^+\text{SO}_3^-$</td>
<td>Merocyaninesulphonic acid</td>
</tr>
<tr>
<td>MGCB</td>
<td>Malachite green carbinol base</td>
</tr>
<tr>
<td>MHz</td>
<td>Megahertz</td>
</tr>
<tr>
<td>$\text{min}$</td>
<td>Minute</td>
</tr>
<tr>
<td>$\text{mm}$</td>
<td>Millimetre</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>mM</td>
<td>Millimolar</td>
</tr>
<tr>
<td>mN</td>
<td>Millinewton</td>
</tr>
<tr>
<td>mol</td>
<td>Mole</td>
</tr>
<tr>
<td>mW</td>
<td>Milliwatt</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>NBA</td>
<td>2-Nitrobenzaldehyde</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>nN</td>
<td>Nanonewton</td>
</tr>
<tr>
<td>NSBA</td>
<td>2-Nitrosobenzoic acid</td>
</tr>
<tr>
<td>oil-in-water</td>
<td>Organic droplets in water</td>
</tr>
<tr>
<td>p</td>
<td>Momentum</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts per million</td>
</tr>
<tr>
<td>R</td>
<td>Radius</td>
</tr>
<tr>
<td>s</td>
<td>Second</td>
</tr>
<tr>
<td>SDBS</td>
<td>Sodium dodecylbenzenesulphonate</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulphate</td>
</tr>
<tr>
<td>SP</td>
<td>Spiropyran</td>
</tr>
<tr>
<td>SPH⁺</td>
<td>Protonated spiropyran</td>
</tr>
<tr>
<td>SPSO₃H</td>
<td>Spiropyansulphonic acid</td>
</tr>
<tr>
<td>STAC</td>
<td>Trimethyloctadecylammonium chloride</td>
</tr>
<tr>
<td>TEA</td>
<td>Triethylamine</td>
</tr>
<tr>
<td>TMS</td>
<td>Tetramethylsilane</td>
</tr>
<tr>
<td>TOF-MS</td>
<td>Time-of-flight mass spectrometry</td>
</tr>
<tr>
<td>UV/Vis</td>
<td>Ultraviolet/visible</td>
</tr>
</tbody>
</table>
\begin{align*}
\nu & \quad \text{Velocity} \\
\text{V} & \quad \text{Volume} \\
\text{v/v} & \quad \text{Volume/volume} \\
\text{water-in-oil} & \quad \text{Water droplets in organic medium} \\
\text{wt} & \quad \text{Weight} \\
\text{Z} & \quad \text{Zusammen (German) – together} \\
\text{\(\mu\)N} & \quad \text{Micronewton} \\
\rho & \quad \text{Density}
\end{align*}
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MC₆H⁺SO₃⁻ (cyan), MC₇H⁺SO₃⁻ (magenta), MC₈H⁺SO₃⁻ (purple) in DMSO (3×10⁻⁵ M): (b) just prepared and then (c) illuminated by 365 nm light for 10-30 s.

Figure 3.11 UV/Vis spectra of merocyaninesulphonic acids MC₁H⁺SO₃⁻ (black), MC₂H⁺SO₃⁻ (red), MC₃H⁺SO₃⁻ (blue), MC₄H⁺SO₃⁻ (olive), MC₅H⁺SO₃⁻ (green), MC₇H⁺SO₃⁻ (magenta) and MC₈H⁺SO₃⁻ (purple) in water: (a) just prepared and then (b) illuminated by 365 nm light for 10-30 s. A saturated solution was used for MC₅H⁺SO₃⁻ due to its poor solubility. For the other merocyaninesulphonic acids, the concentration was 3×10⁻⁵ M.

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Chapter 1 Introduction

1.1 Biological transport process and artificial motion systems

The transport process in fluidic systems plays a crucial role in life on Earth.\(^1\) At the molecular level, there is the transport of ions (Na\(^+\), K\(^+\), Ca\(^{2+}\), and Cl\(^-\)) across the membranes of cells and organelles against concentration or electrochemical gradients, which can maintain the physiological balance of living systems.\(^3\) At the cellular level, there is locomotion or transport of organisms like bacteria, somatic cells, and other single cell or multicellular organisms in response to stimuli such as nutrients, light or something else essential for life, which are known as the taxis behaviours and include chemotaxis,\(^4\) phototaxis,\(^5,6\) thermotaxis,\(^7\) magnetotaxis,\(^8\) aerotaxis,\(^9\) etc. Taxis behaviours are the fundamental properties of living organisms and can be widely found in Nature. Escherichia coli cells migrate to organic nutrients due to chemical gradients, which is chemotaxis.\(^4\) Volvox, a green algae, moves towards a light source for photosynthesis (positive phototaxis),\(^5\) while Euglena gracilis, a single-celled alga, moves away from light to find suitable environmental conditions (negative phototaxis).\(^6\) In 2013, the Nobel Prize in Physiology or Medicine was awarded to Rothman, Schekman and Südhof "for their discoveries of machinery regulating vesicle traffic, a major transport system in our cells", indicating that increasing attention has been focused on the field of biological transport.\(^10\) Emulating the biological transport process in an artificial motion system could help further understand the transport mechanism, and provide functionalities for applications in the fields of microfluidics,\(^11,12\) diagnostics,\(^13\) cargo transport\(^14,15\) and drug-delivery.\(^16\) To construct a man-made motion system, a “vehicle” is required to carry a molecular or cellular cargo in liquid media as well as a driving force to move the vehicle, analogous to vesicle trafficking that allows transport of materials between different organelles in the same cell, between different cellular compartments, or between the cells and the environment. The vehicle can be solid particles or liquid droplets, which are immiscible with the surrounding medium. Based on the state of the vehicle, the systems can be divided into particle motion systems and droplet motion systems. Since liquid droplets have a soft and flexible boundary that can provide relatively good mass exchange...
between the vehicle and the surrounding environment, which is essential for living biological systems, droplet motion systems have attracted increasing attention in recent years. The driving force for artificial motion systems can be produced in a variety of ways, using mechanical motion like flagella, catalytic or electrochemical reactions, bubble propulsion or tension gradients; these can largely be considered to result from as phoretic effects or Marangoni effects.

1.2 Principles of artificial motion systems

1.2.1 Marangoni effect

In droplet moving systems, tension gradients play a crucial role to initialise and control the droplet motion. Tension gradients are able to cause a directional mass transfer along the interface between two phases, which is known as the Marangoni effect. The Marangoni effect was first identified in the phenomenon "tears of wine" (Figure 1.1) by James Thomson in 1855 and systematically studied by Carlo Marangoni in his doctoral dissertation. The Marangoni effect causes the liquid to move away from areas of low surface/interfacial tension to areas of high surface/interfacial tension. The tension gradients can be either generated from the external medium surrounding the droplet or from the droplet itself due to temperature change or chemical reactions. In the phenomenon "tears of wine", capillary effect makes the liquid slightly climb up the glass wall after the glass is filled with red wine which can be viewed as the mixture of water and alcohol. Alcohol in the liquid near the wall evaporates faster than that in the bulk solution, thus generating a gradient of alcohol concentration. Since alcohol has a lower surface tension than water, surface tension near the wall is higher than that in the bulk solution. As a result, the liquid is driven from the bulk solution to the side of the glass and then further up along the wall until the liquid drops with gravity. Small particles or droplets located in tension gradients are also moved towards the high surface/interfacial tension area. A good example is the pepper-soap experiment, in which pepper particles floating on water in a Petri dish move to the edge of the dish when a drop of soap is introduced into the water at the centre of the dish.
As long as interfacial tension (IFT) gradients are generated at the interface between a droplet and the surrounding liquid medium, mass transfer from the area of low IFT to the high IFT area occurs due to the Marangoni effect, thus initiating a flow in the same direction on the droplet interface (Figure 1.2). Subsequently, an internal flow directed back to the low IFT area through the inner centre part of the droplet is generated (red lines, Figure 1.2). The external and the internal flow form an entire circular flow within the droplet, which is Marangoni flow.\textsuperscript{24-28} The droplet moves in the opposite direction to the external flow but in the same direction as internal flow by conservation of momentum. The motion direction of droplet changes as the Marangoni flow changes direction. Almost all the reported motion of liquid droplets through an immiscible liquid medium is related to the Marangoni effect and Marangoni flow.\textsuperscript{24-28}

\textbf{Figure 1.1} The phenomenon “tears of wine” due to the Marangoni effect and its explanation. The pictures are from the website of Comsol.\textsuperscript{31}

\textbf{Figure 1.2} Relation between surface tension and Marangoni flow.\textsuperscript{27}
Since tension gradients can be easily created and used to move droplets, droplet motion systems have been widely developed and investigated. The droplet motion systems provide a simple but efficient way to mimic the biological transport and motion process.

1.2.2 Phoretic effect

In particle motion systems, the phoretic effect, which is the interaction between the particle and local field gradient, plays an important role. Phoretic motion is a force-free and torque-free propulsion. The field gradient originates from either the external environment or the particle itself. As has been widely reported before, externally imposed gradients can be generated by the variation in solute concentration, electric field or temperature. For a symmetric spherical particle, motion can be obtained if the particle is placed in such gradient field (Figure 1.3a). The corresponding motion is diffusiophoresis, electrophoresis or thermophoresis, respectively. However, for an asymmetric spherical particle like Janus particle whose hemispheres have different chemical or physical properties, propulsion can be achieved without external gradient as long as the particle has certain chemical interaction with the surrounding solution to break the symmetry (Figure 1.3b). In this case, the gradient is self-generated. The phoretic effect has been investigated by both experiments and calculations, and widely used to explain the motion of colloids in particle motion systems. Generally, even though the phoretic effect can also contribute to propulsion in droplet motion systems under certain circumstances, however, the Marangoni effect still largely dominates the motion process, which has been demonstrated by theoretical calculations.

![Figure 1.3](image)

*Figure 1.3* (a) Motion of a symmetric particle in an external temperature gradient field. (b) Motion of a Janus particle in a uniform solution. Half of the particle is coated with a catalyst which can cause catalytic reaction in the surrounding medium.
1.3 Self-motion

Self-motion is the simplest motion type in droplet systems. The self-propelled droplets can be perfect protocell models to emulate some essential functions of living cells. The origin of this kind of automatic movement is the irregular change in surface/interfacial tension, which generates tension gradients thus initiating the motion by the Marangoni effect. This irregular change can be induced by the diffusion of a surfactant species or chemical reaction at the droplet/medium interface.

1.3.1 Self-motion by diffusion of surfactant

The diffusion of surfactant molecules from the droplets into the surrounding medium, which is able to form tension gradients around the droplet spontaneously, is a simple way to generate self-motion. The precursor for this was the self-motion of camphor particles on the surface of water, which was investigated by Lord Rayleigh a century ago. Tension gradients generated by the heterogeneous distribution of camphor molecules on the water surface around the particles was found to be the origin of the automatic propulsion. These findings opened the way to self-motion of particles as well as droplets by diffusion of surfactant.

As discussed previously, the “tears of wine” phenomenon results from the imbalanced diffusion of ethanol. However, since ethanol is miscible with water, this cannot be used to form droplets to move through another immiscible liquid medium. In contrast, 1-pentanol, which is nearly immiscible with water, has been used by Nagai et al. to create a simple type of self-motion. By adding pentanol to an aqueous solution, droplets formed and moved spontaneously (Figure 1.4a); a pentanol droplet with a volume of 0.3 µL moved randomly on the aqueous surface with a speed of up to more than 10 mm/s. For a droplet with a large volume, the self-motion was observed to be accompanied by a deformation. The asymmetric distribution of pentanol molecules on the water interface generated IFT gradients around the droplet (Figure 1.4b) thus initiating the automatic motion of the droplet due to the Marangoni effect. Since the distribution of pentanol is a spontaneous and random process, directionless motion was obtained in this case.
A similar type of self-motion was obtained by using butyl salicylate (BS) in the droplet and sodium dodecyl sulphate (SDS) in the surrounding aqueous phase. Contact angle change of the BS droplet due to the heterogeneous absorption of the surfactant SDS on BS droplet surface and Marangoni flow induced by the imbalanced diffusion of BS into aqueous phase together with SDS played important roles in the spontaneous motion (Figure 1.4c). The BS droplet was able to undergo reciprocation with a small or a large amplitude depending on the concentration of SDS.

**Figure 1.4** (a) Random motion of a 1-pentanol droplet in aqueous medium which resulted from (b) differential distribution of the 1-pentanol in the aqueous solution. (c) Self-motion generated by diffusion of SDS and BS.

### 1.3.2 Self-motion by chemical reaction

Chemical reaction at the droplet/medium interface is also able to change local surface/interface tension, leading to spontaneous motion. This method had scarcely been investigated until 1978 when Dupeyrat et al. reported a spontaneous motion of a nitrobenzene droplet containing potassium iodide (KI) and iodine (I₂) on a glass substrate in the aqueous solution of a cationic surfactant trimethyloctadecylammonium chloride (STAC) (Figure 1.5a). The droplet underwent an amoeboid locomotion along the glass wall in the aqueous surfactant solution. Typically, for a droplet with a volume of 30 µL, the velocity of self-motion can be up to 20 mm/s. This kind of self-motion was further investigated by Magome et al. in 2005 (Figure 1.5). The chemical reaction of KI and I₂ which generated I₃⁻ was the determining process for the movement. The resulting I₃⁻
formed a hydrophobic ion pair with STA\(^+\), leading to the transfer of the cationic surfactant from the droplet/water interface into the droplet.\(^{47,48}\) As a result of the surfactant diffusion, an IFT difference between the front and the back of the droplet was created, thus initiating droplet motion due to the Marangoni effect. Since the chemical reaction occurred on the droplet surface spontaneously, which made the imbalance in IFT randomly generated, the motion was also random in a spatially symmetric environment (Figure 1.5b). By changing the spatial geometry of the glass substrate for the movement, the irregular motion was converted to a periodic regular one, thus realizing partial control on self-motion. For example, rotational motion of the droplet was obtained by using a vertical circular substrate (Figure 1.5b).\(^{48,49}\) In this type of self-motion, the chemical reaction was used to change the mass transfer at the droplet/water interface.

![Diagram of self-motion of an oil droplet](image1.png)

**Figure 1.5** Self-motion of an oil droplet: (a) time lapse photo of random motion under isotropic conditions and structure of the cationic surfactant STAC, and (b) diagram of a ring immersed in the aqueous medium with a time lapse photo of the rotational motion within the ring.\(^{48}\)

In 2007, Hanczyc and his co-workers took advantage of the hydrolysis reaction of an anhydride to initiate an automatic motion of droplets with a volume of 0.2 µL through the generation of surfactant.\(^{50}\) In their system, oleic anhydride (Figure 1.6a) was used in the droplet and alkaline water containing oleate micelles was the
surrounding medium. In the presence of alkaline water, oleic anhydride was hydrolysed at the droplet/water interface to generate oleate surfactant (Figure 1.6a) thus decreasing the IFT at certain site on the droplet surface where the reaction occurred. As a result of internal convection, a Marangoni flow on the droplet surface was generated. The droplet moved in the same direction as the internal convection (Figure 1.6b-c). The motion speed was decreased as Marangoni flow reduced over time and the movement stopped several minutes before the flow ceased. The release of product trailing at the rear of the droplet was observed, which seemed to have an effect on the directional motion. This release created a lower pH zone trailing the droplet, which can be visualised using a pH indicator thymolphthalein (Figure 1.6d). It was believed that the Marangoni flow brought fresh oleic anhydride to the droplet/water interface for hydrolysis at one pole of the droplet while releasing the product at the opposite pole. The release of products contributed to forming a positive feedback cycle for continuous hydrolysis therefore maintaining the movement. Since the hydrolysis took place automatically, the Marangoni flow formed in a random fashion. Consequently, the droplet exhibited a random self-motion. However, this self-motion could be partly controlled by an imposed pH gradient near the droplet. The droplet was found to move away from the low-pH solution and toward the high-pH solution over a short distance. In this case, the droplet can be viewed as a sensory-motor system, in which the boundary at the droplet/water interface senses chemical change like pH in the external environment and then the droplet “decides” to move towards or away from the change in response to the information. This mechanism is similar to that of chemotaxis in the unicellular living systems. Furthermore, a deformation of the droplet occurred in the pH gradient if the droplet size was larger than 100 µm and up to 5 mm in diameter. The deformation became more dramatic for larger droplet. This property made the droplet a simple model to investigate an autopoietic system like a biological cell, a system capable of maintaining itself. This self-motion system provided a simple physical way to mimic and study complex behaviour in living systems.
The hydrolysis of different types of imine-containing compounds can be used to consume or generate surfactant to propel droplet motion. Based on this, two different types of self-propelled oil droplet systems were developed by Toyota and his co-workers.\textsuperscript{54,55} For the first one reported in 2009, the imine they used in the droplet was N-(4-[3-[trimethylammonio]ethoxy]benzylidene)-4-octylaniline bromide, which was a surfactant (Figure 1.7a).\textsuperscript{54} In the presence of catalyst, this surfactant imine derivative was hydrolysed at the organic/water interface to generate the less surface active aniline and benzaldehyde species, generating an IFT imbalance. Since the products were less surface active, the hydrolysis was a surfactant consuming process. The droplet moved in the opposite direction to where the hydrolysis happened. In this work, the size of the droplet was varied from 10 to 140 µm in diameter and the initial speed of the self-propulsion was in the range of 3 to 40 µm/s. In 2016, these authors reported a similar system, in which, the imine

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure16.png}
\caption{(a) Hydrolysis of oleic anhydride in the presence of an alkaline aqueous solution, and (b) the resulting internal convective flow within the droplet.\textsuperscript{50} (c) Differential interference contrast (DIC) micrograph of the self-propelled droplet showing the internal convection.\textsuperscript{51} (d) Visualisation of the release from the self-motion droplet into the aqueous solution by using thymolphthalein, a pH indicator which appears blue at high pH and becomes colourless below pH 11. The colourless “tail” trailing the droplet, which is the low pH release, can be clearly seen.\textsuperscript{52}}
\end{figure}

\[\begin{array}{c}
\text{CH}_3\text{(CH}_2)_8\text{CH}_2\text{CH}_2\text{(CH}_2)_6\text{CH}_2\text{CH}_2\text{(CH}_2)_6\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}^- + 2 \text{H}^+ \\
2\text{CH}_3\text{(CH}_2)_8\text{CH}_2\text{CH}_2\text{(CH}_2)_6\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{H}_2 \\
\end{array}\]
species (N-(4-(heptyloxy)benzylidene)decyl-1-amine), a surfactant precursor, was used (Figure 1.7b);\textsuperscript{55} a cationic ammonium surfactant was generated on the surface of flocculated oil particles by the protonation of the primary amine that resulted from the hydrolysis of the imine derivative, leading to the formation of spherical oil droplets (upper image, Figure 1.7b). This was a surfactant generating process and the internal Marangoni convective flow was directed towards the surfactant generation through the centre of the droplet. As a result, the droplet moved in the same direction where the surfactant was formed. In this study, the droplets size was varied from 10 to 250 µm in diameter and the initial speeds of the self-propulsion were in the range of 2 to 30 µm/s. Since the hydrolysis was random in both systems (Figure 1.7), the motion was also random.

The deprotonation of acid has also been used to create spontaneous movement of droplets. In 2012, Ban \textit{et al.} developed pH-dependent self-motion of nitrobenzene droplets containing di(2-ethylhexyl)phosphoric acid (DEHPA), which underwent a deprotonation reaction at the droplet/water interface at pH 11.2-13.0 causing an IFT (\(\gamma\)) change (Figure 1.8).\textsuperscript{56} The size of the droplet ranged from 0.5 mm to 10 mm and the motion speed was up to 6 mm/s. As was measured by the pendant drop method, the generation of deprotonated DEHPA was able to decrease IFT. When the pH of the aqueous solution surrounding the droplet was above the threshold for deprotonation, which was 11.2, DEHPA was deprotonated at a certain site on the

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1}
\caption{Figure 1.7 (a) Hydrolysis of an imine-containing surfactant and the resulting movement.\textsuperscript{54} (b) Hydrolysis of an imine derivative with the generation of surfactant and diagram of the droplet transformation.\textsuperscript{55}}
\end{figure}
droplet surface thus decreasing IFT change in this area. As a consequence of this change, a random motion of the droplet was initiated due to the Marangoni effect. Release of the resulting deprotonated DEHPA from the droplet and interfacial turbulence were observed, which were considered important to the movement. In this work, it was demonstrated that pH was able to be used as a switch to initiate or terminate the motion of the droplet, which can be regarded as a limited control over the motion.

![Figure 1.8](image)

**Figure 1.8** (a) Conversion between DEHPA and its deprotonated form with a change in IFT (\(\gamma\)), and (b) the resulting random motion.\(^{36}\)

### 1.4 Controlled motion

Even though self-motion droplets have become ideal protocell models, the inability to fully control the motion makes it nearly impossible to emulate more advanced functions of organisms like taxis behaviours. To overcome this drawback, controlled motion systems have been developed to mimic regular biological transport and motion processes in Nature. The key to controlled motion is to create a regularly sustained change in surface/interface tension, which can be achieved by producing directional internal or external gradients.

#### 1.4.1 Motion controlled by external gradients

Creating external gradients in the surrounding medium is an indirect strategy to control droplet motion. In this case, droplet motion is controlled by controlling its environment. This control can be viewed as an indirect control. This is a passive motion. This strategy has been widely used to control droplet movement, however, as has been reported, the droplet can only be moved in limited directions, along or against the gradient.
1.4.1.1 Controlled motion by thermal gradients

It has been reported that temperature has a significant effect on IFT.\textsuperscript{57-59} Hence, temperature change can be used to generate IFT gradients for droplet motion. The Marangoni effect in this case is referred to as the thermocapillary effect. Since temperature gradient is easily created, the thermocapillary effect has been widely investigated and used for droplet motion. In 2016, Muto \textit{et al.} created interfacial flow by a light-induced temperature gradient in a tetraborate pH standard buffer solution containing Brilliant Blue to increase the absorption of light, thus moving an oleic acid droplet with a volume of 5 to 65 pL surrounded by this gradient.\textsuperscript{60} They found that the IFT increased along with the increase in temperature in the system (Figure 1.9a). Under the temperature gradient created by laser heating, Marangoni flow occurred in the direction of the high temperature area due to the high IFT on the droplet surface, and the droplet moved in the direction away from the heated area (Figure 1.9b). The driving force was estimated to be at the nanonewton (nN) scale. The authors found that, with the same gradient, the larger droplet received a stronger driving force and the corresponding displacement was greater. In this work, by creating temperature gradients in the external environment by laser heating, noncontact manipulation of the droplet was realised.

![Figure 1.9](image)

\textbf{Figure 1.9} (a) IFT vs temperature standard curve for water in oleic acid indicating a positive temperature coefficient for IFT between 30 to 60 °C. (b) Marangoni flow induced by laser-generated temperature gradient and the resulting motion.\textsuperscript{60}

1.4.1.2 Controlled motion by chemical gradients

As an isothermal method, chemical gradients in the environment surrounding the droplet can not only provide energy for the motion but also control the direction of
the movement. For a self-propelled droplet, externally imposed chemical gradients are able to convert the irregular change in surface/interfacial tension at the droplet/medium interface into a regular one, thus controlling random droplet motion. Once a chemical gradient is created, however, it is hard to change the direction. The flexibility of this kind of control is limited and once the droplet moves in this gradient, the termination of the movement is another problem.

As a readily available chemical gradient, pH gradient has been extensively applied to control droplet motion since Sugawara et al. controlled the moving direction of a self-propelled droplet by using an imposed pH gradient, as previously discussed. In 2010, Grzybowski et al. demonstrated that a small oil-based droplet could move through the channels of a microfluidic maze filled with alkaline solution containing surfactant, in the direction of a pH gradient. The 2-hexyldecanoic acid (HDA)/dichloromethane (DCM) droplet was attracted by an acid-soaked gel placed at the exit of the maze channel, thus allowing the droplet to solve the maze (Figure 1.10a). The volume of the HDA/DCM droplet used was around 1 µL and the velocity of the motion was up to around 10 mm s⁻¹. The directed movement of the droplet could be explained by the surface tension differential that resulted from the heterogeneous distribution of HDA/DA⁻ at the liquid-air interface as a result of the greater concentration of HDA on the droplet surface facing the lower pH (Figure 1.10b). A detailed investigation of this system in 2014 showed that Marangoni flow induced by the pH gradient played a key role in the movement. This maze solving system showed that an artificial droplet can undertake intelligent tasks.

In 2014, Toyota and his co-workers reported another directed movement based on a hydrolysis reaction in a pH gradient generated by sodium hydroxide (NaOH) in
an emulsion system. The emulsion was obtained by distributing 10 µL of 4-heptyloxybenzaldehyde (HBA) in to 200 µL of a solution of a Gemini cationic surfactant with carbonate linkages (2G12C, Figure 1.11a). The 2G12C in the emulsion droplets gradually underwent hydrolysis to generate two units of monomeric surfactant (Figure 1.11a) following the addition of NaOH (Figure 1.11b), decreasing the IFT at the oil/water interface. Marangoni flow was directed to the surface area with less hydrolysis and internal convection flow through the droplet centre towards the area of greater hydrolysis on the more concentrated NaOH side (Figure 1.11c). As a result, the droplet moved towards more concentrated NaOH in the microchannel. The motion speed was up to 0.3 mm/s. Since the droplet had no contact with the channel wall, this was a three-dimensional motion. It should be noted that the droplet exhibited a random self-motion without the pH gradient.

![Figure 1.11](image)

Figure 1.11 (a) Hydrolysis of 2G12C in the presence of base and (b) a schematic of the experimental apparatus. (c) The resulting directed droplet motion under a pH gradient in the small channel with indicated Marangoni flow and the pH gradient.

The movement of organic droplets controlled by concentration gradients of other chemical species has also been investigated. In 2014, Hanczyc and his co-workers reported the chemotactic motion of decanol droplets in sodium decanoate aqueous solution along sodium chloride (NaCl) concentration gradients (Figure 1.12a). The motion speed was up to 3 mm/s. The decanol droplets underwent weak self-motion in the solution of sodium decanoate without NaCl because of the mass transfer from the droplet into the soapy solution. The introduction of a NaCl gradient generated a surface tension gradient thus moving the droplet due to the Marangoni effect. The droplet was able to move in a nonlinear path in a channel.
toward the NaCl source. Its usefulness was demonstrated by showing that it could be used to carry iodine as a cargo to initiate an iodination reaction of β-carotene at a desired location. In an intelligent way, the droplet was able to select the stronger of two concentration gradients (Figure 1.12b).

![Figure 1.12](image)

**Figure 1.12** (a) The chemotactic motion of a decanol droplet due to NaCl gradients. (b) Illustration of droplet movement towards the stronger concentration gradient after the introduction at each end of the channel of different amounts of NaCl at 60 s.64

In 2015, Francis et al. also used chloride gradients to direct droplet motion. They reported the movement of an ionic liquid droplet consisting of trihexyl(tetradecyl)phosphonium chloride ([P₆,₆,₆,₁₄]⁺Cl⁻) in the direction of an aqueous chloride gradient in a channel (Figure 1.13).65 This ionic liquid was able to release the cationic surfactant [P₆,₆,₆,₁₄]⁺ into water, thus decreasing the surface tension. The presence of the Cl⁻ gradient in the aqueous solution surrounding the droplet caused asymmetric release of surfactant due to the association between [P₆,₆,₆,₁₄]⁺ and Cl⁻, thus generating a surface tension gradient. The droplet moved towards the higher surface tension area with more concentrated Cl⁻. Typically, the velocity of the directional motion was in the range of 0.5-4 mm/s for a droplet with a volume of around 10 µL. In a following study, they used an electrical potential to generate the Cl⁻ gradient, thus developing an electrotactic droplet system in which the droplet moved on the aqueous electrolyte solution in the channel towards the anode side, which had higher concentration of Cl⁻.66 In this case, better control over the motion was obtained. The initiation, termination, moving direction and moving speed of this motion can be readily controlled by adjusting the applied voltage. The limitation is that specially designed channel need to be used, as well as 3D printed titanium mesh electrode.
1.4.1.3 Motion controlled by photochemical gradients

In recent years, photoactive materials have been used to generate external photochemical gradients by light in order to move droplets. This strategy provides another isothermal method. As an external stimulus, light is contactless and tuneable in space, time and intensity. While it is possible to create heat gradient by light/laser illumination, here only photochemical systems will be discussed.

Unlike normal chemical gradients mentioned before, photochemical gradients induced by light illumination can be readily created, changed or terminated by changing the light source even after the gradient is generated. As a consequence, the initiation, direction control and termination of the droplet motion can be easily achieved. The development of these photoinduced droplet motion systems has opened the door to mimicking and further understanding phototactic behaviour in the biological world. In these cases, the external gradients, which provide the driving force, can be generated by photoinduced isomerisation or photoinduced reaction of the photoactive materials like \( E/Z \) azobenzene and spiropyran/merocyanine systems.

Azobenzene is a photoactive molecule that can undergo reversible photoisomerisation between its \( E \) (from entgegen (German) – opposite) and \( Z \) (from
zusammen (German) – together) isomers (Figure 1.14). The two isomers can interconvert by irradiation with particular wavelengths of light: UV light for $E$-to-$Z$ conversion, and visible light for $Z$-to-$E$ isomerisation.

![Figure 1.14](image)

**Figure 1.14** Photoisomerisation between the $E$ and $Z$ isomers of azobenzene.

Baigl *et al.* modified azobenzene into a surfactant (AzoTAB) by introducing a trimethylammonium group in this compound. As a result, the photoisomerisation between the $E$ ($E$-AzoTAB) and $Z$ isomer ($Z$-AzoTAB) is accompanied by a surface activity change (Figure 1.15a). By dissolving AzoTAB in the aqueous solution, they were able to generate surface tension gradients by simply illuminating the solution with UV light (365 nm) or blue light (475 nm). Consequently, they moved a 3 µL oleic acid droplet floating on the aqueous solution of AzoTAB with a velocity of up to 300 µm/s. They found that $E$-AzoTAB has a lower surface tension than $Z$-AzoTAB. Under UV light (365 nm) illumination, the droplet spontaneously moved away from the illuminated area to the non-illuminated area by the generation of $Z$-AzoTAB (Figure 1.15b). However, if blue light (475 nm) was used instead of UV light, the droplet moved to the illuminated area as a result of the generation of $E$-AzoTAB. It should be noted that light irradiation required a unique illumination arrangement that was moved in time with the droplet.

![Figure 1.15](image)

**Figure 1.15** (a) Photoinduced isomerisation and IFT change of AzoTAB, and the resulting motion of the oil droplet upon (b) UV or (c) blue light radiation.
Spiropyrans have been widely used as photoactive materials since their photochromism was first reported by Fischer and Hirshberg in 1952. Spiropyrans can photoisomerise from the ring-closed spiropyranyl (SP) form to the ring-opened merocyanine (MC) form under UV light illumination, or the reverse under visible light (Figure 1.16). The vastly different properties of SP and MC, their reversible photoisomerisation and good photostability upon irradiation with light of different wavelengths, and their excellent processability and biocompatibility have made spiropyrans widely used for photoswitching, reusable sensing, fluorescent probing and biological imaging.

Under acidic conditions, the merocyanine isomer can be easily protonated to generate protonated merocyanine (MCH⁺). The resulting MCH⁺ is converted to SP upon visible light irradiation via a protonated SP (SPH⁺) intermediate with a change in acidity (Figure 1.16).

![Figure 1.16 Photo and pH induced conversion of SP, MC and MCH⁺.](image)

A spiropyran substituted with a strong acidic group such as sulphonic acid normally exists as MCH⁺ and can act as a photoacid. An example of this is the spiropyran-8-sulphonic acid, which exists in the protonated ring-opening form (MCH⁺SO₃⁻) as shown in Figure 1.17. Upon dissolution in water, the compound is an equilibrium mixture of the merocyanine forms (MCH⁺SO₃⁻ and MCSO₃⁻) with a pH of 5. Upon white light irradiation, the merocyanine forms are converted to the
spiropyran sulphonate (SPSO₃⁻) and a larger population of free protons, decreasing the pH to 3.5.⁸¹

**Figure 1.17** pH change generated by photoisomerisation of the protonated merocyaninesulphonic acid MCH⁺SO₃⁻.⁸¹

By using this photoacidic MCH⁺SO₃⁻ in aqueous solution, Florea *et al.* created a pH gradient by partly illuminating the solution with light, thus driving an organic droplet on water by a pH-induced surface tension gradient.⁸¹ The organic droplet was made up of a dichloromethane (DCM) solution of Chromoionophore I (CI) and 2-hexyldecanoic acid (HDA), which existed as CI-H⁺ and DA⁻ at the boundary of the droplet (Figure 1.18a). Under white light illumination, the isomerisation of MCH⁺SO₃⁻ to SPSO₃H in the aqueous medium resulted in a pH drop (Figure 1.17). As a result, DA⁻ at the droplet boundary was protonated to generate HDA, which
migrated towards the less polar bulk droplet region. At the same time, CI-H+ migrated into the bulk aqueous region. In this way, the surface tension around the droplet in the region closer to the white light illumination was decreased and a pH gradient was therefore generated (Figure 1.18b). The resulting pH gradient caused Marangoni flows and the movement of the droplet away from the illuminated area. For a microliter sized DCM droplet, the propulsion velocity was up to 4000 µm/s when the solution close to the droplet in the channel was illuminated by white light (~100 klx).

In the above two droplet motion systems, efficient control over the movement has been realised by the use of photoactive materials in the external environment to generate gradients upon light irradiation. However, in both systems, the droplet motion was limited to the aqueous surface. In addition, the AzoTAB based system required a complex operation of the light source for movement and in the MCH+SO3− based system, specific channels had to be used. These limitations originate from the fact that the droplet motion still depended on the external change in the environment.

1.4.2 Motion controlled by internal gradients

Creating a continuous gradient within the droplet itself provides a direct strategy to realise the effective control over droplet motion. In this case, the droplet is able to respond to stimuli such as heat and light directly and the movement depends on the droplet itself but is independent of the external environment. This represents direct control of the motion, which is considered active motion. This kind of control has been realised using the thermocapillary effect or a photoinduced chemical reaction within the droplet.

1.4.2.1 Motion controlled by the thermo capillary effect

Surface/interfacial tension is so sensitive to temperature that tension gradients can be easily generated by heat. In this case, the resulting Marangoni effect is also known as the thermocapillary effect that provides a direct physical way to move the droplet. As a simple and flexible method, laser heating has been used to generate thermal gradients. In 2004, Faris’ group moved aqueous droplets in 1-decanol by
using laser heating to generate an IFT gradient across the droplet width.\textsuperscript{82} To increase the absorption and heating effect of the laser, the dyes FD&C Red No. 40 and Red No. 3 were used in the droplet (Figure 1.19a). In 2005, This group used an infrared laser (1525 nm) to heat a pure water droplet, thus moving it in 1-decanol.\textsuperscript{83} Furthermore, the group undertook a chemical assay by moving and then merging two droplets contained an enzyme – horseradish peroxidase (HRP) and the chromogenic substrates: 2,2’-azino-bis(3-ethylbenzthiazoline-6-sulphonic acid) diammonium salt (ABTS) and hydrogen peroxide (H\textsubscript{2}O\textsubscript{2}), respectively (Figure 1.19b).\textsuperscript{83} The merger of the two droplets initiated the enzyme-catalysed decomposition of H\textsubscript{2}O\textsubscript{2} and the following oxidation of ABTS to generate a dark-green droplet. Since heating decreased the IFT in the illuminated area, the tension gradient is from the illuminated area towards the non-illuminated area and the droplet moved with a speed of 3 mm s\textsuperscript{-1} towards the colder non-illuminated region. In order to create a thermal gradient for the movement, a special laser heating apparatus was applied to keep the laser beam just across the trailing edge of the droplet all the time (Figure 1.19a). This is just like pushing a ball with a stick, but the control of the motion direction and distance were limited by the movement of the apparatus. Furthermore, their calculations showed a temperature rise of about 10 °C in this system, which also limited its application in temperature-sensitive biological systems.\textsuperscript{67}

\textbf{Figure 1.19} (a) Schematic diagram of the apparatus used for a laser-heating induced motion system. (b) Laser-induced movement of a small droplet containing the HRP enzyme to combine with a big droplet with chromogenic substrates, ABTS and H\textsubscript{2}O\textsubscript{2}, in order to perform a chemical assay.\textsuperscript{82,83}
1.4.2.2 Motion controlled by photochemical reactions

Photochemical reactions can also be used to generate surface/interfacial tension gradients isothermally. The generation of a surface active compound by photochemical reaction can cause a drop in IFT at a liquid/liquid interface in the illuminated area. However, using this strategy to move a droplet has scarcely been reported.

2-Nitrobenzyl alcohol is a photoactive molecule that can irreversibly convert to 2-nitrosobenzaldehyde in the presence of UV light (Figure 1.20) and it is widely used in organic synthesis as a photoremovable protecting group to protect carboxylic acids, amines, ketones, alcohols, etc.

![Figure 1.20 Photoinduced reaction of 2-nitrobenzyl alcohol.](image)

Based on this photochemical reaction, a photoactivated droplet movement was created. The photodriven system was built by introducing 2-nitrobenzyl oleate (NBO), an oleic acid protected by 2-nitrobenzyl alcohol, into the organic droplet (Figure 1.21a). This NBO droplet can be slowly attracted by UV light (365 nm)
through the basic aqueous solution, with a maximum speed of 5.6 µm s\(^{-1}\) (Figure 1.21b). Under UV illumination, photocleavage of the 2-nitrobenzyl group gives 2-nitrosobenzaldehyde and oleic acid. The photogenerated oleic acid is in equilibrium with oleate at the oil/water boundary, decreasing the surface tension of the droplet, making the droplet move toward the UV light source. The movement was maintained by the convection flow inside the NBO droplet. However, the extremely slow reaction and therefore slow speed of the movement has largely limited its application.

1.5 Summary and thesis structure

Light-controlled droplet motion systems, in which photoactive materials are used to generate photochemical gradients, provide an efficient isothermal method to realise control of the droplet movement, thus emulating the biological transport and motion process in living systems. However, this kind of droplet motion has scarcely been reported, with only three reports in the existing literature.\(^{71,81,89}\) The photoactive materials developed for these droplet motion systems are limited to an azobenzene surfactant AzoTAB, a spiropyran sulphonic acid SPSO\(_3\)H and a nitrobenzyl ester NBO. For the AzoTAB and SPSO\(_3\)H motion systems, the application of photoactive materials in the environment to create external gradients limited the total control of the motion.\(^{71,81}\) For the NBO system, better control was achieved by using the photoactive material within the droplet to generate the internal gradients, but the motion speed of the droplet was extremely slow.\(^{89}\) Furthermore, the three reported light-controlled droplet motion systems are all organic droplet in water systems. The light-controlled isothermal motion of a water droplet in an organic system has never been reported.

The motivation of this work was to develop better light-controlled droplet motion systems with photoactive materials. This aim was achieved through varying the two key components of droplet motion, the photoactive materials and the system structure. The photoactive materials used in this work are different types of spiropryan/merocyanine species, which were chosen due to their reversible photoisomerisation and reduced photodegradation upon irradiation of light with different wavelengths, high solvent compatibility, and significant difference
between the SP and MC forms in structure, polarity and hydrophobicity/hydrophilicity. Furthermore, spiropyran species can be relatively easily synthesised according to literature procedures and some derivatives are commercially available. To achieve better control of the motion, the photoactive materials were used in the droplet and not in its external environment. Based on the solubility of photoactive materials, two types of droplet motion systems were developed, that is, an organic droplet in water system and a water droplet in organic system. The mechanism of motion based on the Marangoni effect and Marangoni flow was also investigated.

In Chapter 3, spiropyrans, that had the potential to be water soluble and to act as photoacids, were synthesised and characterised. These spiropyrans are merocyaninesulphonic acids, most of which were able to change pH upon light irradiation. The investigation of these compounds helped to further understand the unique photo properties of spiropyrans and one of the most water soluble materials was used in Chapter 6 to extend the droplet motion system developed in Chapter 4. In addition, the deprotonation of these merocyaninesulphonic acids by bases such as triethylamine and ammonia, which could generate spiropyrans via a purple or blue intermediate MC, was investigated. Based on this, a basic gas sensor was developed.

In Chapter 4, a commercial organic solvent soluble spiropyran was used in organic droplets to achieve light-controlled droplet motion in aqueous solution. The scope of this droplet motion was studied to construct a series of organic droplet in water systems, with the spiropyran being used alone or together with other materials such as surfactants and a range of acids. It was found that the droplets were able to move away from or towards light sources under the different conditions operating in these systems.

In Chapter 5, a different type of photoactive material, a protonated merocyanine/surfactant salt, was prepared by treating the spiropyran used in the previous chapter with a surfactant acid. An organic droplet in water system was developed using this protonated merocyanine/surfactant salt in the organic droplet. It was found that this droplet could be moved towards light in pure water, that is, no specific modification of the environment surrounding the droplet was needed. In this way, droplet motion could be achieved in 3D for the first time and was
relatively independent of the external environment, similar to the movement of biological entities in natural systems.

In Chapter 6, the water soluble sodium sulphonate-substituted merocyaninesulphonic acids synthesised in Chapter 3 was used to construct a photoactive water droplet that was able to move towards light in fatty alcohol. A water droplet in organic system was therefore developed, demonstrating the true versatility of these droplet motion systems.

In Chapter 7, having successfully developed the versatile light-controlled droplet motion systems in the previous chapters, their possible applications were explored. The use of the photoactive droplets as carriers to transport particles was demonstrated. This ability was then extended to move chemicals to a desired place to initiate chemical reactions in both aqueous and organic media. Light-controlled movement of photoactive liquids in a confined space such as capillaries and narrow tubes was also investigated.

Mechanistic studies of each of the different droplet motion systems were carried out in Chapters 4, 5 and 6. In these light-controlled droplet motion systems, some droplets moved towards light and some moved away. The movement mechanisms were investigated using IFT measurements and capturing Marangoni convective flows on camera. It was found that as long as light illumination decreased the IFT of the system, Marangoni flow was directed from the illuminated area to the non-illuminated area on the droplet surface and the droplet moved in the opposite direction, towards the light source. If light illumination increased the IFT of the system, Marangoni flow was directed from the non-illuminated area to the illuminated area on the droplet surface and the droplet moved away from the light source. In Chapters 5 and 6, calculations on the driving force provided by IFT change was carried out, which provided a quantitative estimation of the force. The studies on mechanism contributed to further understanding of these droplet motion systems, and in turn, assisted in the design of new systems.

1.6 References

(1) Kay, E. R.; Leigh, D. A.; Zerbetto, F. Synthetic Molecular Motors and


(47) Dupeyrat, M.; Nakache, E. Direct Conversion of Chemical Energy into


(58) Ye, Z.; Zhang, F.; Han, L.; Luo, P.; Yang, J.; Chen, H. The Effect of


(69) Kumar, G. S.; Neckers, D. C. Photochemistry of Azobenzene-Containing


(37), 14699-14703.


(90) Suzuki, K.; Sugawara, T. Phototaxis of Oil Droplets Comprising a Caged Fatty
Chapter 2  General Experimental

2.1  Reagents and Materials

The chemical reagents and materials used in this work, and their grades and sources are listed in Table 2.1. All the chemicals were used as received without any purification.

Table 2.1 Chemical reagents and materials.

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<th>Company</th>
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<td>Kindly provided by Dr Pawel Wagner</td>
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</table>
2.2 Synthesis and Characterisation of Materials

2.2.1 General

Generally, ultraviolet/visible (UV/Vis) absorption spectra were obtained at room temperature using a Shimadzu UV-1800 spectrophotometer. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) relative to TMS (δ 0.0). Fourier-transform infrared spectroscopy (FT-IR) were obtained by a Shimadzu FT-IR spectrophotometer equipped with a MCT AIM-8800 detector.

2.2.2 Synthesis and Characterisation

Synthesis of 2-hydroxy-5-nitrobenzaldehyde.\textsuperscript{1-3} 2-Hydroxy benzaldehyde (11.8 mL, 111 mmol) and 63% aqueous HNO\textsubscript{3} (10.0 mL, 219 mmol) were dissolved in acetic acid (75 mL) in a 2-necked flask equipped with a thermometer and stirring bar and the solution was kept at 0-5 °C in ice-water bath under stirring for 140 min. Then the ice-water bath was removed and the temperature of the solution kept increasing due to the exothermic nitration reaction. When the temperature reached 50 °C, the solution was poured into a beaker filled with ice water (250 mL). Yellow precipitates was formed and filtered. The solid was put into 8% NaOH (125 mL) solution and heated in water bath under stirring for h and then allowed to stand for overnight. Dark red solution was obtained by filtration and then added to 4 M HCl (100 mL). The yellow solid was filtered, washed with water and dried (1.352 g, 7%). The \textsuperscript{1}H NMR spectrum was similar to that reported in the literature, which was obtained in DMSO-\textsubscript{d6}.\textsuperscript{3} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 11.60 (s, 1H), 10.00 (s, 1H), 8.56 (d, J = 2.8 Hz, 1H), 8.41 (dd, J = 9.2, 2.8 Hz, 1H), 7.13 (d, J = 9.2 Hz, 1H).
Synthesis of SPCH₃.⁴⁻⁶ 1,3,3-Trimethyl-2-methyleneindoline (1.739 g, 10 mmol) and 2-hydroxy-5-nitrobenzaldehyde (1.701 g, 10 mmol) which was dissolved in ethanol (10 mL). The mixture was stirred under reflux for 12 h. The yellow solid was collected by filtration, washed with chilled ethanol, and dried in vacuo (0.333 g, 41%). The ¹H NMR spectrum was similar to that reported in the literature, which was obtained in CD₃CN.⁶,⁷ ¹H NMR (400 MHz, CDCl₃) δ 8.07-7.97 (m, 2H), 7.21 (t, J = 7.5 Hz, 1H), 7.09 (d, J = 7.5 Hz, 1H), 6.93 (d, J = 10.4 Hz, 1H), 6.89 (t, J = 7.5 Hz, 1H), 6.77 (d, J = 8.5 Hz, 1H), 6.56 (d, J = 7.5 Hz, 1H), 5.86 (d, J = 10.4 Hz, 1H), 2.74 (s, 3H), 1.30 (s, 3H), 1.19 (s, 3H).

Synthesis of SP(NO₂)₂.⁶,⁸⁻¹² 1-(2-Hydroxyethyl)-2,3,3-trimethyl-3H-indolium iodide (3.019 g, 9.1 mmol) and potassium hydroxide (1.303 g, 23.2 mmol) were dissolved in DI water (20 mL). The mixture was stirred at room temperature for 30 min and then extracted with ethyl acetate (3×20 mL). The organic phase was dried with MgSO₄. A yellow oil was obtain after evaporation under reduced pressure. 0.1646 g (0.8 mmol) of the resulting oil was dissolved in ethanol (4 mL) and the resulting solution was added into 4 mL ethanol solution of 3,5-dinitrosalicylaldehyde (0.174 g, 0.8 mmol) in 10 min. The mixture was stirred for 2 h and then kept still in dark for 20 h. The dark purple solid was collected by filtration, washed with ethanol, and dried in vacuo (0.265 g, 82%). ¹H NMR (400 MHz, DMSO-d₆) δ 8.88 (d, J = 3.2 Hz, 1H), 8.57 (d, J = 3.2 Hz, 1H), 8.54 (d, J = 15.8 Hz, 1H), 8.43 (d, J = 15.8 Hz, 1H), 7.89-7.76 (m, 2H), 7.62-7.49 (m, 2H), 5.21 (s, 1H), 4.58 (m, 2H), 3.92 (m, 2H), 1.79 (s, 6H).
Synthesis of phenylhydrazine hydrochloride (1a). Aniline (1.863 g, 20.0 mmol) was dissolved in 6 M HCl (24 mL) in a 3-necked flask equipped with a thermometer and stirring bar and the solution was cooled down to 0-5 °C by an ice bath. After dropwise addition of sodium nitrite (1.468 g, 21.3 mmol) in water (6 mL), the resulting solution was kept under stirring at 0 °C for 45 min. Then a solution of SnCl₂•2H₂O (15.801 g, 70.0 mmol) in 6 M HCl solution (24 mL) was added over 2 h with the temperature below 0 °C. After stirring at the same temperature for 2.5 h, the mixture was filtered. The resulting solid was dissolved in 40% KOH solution (30 mL) and extracted with ethyl acetate (4×30 mL). The organic phase was combined and shaken with 32% HCl (5 mL) in ethyl acetate (10 mL). The pale solid was collected by filtration, washed with ethyl acetate, and dried in vacuo (1.539 g, 53%). The ¹H NMR spectrum was similar to that in the Spectral Database for Organic Compounds managed and maintained by National Institute of Advanced Industrial Science and Technology (AIST). ¹H NMR (400 MHz, DMSO-d₆) δ 10.17 (s, 3H), 8.23 (s, 1H), 7.39-7.17 (m, 2H), 7.08-6.83 (m, 3H).

Synthesis of 2,3,3-trimethyl-3H-indole (2a). Phenylhydrazine hydrochloride (5.841 g, 7.0 mmol) and 3-methyl-2-butanone (0.666 g, 7.7 mmol) were dissolved in ethanol (25 mL) at room temperature, and heated to reflux under nitrogen for 24 h. After evaporation under reduced pressure, the residue was separated on a silica gel column with hexane/ethyl acetate as the eluent and dried in vacuo to afford 2a as orange oil (1.039 g, 93%). The ¹H NMR spectrum was similar to that reported in the literature, which was obtained in CDCl₃. ¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, J = 8.0 Hz, 1H), 7.33-7.26 (m, 2H), 7.19 (t, J = 7.2 Hz, 1H), 2.28 (s, 3H), 1.30 (s, 6H).

Synthesis of MC₃H⁺SO₃⁻. 2,3,3-Trimethyl-3H-indole (1.039 g, 6.5 mmol) and 1,3-propanesultone (0.879 g, 7.2 mmol) were dissolved in toluene (6 mL). The mixture was precipitated to the bottom of the flask and the solvent was removed carefully.
with a pipette.\textsuperscript{20-25} The resulting purple solid was washed with diethyl ether, dried in vacuum and then dissolved in ethanol (36 mL). After addition of salicylaldehyde (0.879 g, 7.2 mmol), the mixture was allowed to reflux for 18 h. The orange solid was collected by filtration, washed with ethanol, and dried in vacuo (1.509 g, 60%). The \textsuperscript{1}H NMR spectrum was similar to that reported in the literature, which was obtained in DMSO-\textit{d}_6.\textsuperscript{18} \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6) \( \delta \) 11.00 (s, 1H), 8.58 (d, \( J = 16.4 \) Hz, 1H), 8.28 (dd, \( J = 8.0, 1.6 \) Hz, 1H), 8.02 (dd, \( J = 7.0, 1.8 \) Hz, 1H), 7.87 (d, \( J = 16.4 \) Hz, 1H), 7.86 (dd, \( J = 6.2, 2.2 \) Hz, 1H), 7.62 (m, 2H), 7.47 (m, 1H), 7.06-6.94 (m, 2H), 4.81 (m, 2H), 2.65 (m, 2H), 2.19 (m, 2H), 1.77 (s, 6H); UV/Vis (DMSO) \( \lambda_{\text{max}} \) nm (log \( \varepsilon \)) 437 (4.38); FT-IR \( \nu \)/cm\(^{-1}\) 1589, 1531, 1501, 1474, 1462, 1308, 1258, 1227, 1146, 1026, 764, 718.

\textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6) of MC\textsubscript{1}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−} after treatment with 1.2 equivalent of triethylamine: \( \delta \) 7.15 (dd, \( J = 7.6, 1.6 \) Hz, 1H), 7.11-7.03 (m, 3H), 6.98 (d, \( J = 10.4 \) Hz, 1H), 6.81 (app td, 1H), 6.73 (app td 1H), 6.66-6.59 (m, 2H), 5.74 (d, \( J = 10.4 \) Hz, 1H), 3.25-3.11 (m, 2H), 2.48-2.30 (m, 2H), 1.93-1.74 (m, 2H), 1.19 (s, 3H), 1.08 (s, 3H); \textsuperscript{13}C NMR (100 MHz, all 1C unless indicated) \( \delta \) 153.79, 147.26, 135.90, 129.62, 129.01, 127.28, 126.85, 121.36, 120.04, 119.71, 118.47, 118.24, 114.36, 106.26, 104.15, 51.75, 49.20, 42.36, 25.68, 24.96, 19.71.

Synthesis of 5-methoxy-2,3,3-trimethyl-3H-indole (2b).\textsuperscript{16,17,26} (4-Methoxy)-phenylhydrazine hydrochloride (2.002 g, 11.5 mmol) and 3-methyl-2-butanone (1.4 mL, 13.1 mmol) were dissolved in ethanol (40 mL) at room temperature, and then heated to reflux under nitrogen for 24 h. After evaporation under reduced pressure, the residue was separated on a silica gel column with hexane/ethyl acetate as the eluent and dried in vacuo to afford 3c as orange oil (1.773 g, 83%). The \textsuperscript{1}H NMR spectrum was similar to that reported in the literature, which was obtained in CDCl\textsubscript{3}.\textsuperscript{17,26} \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.42 (d, \( J = 8.4 \) Hz, 1H), 6.86-6.78 (m, 2H), 3.83 (s, 3H), 2.24 (s, 3H), 1.28 (s, 6H).
Synthesis of $\text{MC}_2\text{H}^+\text{SO}_3^-$.\textsuperscript{18,19} 5-Methoxy-2,3,3-trimethyl-3H-indole (1.602 g, 8.6 mmol) and 1,3-propanesultone (1.244 g, 10.2 mmol) were dissolved in toluene (8 mL). The mixture was stirred under reflux under a nitrogen atmosphere for 24 h. The product was precipitated to the bottom of the flask and the solvent was removed carefully with a pipette. The resulting purple solid was washed with diethyl ether, dried in vacuum and then dissolved in ethanol (50 mL). After addition of salicylaldehyde (1.32 mL, 12.4 mmol), the mixture was allowed to reflux for 21 h. The orange solid was collected by filtration, washed with ethanol, and dried in vacuo (2.247 g, 63%). \textsuperscript{1}H NMR (400 MHz, DMSO-$d_6$) δ 10.90 (s, 1H), 8.50 (d, $J = 16.6$ Hz, 1H), 8.23 (dd, $J = 8.0$, 1.2 Hz, 1H), 7.94 (d, $J = 8.9$ Hz, 1H), 7.81 (d, $J = 16.6$ Hz, 1H), 7.50 (d, $J = 2.5$ Hz, 1H), 7.44 (m, 1H), 7.17 (dd, $J = 8.9$, 2.5 Hz, 1H), 7.06-6.92 (m, 2H), 4.77 (m, 2H), 2.63 (m, 2H), 2.16 (m, 2H), 1.76 (s, 6H); \textsuperscript{13}C NMR (100 MHz, DMSO-$d_6$, all 1C unless indicated) δ 179.48, 160.70, 158.58, 146.75, 145.66, 135.10, 134.16, 129.51, 121.40, 119.95, 116.51, 116.19, 114.83, 111.53, 108.80, 55.97, 51.79, 47.29, 45.57, 26.40 (2C), 24.68; UV/Vis (DMSO) $\lambda_{max}$ nm (log ε) 319 (3.77), 447 (4.12); FT-IR $\nu$/cm$^{-1}$ 1605, 15223, 1481, 1462, 1300, 1219, 1169, 1146, 1034, 988, 768; ESI-MS $m$/z calcd for C$_{22}$H$_{24}$NO$_5$S $[M-H]^{-}$ 414.1375, found 414.1369.

$\textsuperscript{1}$H NMR (400 MHz, DMSO-$d_6$) of $\text{MC}_2\text{H}^+\text{SO}_3^-$ after treatment with 1.2 equivalent of triethylamine: δ 7.14 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.07 (app td, 1H), 6.96 (d, $J = 10.2$ Hz, 1H), 6.80 (app td, 1H), 6.73 (d, $J = 2.4$ Hz, 1H), 6.67-6.59 (m, 2H), 6.53 (d, $J = 8.4$ Hz, 1H), 5.72 (d, $J = 10.2$ Hz, 1H), 3.16-3.06 (m, 2H), 2.47-2.30 (m, 2H), 1.93-1.72 (m, 2H), 1.17 (s, 3H), 1.08 (s, 3H)

Synthesis of $\text{MC}_3\text{H}^+\text{SO}_3^-$.\textsuperscript{18,19} 2,3,3-Trimethyl-3H-indole (1.590 g, 10.0 mmol) and 1,3-propanesultone (1.393 g, 11.4 mmol) were dissolved in toluene (10 mL). The mixture was stirred under reflux under a nitrogen atmosphere for 24 h. The product was precipitated to the bottom of the flask and the solvent was removed carefully with a pipette. The resulting purple solid was washed with diethyl ether,
dried in vacuum and then dissolved in ethanol (50 mL). After addition of 2-hydroxy-5-nitrobenzaldehyde (1.669 g, 10.0 mmol), the mixture was allowed to reflux overnight. The orange solid was collected by filtration, washed with ethanol, and dried in vacuo (2.641 g, 61%). \( ^1\)H NMR (400 MHz, DMSO-\( d_6\) ) \( \delta \) 9.09 (d, \( J = 2.8 \) Hz, 1H), 8.50 (d, \( J = 16.6 \) Hz, 1H), 8.30 (dd, \( J = 9.2, 2.8 \) Hz, 1H), 8.10 (m, 1H), 8.08 (d, \( J = 16.6 \) Hz, 1H), 7.89 (m, 1H), 7.65 (m, 2H), 7.21 (d, \( J = 9.2 \) Hz, 1H), 4.84 (m, 2H), 2.65 (m, 2H), 2.21 (m, 2H), 1.80 (s, 6H); UV/Vis (DMSO) \( \lambda_{\text{max}} \) nm (log \( c_\text{e} \) ) 318.5 (4.22), 412 (4.40), 563 (3.19); FT-IR \( \nu/cm^{-1} \) 1605, 1539, 1339, 1300, 1234, 1157, 1130, 1034, 980, 860, 745.

\( ^1\)H NMR (400 MHz, DMSO-\( d_6\) ) of MC\( 3\)H\( ^+\)SO\( 3^-\) after treatment with 1.2 equivalent of triethylamine within 5 min: merocyanine form (71%) \( \delta \) 8.69 (d, \( J = 3.2 \) Hz, 1H), 8.42 (bd s, 2H), 7.84 (d, \( J = 7.9 \) Hz, 1H), 7.81 (dd, \( J = 9.8, 3.2 \) Hz, 1H), 7.75 (dd, \( J = 7.5, 0.8 \) Hz, 1H), 7.53 (app td, 1H), 7.45 (app td, 1H), 6.26 (d, \( J = 9.8 \) Hz, 1H), 4.50 (m, 2H), 2.57 (m, 2H), 2.13 (m, 2H), 1.7 (s, 6H); spiropyran form (29%) \( \delta \) 8.20 (d, \( J = 2.8 \) Hz, 1H), 7.99 (dd, \( J = 9.0, 2.8 \) Hz, 1H), 7.20 (d, \( J = 10.4 \) Hz, 1H), 7.15-7.06 (m, 2H), 6.85 (d, \( J = 9.0 \) Hz, 1H), 6.77 (app td, 1H), 6.70 (dd, \( J = 7.4, 0.8 \) Hz, 1H), 5.98 (d, \( J = 10.4 \) Hz, 1H), 3.50-3.10 (m, 2H), 2.48-2.31 (m, 2H), 1.94-1.76 (m, 2H), 1.19 (s, 3H), 1.10 (s, 3H).

**Synthesis of MC\( 4\)H\(^+\)SO\(^-\).**\(^{18,19}\) 5-Methoxy-2,3,3-trimethyl-3\( H\)-indole (0.800 g, 4.2 mmol) and 1,3-propanesultone (0.708 g, 4.3 mmol) were dissolved in toluene (5 mL). The mixture was stirred under reflux under a nitrogen atmosphere for 24 h. The product precipitated and the solvent was removed carefully with a pipette. The resulting purple solid was washed with diethyl ether, dried in vacuum and then dissolved in ethanol (2 mL). After addition of 2-hydroxy-5-nitrobenzaldehyde (0.715 mg, 4.3 mmol), the mixture was allowed to reflux overnight. The orange solid was collected by filtration, washed with ethanol, and dried in vacuo (0.802 g, 41%). \( ^1\)H NMR (400 MHz, DMSO-\( d_6\) ) \( \delta \) 9.05 (d, \( J = 2.8 \) Hz, 1H), 8.40 (d, \( J = 16.6 \) Hz, 1H), 8.08 (d, \( J = 16.6 \) Hz, 1H), 7.89 (m, 1H), 7.65 (m, 2H), 7.21 (d, \( J = 9.2 \) Hz, 1H), 4.84 (m, 2H), 2.65 (m, 2H), 2.21 (m, 2H), 1.80 (s, 6H); UV/Vis (DMSO) \( \lambda_{\text{max}} \) nm (log \( c_\text{e} \) ) 318.5 (4.22), 412 (4.40), 563 (3.19); FT-IR \( \nu/cm^{-1} \) 1605, 1539, 1339, 1300, 1234, 1157, 1130, 1034, 980, 860, 745.
Hz, 1H), 8.28 (dd, J = 9.2, 2.8 Hz, 1H), 8.02 (d, J = 9.0 Hz, 1H), 8.00 (d, J = 16.6 Hz, 1H), 7.53 (d, J = 2.2 Hz, 1H), 7.20 (d, J = 9.2 Hz, 1H), 7.20 (dd, J = 9.0, 2.2 Hz, 1H), 4.8 (m, 2H), 3.91 (s, 1H), 2.62 (m, 2H), 2.19 (m, 2H), 1.79 (s, 6H); UV/Vis (DMSO) λ_max nm (log ε) 312 (4.13), 431 (4.25); FT-IR ν/cm\(^{-1}\) 1605, 1535, 1342, 1304, 1261, 1219, 1153, 1038, 864, 822, 748, 721; ESI-MS m/z calcd for C\(_{22}\)H\(_{23}\)N\(_2\)O\(_7\)S [M–H]\(^{-}\) 459.1226, found 459.1242.

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) of MC\(_4\)H\(^+\)SO\(_3\)\(^-\) after treatment with 1.2 equivalent of triethylamine within 5 min: merocyanine form (96%) δ 8.65 (d, J = 3.2 Hz, 1H), 8.35 (bd s, 2H), 7.80 (dd, J = 9.8, 3.2 Hz, 1H), 7.78 (d, J = 8.8 Hz, 1H), 7.42 (d, J = 2.4 Hz, 1H), 7.08 (dd, J = 8.8, 2.4 Hz, 1H), 6.23 (d, J = 9.8 Hz, 1H), 4.47 (m, 2H), 3.86 (s, 3H), 2.56 (m, 2H), 2.12 (m, 2H), 1.74 (s, 6H); spiropyran form (4%) δ 8.18 (d, J = 2.8 Hz, 1H), 7.98 (dd, J = 9.0, 2.8 Hz, 1H), 7.17 (d, J = 10.4 Hz, 1H), 6.84 (d, J = 9.0 Hz, 1H), 6.77 (d, J = 2.6 Hz, 1H), 6.67 (dd, J = 8.4, 2.6 Hz, 1H), 6.60 (d, J = 8.4 Hz, 1H), 5.95 (d, J = 10.4 Hz, 1H), 3.70 (s, 3H), 3.48-3.41 (m, 2H), 2.48-2.32 (m, 2H), 1.90-1.76 (m, 2H), 1.18 (s, 3H), 1.10 (s, 3H).

**Preparation of MC\(_4\)H\(^+\)SO\(_3\)\(^-\)/DBSA-PDMS sensor.**\(^{27}\) MC\(_4\)H\(^+\)SO\(_3\)\(^-\) (4.70 mg, 0.01 mmol) and 4-dodecylbenzenesulphonic acid (DBSA) (3.27 mg, 0.01 mmol) were dissolved in dichloromethane (200 mL). 11.7 mL of the above solution was mixed with 551.4 mg of Sylgard 184 silicone elastomer base and 55.4 mg of Sylgard 184 silicone elastomer curing agent by vigorous stirring. After dichloromethane was removed by evaporation in vacuo, the viscous liquid was poured to a glass Petri dish (~6 mm in diameter) and kept in vacuo under 70 ℃ for 12 h.

**2,3,3-Trimethylindolenine-5-sulphonic acid (2c).**\(^{28}\) 4-Hydrizinobenzenesulphonic acid hemihydrate (4.00 g, 20.3 mmol) and 3-methyl-2-butanone (2.5 mL, 23.4 mmol) were dissolved in acetic acid (15 mL) at room temperature, heated to reflux under nitrogen for 16 h and then cooled to room temperature. The solid was obtained by adding ethyl acetate, collected by filtration, washed with ethanol, and dried in vacuo (3.81 g, 75%). The \(^1\)H NMR
spectrum was similar to that reported in the literature, which was obtained in DMSO-d6.\textsuperscript{28} \textsuperscript{1}H NMR (400 MHz, DMSO-d6) \(\delta\) 7.75 (d, \(J = 1.4\) Hz, 1H), 7.62 (dd, \(J = 8.0, 1.4\) Hz, 1H), 7.42 (d, \(J = 8.0\) Hz, 1H), 2.38 (s, 3H), 1.34 (s, 6H).

\textbf{1,2,3,3-Tetramethylindolinium-5-sulphonate potassium iodide salt (3c).}\textsuperscript{28}

2,3,3-Trimethylindolenine-5-sulphonic acid (3.597 g, 15 mmol) was dissolved in methanol (15 mL). A yellow solid was precipitated by adding saturated 2-propanol solution of potassium hydroxide under stirring and collected by filtration. The solid was added to 50 mL 1-propanol solution of methyl iodide (1.13 mL, 18 mol). The resulting suspension was refluxed for 24 h and cooled to room temperature. The pink solid was collected by filtration, quickly washed with 1-propanol, and dried in vacuo (3.069, 48%). The \textsuperscript{1}H NMR spectrum was similar to that reported in the literature, which was obtained in DMSO-d6.\textsuperscript{28} \textsuperscript{1}H NMR (400 MHz, DMSO-d6) \(\delta\) 8.00 (s, 1H), 7.89-7.77 (m, 2H), 7.42 (d, \(J = 8.0\) Hz, 1H), 3.95 (s, 3H), 2.75 (s, 3H), 1.53 (s, 6H).

\textbf{MC}_5\textsuperscript{H\textsuperscript{+}}\textsuperscript{SO}_3\textsuperscript{−}.\textsuperscript{28} 5-Decyl-2,3,3-trimethyl-3H-indolium iodide (0.837 g, 3.3 mmol), 2-hydroxy-5-nitrobenzaldehyde (0.451 g, 2.7 mmol) and piperidine (0.42 mL, 4.3 mmol) were dissolved in ethanol (20 mL). The mixture was stirred under reflux for 20 h and cooled to room temperature. After neutralisation with 32% HCl, the yellow solid was collected by filtration, washed with boiling ethanol and dried in vacuo (0.719 g, 66%). The \textsuperscript{1}H NMR spectrum was similar to that reported in the literature, which was obtained in DMSO-d6.\textsuperscript{28} \textsuperscript{1}H NMR (400 MHz, DMSO-d6) \(\delta\) 9.08 (d, \(J = 2.2\) Hz, 1H), 8.45 (d, \(J = 16.2\) Hz, 1H), 8.30 (dd, \(J = 9.2, 2.3\) Hz, 1H), 8.07 (s, 1H), 7.95 (d, \(J = 16.2\) Hz, 1H), 7.82-7.91 (m, 2H), 7.22 (d, \(J = 9.2\) Hz, 1H), 4.14 (s, 3H), 1.79 (s, 6H).

\textbf{MC}_5\textsuperscript{H\textsuperscript{+}}\textsuperscript{SO}_3\textsuperscript{−} after treatment with 1.2 equivalent of triethylamine within 5 min: merocyanine form (33%) \(\delta\) 8.67 (d, \(J = 2.9\) Hz, 1H), 8.38 (bd s, 2H), 7.91 (s, 1H), 7.81 (dd, \(J = 9.8, 2.9\) Hz, 1H), 7.76 (d, \(J = 8.4\) Hz, 1H), 7.63 (d, \(J = 8.4\) Hz, 1H), 6.26 (d, \(J = 9.8\) Hz, 1H), 3.84 (s, 3H), 1.75 (s, 6H); spiropyran form (67%) \(\delta\) 8.21 (d, \(J = 2.8\) Hz, 1H), 8.00 (dd, \(J = 8.8, 2.8\) Hz, 1H), 7.43 (dd, \(J = 8.0, 1.6\) Hz, 1H), 7.34 (d, \(J = 1.6\) Hz, 1H), 7.23 (d, \(J = 10.2\) Hz, 1H), 6.93 (d, \(J = 8.8\) Hz, 1H), 6.54 (d, \(J = 8.0\) Hz, 1H), 6.01 (d, \(J = 10.2\) Hz, 1H), 2.68 (s, 3H), 1.22 (s, 3H), 1.13 (s, 3H).
Synthesis of 3,4,5-trimethoxyphenylhydrazine hydrochloride (1d). \(^{13,29}\) 3,4,5-Trimethoxyaniline (1.837 g, 10.0 mmol) was dissolved in 6 M HCl (30 mL) in a 3-necked flask equipped with a thermometer and stirring bar and the solution was cooled down to 0 °C by an ice bath. After dropwise addition of sodium nitrite (0.7588 g, 11.0 mmol) in DI water (3 mL), the resulting solution was kept under stirring at 0 °C for 60 min. Then a solution of SnCl\(_2\)•2H\(_2\)O (7.916 g, 34.5 mmol) in 6 M HCl solution (12 mL) was added slowly with the temperature at 0 °C. After stirring at the same temperature for 4 h, the mixture was filtered. The resulting solid was mixed with 40% KOH solution (15 mL) and extracted with ethyl acetate (4×15 mL). The organic phase was combined and shaken with 32% HCl (2.5 mL) in ethyl acetate (5 mL). The pale solid was collected by filtration, washed with ethyl acetate, and dried in vacuo (0.582 g, 25%). The \(^1\)H NMR spectrum was similar to that reported in the literature, which was obtained in DMSO-\(d_6\). \(^{29}\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 10.08 (s, 3H), 7.97 (s, 1H), 6.41 (m, 2H), 3.74 (s, 6H), 3.50 (s, 3H).

Synthesis of 4,5,6-trimethoxy-2,3,3-trimethyl-3H-indole (2d). \(^{16,17,26}\) 3,4,5-Trimethoxyphenylhydrazine hydrochloride (0.470 g, 2.0 mmol) and 3-methyl-2-butanone (0.193 g, 2.2 mmol) were dissolved in ethanol (10 mL) at room temperature, and heated to reflux under nitrogen for 24 h. After evaporation under reduced pressure, the residue was separated on a silica gel column with hexane/ethyl acetate as the eluent and dried in vacuo to afford 2c as orange solid (0.498 g, 99.8%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.91 (s, 1H), 3.98 (s, 3H), 3.88 (s, 3H), 3.86 (s, 3H), 2.21 (s, 3H), 1.37 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), all 1C unless indicated) \(\delta\) 188.74, 153.98, 149.78, 149.63, 140.15, 128.80, 100.28, 61.16, 61.08, 56.43, 55.19, 21.94, 15.16, 15.15; FT-IR \(\nu/\text{cm}^{-1}\) 2967, 2932, 1578, 1458, 1412, 1327, 1273, 1215, 1107, 1026, 941, 926, 829, 729.
Synthesis of 4,5,6-trimethoxy-2,3,3-trimethyl-3H-indolium iodide (3d).\textsuperscript{17} 4,5,6-Trimethoxy-2,3,3-trimethyl-3H-indole (0.457 g, 1.8 mmol) was dissolved in methyl iodide (8 mL) at room temperature, and heated to reflux for 24 h. Then after cooled to room temperature, the reaction mixture was treated with diethyl ether (50 mL). The orange solid was collected by filtration, washed with diethyl ether, and dried in vacuo (0.529 g, 74%). \textsuperscript{1}H NMR (400 MHz, DMSO-$d_6$) $\delta$ 7.41 (s, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 3.92 (s, 3H), 3.81 (s, 3H), 2.70 (s, 3H), 1.52 (s, 6H); FT-IR $\nu$/cm\textsuperscript{-1} 3622, 3460, 3021, 2940, 1636, 1481, 1420, 1354, 1319, 1238, 1119, 1107, 1022, 995, 961, 934, 837.

Synthesis of 5-sulphosalicylaldehyde sodium salt.\textsuperscript{30-32} 98% H$_2$SO$_4$ (86 mL) was added dropwise to salicylaldehyde (10.001 g, 82.0 mmol) at 0-10 °C in about 1 h. The resulting red brown mixture was stirred at 34 °C for 16 h and poured into cracked ice (180 g). DI water (180 mL) was added to the solution, followed by the slow addition of NaCO$_3$ (87 g) by portion. The precipitate was filtered, washed with acetone and dried in vacuum to give white powder (17.127 g, 93%). The \textsuperscript{1}H NMR spectrum was similar to that reported in the literature, which was obtained in DMSO-$d_6$.\textsuperscript{30} \textsuperscript{1}H NMR (400 MHz, DMSO-$d_6$) $\delta$ 10.83 (s, 1H), 10.25 (s, 1H), 7.90 (d, $J = 2.2$ Hz, 1H), 7.71 (dd, $J = 8.5$, 2.2 Hz, 1H), 6.93 (d, $J = 8.5$ Hz, 1H).

Synthesis of MC$_6$H$^+$SO$_3$\textsuperscript{−}.\textsuperscript{26,33,34} 4,5,6-Trimethoxy-2,3,3-trimethyl-3H-indolium iodide (0.392 g, 1.0 mmol), 5-sulphosalicylaldehyde sodium salt (0.227 g, 1.0 mmol) and piperidine (0.2 mL, 2.0 mmol) were dissolved in ethanol (10 mL). The mixture was stirred under reflux for 22 h. After neutralisation with 32% HCl and evaporation of ethanol, diethyl ether (12 mL) was added and the resulting mixture was cooled to 0 °C with vigorous stirring. The yellow solid was collected by filtration, washed with acetone, recrystallised from ethanol and acetone, and dried in vacuo (0.333 g, 41%). \textsuperscript{1}H NMR (400 MHz, DMSO-$d_6$) $\delta$ 11.19 (s, 1H), 8.42 (d, $J = 16.4$ Hz, 1H), 8.21 (d, $J = 2.0$ Hz, 1H), 7.67 (dd, $J = 8.4$, 2.0 Hz, 1H), 7.65 (d, $J = 16.4$ Hz, 1H), 7.41 (s, 1H), 6.98 (d, $J = 8.4$ Hz, 1H), 4.08 (s, 3H), 4.02 (s, 3H), 3.95 (s, 3H), 3.83 (s, 3H), 1.78 (s, 6H); \textsuperscript{13}C NMR (100 MHz, DMSO-$d_6$, all 1C unless indicated) $\delta$ 181.89, 158.84, 154.85, 148.87, 147.91, 142.23, 140.83, 137.50, 132.66, 127.64, 126.22, 120.08, 115.71, 112.42, 95.70, 61.20, 60.77, 56.88, 52.22, 34.46, 24.08 (2C); UV/Vis (DMSO) $\lambda_{\text{max}}$ nm (log $\varepsilon$) 332 (4.00), 449.5 (4.37);
FT-IR ν/cm\(^{-1}\) 1597, 1539, 1477, 1427, 1335, 1261, 1192, 1092, 1038, 976, 833. ESI-MS \(m/z\) calcd for C\(_{22}\)H\(_{24}\)NO\(_7\)S [M–H]\(^–\) 446.1273, found 446.1278.

\(^1\)H NMR (400 MHz, DMSO-\(d_6\)) of MC\(_6\)H\(^\bullet\)SO\(_3\)^– after treatment with 1.2 equivalent of triethylamine: \(δ\) 7.41 (d, \(J = 2.1\) Hz, 1H), 7.32 (dd, \(J = 8.3, 2.1\) Hz, 1H), 7.03 (d, \(J = 10.2\) Hz, 1H), 6.62 (d, \(J = 8.3\) Hz, 1H), 6.11 (s, 1H), 5.69 (d, \(J = 10.2\) Hz, 1H), 3.82 (s, 3H), 3.79 (s, 3H), 3.67 (s, 3H), 2.61 (s, 3H), 1.27 (s, 3H), 1.11 (s, 3H); \(^{13}\)C NMR (100 MHz, all 1C unless indicated) \(δ\) 153.94, 153.25, 149.79, 144.33, 140.82, 134.60, 129.22, 127.21, 124.36, 119.01, 117.64, 117.29, 113.20, 104.17, 89.39, 60.60, 60.35, 56.04, 51.63, 28.72, 24.10, 20.40.

Synthesis of 4-decylphenylhydrazine hydrochloride (1e).\(^{13}\) 4-Decylaniline (3.842 g, 16.5 mmol) was dissolved in 6 M HCl (20 mL) in a 3-necked flask equipped with a thermometer and stirring bar and the solution was cooled down to 0 °C by an ice bath. After dropwise addition of sodium nitrite (1.256 g, 35 mmol) in DI water (5 mL) over 20 min, the resulting solution was kept under stirring at 0 °C for 50 min. Then a solution of SnCl\(_2\)•2H\(_2\)O (13.042 g, 56.9 mmol) in 6 M HCl solution (20 mL) was added slowly with the temperature at 0 °C. After stirring at the same temperature for 2 h, the mixture was filtered. The resulting solid was mixed with 40% KOH solution (25 mL) and extracted with ethyl acetate (4×25 mL). The organic phase was combined and shaken with 32% HCl (4.2 mL) in ethyl acetate (9 mL). The pale solid was collected by filtration, washed with ethyl acetate, and dried in vacuo (3.672 g, 78%). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)) \(δ\) 10.08 (s, 3H), 8.06 (s, 1H), 7.00 (m, 4H), 2.49 (t, \(J = 7.8\), 2H), 1.51 (m, 2H), 1.35-1.15 (m, 14H), 0.85 (t, \(J = 6.8\), 3H); \(^{13}\)C NMR (100 MHz, DMSO-\(d_6\), all 1C unless indicated) \(δ\) 143.25, 135.63, 128.66 (2C), 114.79 (2C), 34.27, 31.22, 31.07, 28.96, 28.93, 28.80,
28.62, 28.50, 22.02, 13.88; FT-IR ν/cm\(^{-1}\) 3229, 2955, 2916, 2851, 2696, 1574, 1520, 1489, 1474, 864, 810, 714.

**Synthesis of 5-decyl-2,3,3-trimethyl-3H-indole (2e)**.\(^{16,17,26}\) 4-Decylphenylhydrazine hydrochloride (0.952 g, 3.3 mmol) and 3-methyl-2-butanone (0.330 g, 3.8 mmol) were dissolved in ethanol (15 mL) at room temperature, and heated to reflux under nitrogen for 24 h. After evaporation under reduced pressure, the residue was separated on a silica gel column with hexane/ethyl acetate as the eluent and dried in vacuo to afford 2d as orange oil (0.892 g, 89%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.42 (d, J = 8.0 Hz, 1H), 7.14-7.05 (m, 2H), 2.63 (t, J = 7.8, 2H), 1.62 (m, 2H), 1.40-1.19 (m, 20H), 0.88 (t, J = 7.0, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), all 1C unless indicated) δ 187.07, 151.92, 145.90, 140.24, 127.66, 121.48, 119.56, 53.58, 36.19, 32.04, 29.764, 29.756, 29.66, 29.56, 29.48, 23.35 (2C), 22.83, 15.45, 14.23; FT-IR ν/cm\(^{-1}\) 2959, 2924, 2855, 1578, 1462, 1377, 1250, 1204, 964, 945, 826, 721.

**Synthesis of 5-decyl-2,3,3-trimethyl-3H-indolium iodide (3e)**.\(^{17}\) 5-Decyl-2,3,3-trimethyl-3H-indole (0.834 g, 2.8 mmol) was dissolved in methyl iodide (15 mL) at room temperature, and heated to reflux for 25 h. Then after cooled to room temperature, the reaction mixture was treated with diethyl ether. The orange solid was collected by filtration, washed with diethyl ether, and dried in vacuo (1.152 g, 94%). \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) δ 7.80 (d, J = 8.3 Hz, 1H), 7.65 (d, J = 1.3 Hz, 1H), 7.33 (dd, J = 8.3, 1.3 Hz, 1H), 3.94 (s, 3H), 3.73 (s, 3H), 2.70 (t, J = 7.6, 2H), 1.60 (m, 2H), 1.50 (s, 6H), 1.31-1.19 (m, 14H), 0.85 (t, J = 6.8, 3H); \(^{13}\)C NMR (100 MHz, DMSO-d\(_6\), all 1C unless indicated) δ 194.83, 144.38, 141.71, 140.12, 128.57, 122.99, 114.71, 53.63, 34.94, 34.49, 31.21, 30.93, 28.91, 28.88, 28.70, 28.60, 28.50, 22.01, 21.73 (2C), 13.88, 13.77; FT-IR ν/cm\(^{-1}\) 3491, 3445, 2916, 2855, 1636, 1470, 1462, 1366, 1146, 964, 945, 910, 818, 718.

**Synthesis of MC\(_7\)H\(^+\)SO\(_3\)^{-}\(^{26,33}\) 5-Decyl-2,3,3-trimethyl-3H-indolium iodide (1.070 g, 2.4 mmol), 5-sulphosalicylaldehyde sodium salt (0.543 g, 2.4 mmol) and piperidine (0.5 mL, 5.1 mmol) were dissolved in ethanol (25 mL). The mixture was stirred under reflux for 22 h. After neutralisation with 32% HCl and evaporation of ethanol, diethyl ether (12 mL) was added and the resulting mixture was cooled to 0 °C with vigorous stirring. The orange solid was collected by filtration, washed with acetone, recrystallised from ethanol and acetone, and dried in vacuo (0.491 g,
1H NMR (400 MHz, DMSO-d6) δ 11.30 (s, 1H), 8.45 (d, J = 16.4 Hz, 1H), 8.22 (s, 1H), 7.94-7.56 (m, 4H), 7.43 (d, J = 8.4 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 4.08 (s, 3H), 2.72 (m, 2H), 1.75 (s, 3H), 1.55 (m, 2H), 1.36-1.19 (m, 14H), 0.84 (t, J = 6.4 Hz, 6H); 13C NMR (100 MHz, DMSO-d6, all 1C unless indicated) δ 181.22, 158.96, 148.24, 144.37, 143.49, 140.73, 139.86, 132.59, 128.80, 127.82, 122.55, 120.07, 115.75, 114.66, 112.66, 51.67, 35.07, 34.14, 31.22, 30.94, 28.91, 28.90, 28.72, 28.60, 28.53, 22.01 (2C), 13.88; UV/Vis (DMSO) λ max nm (log ε) 305.5 (3.72), 437 (4.06); FT-IR ν/cm–1 2920, 2851, 1601, 1574, 1535, 1485, 1277, 1227, 1169, 1107, 1026, 964, 949, 860, 829. ESI-MS m/z calcd for C29H38NO4S [M–H]– 496.2522, found 496.2534.

1H NMR (400 MHz, DMSO-d6) of MC7'H+SO3– after treatment with 1.2 equivalent of triethylamine: δ 7.41 (d, J = 2.0 Hz, 1H), 7.31 (dd, J = 8.8, 2.0 Hz, 1H), 7.03 (d, J = 10.2 Hz, 1H), 6.97-6.84 (m, 2H), 6.57 (d, J = 8.0 Hz, 1H), 6.45 (d, J = 8.0 Hz, 1H), 5.75 (d, J = 10.2 Hz, 1H), 3.04-2.94 (m, 4H), 2.61 (s, 3H), 1.37-1.22 (m, 14H), 1.20 (s, 3H), 0.86 (t, J = 6.6 Hz, 6H)

1’-(3-sulphopropyl)-3’,3’-dimethyl-6-sulpho-1’,3’-dihydrospiro[chromene-2,2’-indole], sodium salt (1:1) (MC8H3+SO3–)18,19 2,3,3-Trimethyl-3H-indole (8.082 g, 51 mmol) and 1,3-propanesultone (6.845 g, 56 mmol) were dissolved in toluene (100 mL). The mixture was stirred under reflux for 52 h. The product was precipitated to the bottom of the flask and the solvent was removed carefully with a pipette. The resulting purple solid was washed with diethyl ether, dried in vacuum and then dissolved in ethanol (150 mL). After addition of 5-sulphosalicylaldehyde sodium salt (5.999 g, 27 mmol), the mixture was allowed to reflux for 28 h. The orange solid was collected by filtration, washed with ethanol, and dried in vacuo (7.778 g, 31%). 1H NMR (400 MHz, DMSO-d6) δ 11.40 (s, 1H), 8.54 (d, J = 16.2 Hz, 1H), 8.28 (s, 1H), 8.07 (d, J = 7.2 Hz, 1H), 7.91 (d, J = 16.2 Hz, 1H), 7.86 (d, J = 7.2 Hz, 1H), 7.69 (dd, J = 8.6, 1.2 Hz, 1H), 7.61 (m, 2H), 6.99 (d, J = 8.6 Hz,
1H), 4.77 (m, 2H), 2.65 (m, 2H), 2.19 (m, 2H), 1.79 (s, 6H); 13C NMR (100 MHz, DMSO-d6, all 1C unless indicated) δ 182.25, 159.39 (2C), 150.43, 143.60, 140.96, 140.66, 132.93, 129.09, 129.05, 122.88, 120.14, 115.74, 115.19, 112.56, 52.02, 47.64, 45.81, 26.08, 24.42; UV/Vis (DMSO) λmax nm (log ε) 368.5 (4.01), 439 (4.26); FT-IR ν/cm⁻¹ 1597, 1528, 1470, 1312, 1254, 1219, 1034, 968, 937, 860, 829, 764, 733; ESI-MS m/z calcd for C_{21}H_{21}NNaO_{7}S_{2} [M-H] − 486.0662, found 486.0663.

1H NMR (400 MHz, DMSO-d6) of MC_{8}H^{+}SO_{3}^{−} after treatment with 1.2 equivalent of triethylamine: δ 7.40 (d, J = 1.6 Hz, 1H), 7.30 (dd, J = 8.4, 1.6 Hz, 1H), 7.17-6.93 (m, 3H), 6.73 (t, J = 7.4 Hz, 1H), 6.64 (d, J = 7.6 Hz, 1H), 6.54 (d, J = 8.4 Hz, 1H), 5.74 (d, J = 10.4 Hz, 1H), 3.19 (m, 2H), 2.42 (m, 2H), 1.85 (m, 2H), 1.18 (s, 3H), 1.08 (s, 3H).

Synthesis of MCH^{+}DBS^{−}. 1-(2-Hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrlylospiran (250.4 mg, 0.7 mmol) and 4-dodecylbenzenesulphonic acid (255.4 mg, 0.8 mmol) were dissolved in toluene (7.1 mL). The resulting solution was kept in dark at room temperature for 24 h. The orange solid was collected by filtration, washed with toluene and diethyl ether subsequently, and dried in vacuo (392.8 mg, 81%). Since the starting material DBSA is technical grade which is a mixture of isomers, signals for DBS^{−} part in NMR spectra of MCH^{+}DBS^{−} are too complicated to be assigned. To simplify the characterisation, chemical shifts only for the MCH^{+} part in 1H NMR and 13C NMR of MCH^{+}DBS^{−} were listed unless indicated. 1H NMR (400 MHz, CDCl₃) δ 8.81 (d, J = 2.7 Hz, 1H), 8.26 (d, J = 16.5, 1H), 8.17 (d, J = 16.5, 1H), 7.97 (dd, J = 9.2, 2.7 Hz, 1H), 7.97-7.90 (m, 2H from DBS^{−}), 7.61-7.45 (m, 4H), 7.37 (d, J = 9.2 Hz, 1H), 7.25-7.16 (m, 2H from DBS^{−}), 4.72 (t, J = 4.7 Hz, 2H), 3.96 (t, J = 4.7 Hz, 2H), 1.83 (s, 6H). 13C NMR (100 MHz, CDCl₃, all 1C unless indicated) δ 184.62, 164.86, 149.05, 143.95, 140.90, 140.77, 130.15, 129.77, 129.49, 127.03, 126.41, 126.35, 122.99, 121.30, 114.92, 59.56, 52.92, 51.03, 27.57 (2C); FT-IR ν/cm⁻¹ 2955, 2924, 2855, 2361, 2330, 1605, 1535,
2.3 Construction and characterisation of droplet motion systems

2.3.1 General methods for droplet experiments

UV/Vis absorption spectra were obtained at room temperature using a Shimadzu UV-1800 spectrophotometer. NMR spectra were recorded on a Bruker Avance 400 spectrometer. Chemical shifts are reported in parts per million (ppm) relative to TMS (δ 0.0). The surface/interfacial tension was measured using the pendant droplet method and performed on a video-based optical contact angle measuring instrument (DataPhysics OCA20, FTA200 Dynamic Contact Angle Analyzer or USA KINO SL200KS). The interfacial tension values were calculated automatically by the corresponding tensiometer software using the Young-Laplace equation. The pH measurements were made using a Horiba F-71 pH meter. The MALDI MS measurements were carried out on a Shimadzu Axima Mass spectrometer. Fluorescence emission spectra were recorded at room temperature using a Horiba Jobin-Yvon Fluorolog FL3-22 spectrofluorometer. A 365 nm mounted LED (190 mW, M365L2, Thorlabs) equipped with a collimation adapter (SM1P25-A, Thorlabs) and 405 nm lasers (2.7 mW or 63 mW) were used for light illumination. All movies were taken with an iPhone 6 smartphone or a high speed video camera (IDS UI-3370CP, IDS GmbH, Germany). The glass slides or Petri dishes were immersed in piranha solution (conc. H₂SO₄/30% H₂O₂ = 3/1, v/v) at 100 ºC for 1 h, then rinsed thoroughly with deionised water and stored in deionised water, and dried under a stream of nitrogen prior to use. All the experiments were carried out at room temperature unless specifically mentioned.
2.3.2 Construction of droplet motion systems

SPCH$_2$CH$_2$OH droplet in DI water. 2D movement: SPCH$_2$CH$_2$OH was dissolved in DCE/toluene mixture (1:1, v/v) to make the concentration of spiropyran 0.1 M. An organic droplet was generated by loading 2 µL of the above solution onto the bottom of a glass Petri dish filled with DI water and 365 nm light was used to control the movement of the droplet towards the light source along the beam.

3D movement: SPCH$_2$CH$_2$OH was dissolved in DCE/toluene mixture (1:1.7, v/v) to make the concentration of spiropyran 0.1 M. An organic droplet was generated by loading 2 µL of the above solution onto the bottom of a glass cuvette filled with DI water and 365 nm light was used from top to move the droplet up towards the light source.

SPCH$_2$CH$_2$OH droplet in surfactant solution. Motion under water: SPCH$_2$CH$_2$OH was dissolved in DCE or DCE/toluene mixture (1:1, v/v) to make the concentration of spiropyran 0.1 M. A droplet was generated by loading 2 µL of the above solution onto the bottom of a glass Petri dish filled with an aqueous solution containing SDBS (7 mM), SDBS (7 mM) and CaCl$_2$ (0.4 mM) or SDBS (7 mM) and an acid (0.1 M). The acid was hydrochloric acid, methanesulphonic acid, oxalic acid or phthalic acid. 365 nm light was used to control the underwater movement of the droplet away from light and then 405 nm light was used to move the resulting droplet towards light source.

Motion on water: SPCH$_2$CH$_2$OH was dissolved in DCE/toluene mixture (1:2, v/v) to make the concentration of spiropyran 0.1 M. A droplet was generated by loading 2 µL of the above solution under the surface of an aqueous solution of SDBS (7 mM) and CaCl$_2$ (0.4 mM) with or without an acid (0.1 M). 365 nm light was used to control the movement of the droplet away from light on water and then 405 nm light was used to move the resulting droplet towards light source.

SPCH$_2$CH$_2$OH/acid droplet in surfactant solution. Motion under water: SPCH$_2$CH$_2$OH and an acid (1:1, mol/mol) were dissolved in DCE or DCE/toluene mixture (1:1, v/v) to make the concentration of spiropyran 0.1 M. The acid used was 2-hexyldecanoic acid, acetic acid, octanoic acid, lipoic acid or benzoic acid. An organic droplet was generated by loading 2 µL of the above solution onto the
bottom of a glass Petri dish filled with an aqueous solution containing SDBS (7 mM). 365 nm light was used to control the underwater movement of the droplet away from light and then 405 nm light was used to move the resulting droplet towards light source.

Motion on water: SPCH$_2$CH$_2$OH and an acid (1:1, mol/mol) like 2-hexyldecanoic acid, acetic acid, octanoic acid, lipoic acid or benzoic acid were dissolved in DCE/toluene mixture (1:2, v/v) to make the concentration of spiropyran 0.1 M. An organic droplet was generated by loading 2 µL of the above solution under the surface of an aqueous solution containing SDBS (7 mM) and CaCl$_2$ (0.4 mM). 365 nm light was used to control the movement of the droplet away from light on water and then 405 nm light was used to move the resulting droplet towards light source.

**SPCH$_2$CH$_2$OH/C$_7$H$_{15}$COOH/SDBS droplet in DI water.** SPCH$_2$CH$_2$OH, SDBS and octanoic acid (1:0.2:10, mol/mol/mol) were dissolved in chloroform to make the concentration of spiropyran 0.1 M. An organic droplet was generated by loading 2 µL of the above solution onto the bottom of a glass Petri dish filled with DI water. 365 nm light was used to control the movement of the droplet away from the light source.

**MCH$^+$/DBS$^-$ droplet in surfactant solution.** SPCH$_2$CH$_2$OH and DBSA (1:1, mol/mol) was dissolved in DCE and toluene mixture to give a concentration of 0.1 M. The solution was kept in dark for at least 12 h. An organic droplet was generated by loading 2 µL of the above solution using an autopipette onto the bottom of a Petri dish filled with an aqueous solution containing SDBS (7 mM) and CaCl$_2$ (0.4 mM). 365 nm or 405 nm light was used to control the movement of the droplet towards the light source. For droplet moving under water, the ratio of DCE and toluene was 1:1 (v/v) or pure DCE was used. For droplet floating on water, the ratio of DCE and toluene is 1:2 (v/v).

**MCH$^+$/DBS$^-$ droplet in DI water.** Motion in 2D: SPCH$_2$CH$_2$OH and DBSA (1:1, mol/mol) was dissolved in nitrobenzene to give a concentration of 0.1 M. The solution was kept in dark for at least 12 h. An organic droplet was generated by loading 2 µL of the above solution using an autopipette onto the bottom of a Petri dish filled with DI water. 365 nm or 405 nm light was used to control the movement of the droplet on the bottom of the Petri dish towards the light source.
Motion in 3D: \(\text{SPCH}_2\text{CH}_2\text{OH}\) and DBSA (1:1, mol/mol) was dissolved in nitrobenzene and toluene mixture (1:1.9, v/v) to give a concentration of 0.1 M. The solution was kept in dark for at least 12 h. An organic droplet was generated by loading 2 µL of the above solution using an autopipette onto the bottom of a cuvette or a tank filled with DI water. The droplet was illuminated by 405 nm light from vertical, horizontal or any other direction. The droplet moved towards the light source along the beam in 3D.

\(\text{MC}_8\text{H}^+\text{SO}_3^-/\text{H}_2\text{O}\) droplet in fatty alcohol. \(\text{MC}_8\text{H}^+\text{SO}_3^-\) was dissolved in DI water to give a concentration of 0.2 M. A water droplet was generated by loading 2 µL of the above solution using an auto-pipette onto the bottom of a polystyrene Petri dish (5 cm) filled with a fatty alcohol. The fatty alcohol was 1-hexanol, 1-octanol, 1-decanol or cyclohexanol and saturated with water prior to use. A 405 nm laser was used to control the movement of the droplet. In 1-hexanol, 1-octanol or 1-decanol the \(\text{MC}_8\text{H}^+\text{SO}_3^-/\text{H}_2\text{O}\) droplet moved in 2D, on the bottom of the Petri dish. In cyclohexanol, the droplet was able to move in 3D, for example, up towards the light source.

Movement of \(\text{SPCH}_2\text{CH}_2\text{OH}\) droplet in capillaries or tubes filled with surfactant solution. \(\text{SPCH}_2\text{CH}_2\text{OH}\) was dissolved in DCE to make the concentration of spiropyran 0.1 M. One end of a glass melting point capillary (both ends open, inner diameter 1.1 mm) or a plastic tube (both ends open, inner diameter 2 mm) was immersed in a small amount of the above \(\text{SPCH}_2\text{CH}_2\text{OH}\) solution to give a plug of the photoactive organic liquid. Each end of the capillary was then immersed in the aqueous solution of SDBS (7 mM) and HCl (0.1 M), such that both sides of the organic liquid plug was surrounded by the aqueous phase in the capillary.

The capillary was then placed in a Petri dish containing the aqueous solution of SDBS (7 mM) and HCl (0.1 M) or directly on the desktop. 365 or 405 nm light was used to irradiate the organic/water interface to create movement of the liquids in the capillaries or tubes.
2.3.3 Droplet collision experiments

**MCH+DBS− droplet.** The initial moving droplet was a nitrobenzene solution of MCH+DBS− (0.1 M, 2 µL). The droplet (2 µL) for the first collision was a nitrobenzene solution of tetraphenylporphyrin (1.0 mM) containing 1% v/v Triton X-100. The droplet (2 µL) for the second collision was a nitrobenzene solution of oleylamine (0.1 M). The above three droplet was separately placed on a glass slide in a Petri dish filled with DI water. 405 nm light was used to moving the initial photoactive droplet (yellow) to collide with the tetraphenylporphyrin droplet (purple). The colour of droplet changed into green due to the protonation of tetraphenylporphyrin. The resulting larger droplet (green) was guided by 405 nm light to the oleylamine droplet (colourless) to give a purple droplet due to the deprotonation of tetraphenylporphyrin.

**MC₈H⁺SO₃− water droplet.** The moving droplet was 2 µL of MC₈H⁺SO₃− aqueous solution (0.2 M) containing potassium iodide (2.5 M). The droplet for collision was 2 µL of 32% hydrogen peroxide solution. Both droplets were placed into a polystyrene Petri dish and 405 nm light was used to control the movement of the photoactive droplet. A large amount of oxygen bubbles were generated immediately due to the decomposition of hydrogen peroxide catalysed by potassium iodide when the two droplet merged.

2.3.4 Characterisation of droplet motion systems

2.3.4.1 IFT measurements

**SPCH₂CH₂OH droplet.** SPCH₂CH₂OH was dissolved in chloroform or DCE to make the concentration of spiropyran 0.01 M or 0.1 M, respectively. The droplet generated with this solution under DI water or the aqueous solution of SDBS (2.2 mM) was illuminated with 365 nm or 405 nm light. IFT was measured with pendant drop method at the same time. IFT of the droplet with the same composition under the same aqueous solution without light illumination was measured as a control.

**SPCH₂CH₂OH/C₇H₁₅COOH/SDBS droplet.** SPCH₂CH₂OH, SDBS and octanoic acid (1:0.2:10, mol/mol/mol) were dissolved in chloroform to make the concentration of spiropyran 0.1 M. This solution was diluted to 1/10. IFT of the
diluted solution upon alternative irradiation of 365 nm and 405 nm light in DI water was measured with pendant drop method. IFT of the same solution without light illumination was measured as a control. IFTs of the chloroform solution of SPCH$_2$CH$_2$OH/SDBS (1:0.2, mol/mol) and SPCH$_2$CH$_2$OH/octanoic acid (1:10, mol/mol) in DI water alternatively illuminated by 365 nm light and 405 nm light were also measured separately.

**MCH$^+$DBS$^-$ droplet.** SPCH$_2$CH$_2$OH and DBSA (1:1, mol/mol) was dissolved in nitrobenzene to give a concentration of 0.1 M. The solution was kept in dark for at least 12 h and then diluted to 0.002 M. IFT of this solution in DI water was measured before and after 3 min illumination of 365 nm light. IFT of the same solution without light illumination was measured as a control. IFT of nitrobenzene solution of DBSA (0.002 M) was also measured.

**MC$_8$H$^+$SO$_3^-$/H$_2$O droplet.** MC$_8$H$^+$SO$_3^-$ was dissolved in DI water to give a concentration of 0.2 M. IFT of this solution in 1-hexanol or cyclohexanol under 405 nm light illumination was measured. IFT of the same MC$_8$H$^+$SO$_3^-$/H$_2$O solution in 1-hexanol or cyclohexanol without light illumination was measured as a control.

2.3.4.2 Observations of Marangoni flow

**SPCH$_2$CH$_2$OH/HDA acid droplet.** SPCH$_2$CH$_2$OH and 2-hexyldecanoic acid (1:1, mol/mol) were dissolved in 1,2-dichloroethane to make the concentration of spiropyran 0.1 M. An organic droplet was generated by loading 10 µL of the above solution onto the bottom of a glass cuvette filled with an aqueous solution of SDBS (7 mM) and CaCl$_2$ (0.4 mM). 365 nm light from one side was used to move the droplet away from the light source and videos were taken from above. The convective flow in the droplet was indicated by the purple colour generated in the illuminated side. After the droplet became dark purple and stopped moving, 405 nm light from one side was used to move the droplet towards the light source and videos were taken from above. The flow in the droplet was indicated by the colourless current before it became light yellow or colourless and stopped moving.

**MCH$^+$DBS$^-$ droplet.** SPCH$_2$CH$_2$OH and DBSA (1:1, mol/mol) was dissolved in nitrobenzene and toluene mixture (1:1.9, v/v) to give a concentration of 0.1 M. The
solution was kept in dark for at least 12 h. An organic droplet was generated by loading 10 µL of the above solution into a glass cuvette filled with DI water. The droplet was illuminated by 405 nm light from the top and videos were taken from the side with a Goniometer camera at the same time. The droplet moved up towards 405 nm light with a fusiform shape and fast flow within the droplet was observed at the same time.

**MC₈H⁺SO₃⁻/H₂O droplet.** MC₈H⁺SO₃⁻ was dissolved in DI water to give a concentration of 0.2 M. A water droplet was generated by loading 5 µL of the above solution into a plastic cuvette filled with 1-hexanol. The droplet was illuminated by 405 nm light from the front, the top or the side. At the same time, videos were taken from the side with a high speed camera to record the directional movement of the particles within the droplet.

2.2.4.3 Photochemical reaction monitored by UV/Vis and NMR spectroscopy

**SPCH₂CH₂OH droplet.** SPCH₂CH₂OH was dissolved in CDCl₃ to make the concentration of spiropyran 0.025 M. ¹H NMR was recorded before and after 365 nm light illumination for 30 min, which was unchanged.

**SPCH₂CH₂OH** was dissolved in dichloromethane to make the concentration of spiropyran 5×10⁻³ M. UV/Vis spectra of this solution were recorded subsequently after 15 min in dark, 20 s under 365 nm light irradiation and 20 s under 405 nm light or visible light irradiation.

**SPCH₂CH₂OH** was dissolved in dichloroethane to make the concentration of spiropyran 0.1 M. 10 µL of the solution was loaded into a 2 mL vial filled with 1 mL aqueous solution of SDBS (7 mM) and HCl (0.1 M), SDBS (7 mM) and HCl (1 mM), SDBS (7 mM) or HCl (0.1 M), respectively. The droplet was irradiated with 365 nm light 3 min. Then 1.5 µL of the droplet was taken and added to 3 mL of chloroform and UV/Vis spectrum of the resulting chloroform solution was recorded immediately.

**MCH⁺DBS⁻ droplet.** SPCH₂CH₂OH was dissolved in CDCl₃ to make the concentration of spiropyran 0.025 M. ¹H NMR spectra were recorded immediately after addition of 1 equivalent of DBSA, followed by 12 h in dark, and then under 365 nm light illumination for 30 min.
SPCH₂CH₂OH and DBSA (1:1, mol/mol) was dissolved in dichloromethane to make the concentration of spiropyran $5 \times 10^{-5}$ M. UV/Vis spectra were recorded subsequently after preparation, 12 h in dark and then 30 s under illumination of 365 nm light, 405 nm light or visible light.

SPCH₂CH₂OH was dissolved in CDCl₃ to make the concentration of spiropyran 0.1 M. 200 µL of the solution was loaded into a 2 mL vial filled with 1 mL of D₂O. The solution was illuminated with 365 nm light for 15 min and then the organic layer was diluted to 0.025 M to test $^1$H NMR. The aqueous layer was used to run NMR directly. As a control, 200 µL of CDCl₃ solution of SPCH₂CH₂OH (0.1 M) under 1 mL of D₂O was kept in dark for 15 min and NMR spectra of the organic and aqueous layers were measured in the same way, respectively.

MC₈H⁺SO₃⁻ water droplet. SPCH₂CH₂OH was dissolved in D₂O to make the concentration of spiropyran 0.025 M. $^1$H NMR spectra were recorded before and after 405 nm light illumination for 10 min and then in dark for 1 h.

SPCH₂CH₂OH was dissolved in DI water to make the concentration of spiropyran $3 \times 10^{-5}$ M. UV/Vis spectra of this solution were recorded subsequently after preparation, 20 s under 365 nm or 405 light irradiation and then 2 h in dark.

2.3.4.4 Characterisation of release

Characterizing release with pH measurement. pHs of DBSA aqueous solution at concentrations of 0.1, 0.2, 0.4, 0.6, 0.8 and 1 mM were measured and Log[c] vs pH standard curve for DBSA solution was obtained according to the results.

SPCH₂CH₂OH and DBSA (1:1, mol/mol) were dissolved in nitrobenzene to make the concentration of spiropyran 0.1 M and then kept in dark for 12 h. 10 µL of the solution was loaded into a 2 mL vial filled with 1 mL of DI water. pH of the aqueous layer was measured at 10 min, 30 min, 1 h, 2 h and 24 h. As a control, 10 µL nitrobenzene solution of DBSA (0.1 M) was loaded into a 2 mL vial filled with 1 mL of DI water and pH of the aqueous layer was measured in the same way. For light illumination experiments, 10 µL of the above 12 h old SPCH₂CH₂OH:DBSA solution was loaded into a 2 mL vial filled with 1 mL of DI water and pH of the aqueous layer was measured subsequently after 10 min in dark and then under
365 nm light irradiation for 10 min or under 405 nm light irradiation for 5 min. It should be noted that the vial was washed with dilute HCl and DI water prior to use.

**Characterizing release with pH measurement.** SPCH$_2$CH$_2$OH was dissolved in DCE/toluene mixture (1:1, v/v) to make the concentration of spiropyran 0.1 M. An organic droplet was generated by loading 2 µL of the above solution onto the bottom of a glass Petri dish filled with DI water and 365 nm light was used to move the droplet towards the light source. At the same time, some of the aqueous solution containing the red fluorescent plume was collected and the fluorescent emission was measured with an excitation wavelength of 365 nm. The positive ion MALDI-TOF MS spectrum of aqueous solution containing plume was also obtained.

MC$_8$H$^+$SO$_3^-$ was dissolved in DI water to give a concentration of 0.2 M. A water droplet was generated by loading 2 µL of the above solution using an auto-pipette onto the bottom of a polystyrene Petri dish (5 cm) filled with 1-hexanol and a 405 nm laser was used to move the droplet. At the same time, some of the hexanol solution containing the blue fluorescent plume was collected and the fluorescent emission was measured with an excitation wavelength of 405 nm. The negative ion MALDI-TOF MS spectrum was also measured.

### 2.4 References


(33) Sunamoto, J.; Iwamoto, K.; Akutagawa, M.; Nagase, M.; Kondo, H. Rate


Chapter 3 Synthesis and characterisation of photoacidic merocyaninesulphonic acids

3.1 Introduction

Photoacids are a class of compounds, which can generate acid upon light irradiation. In recent years, photoacids have been widely developed due to their important application in the fields of polymerisation, microelectronics and biology.\textsuperscript{1,2} For most of the reported photoacids, the process to generate acid is irreversible.\textsuperscript{1,2} Compounds that can reversibly decrease pH under light illumination have scarcely been reported. For example, malachite green and spiropyran/merocyanine based systems are able to perform this task.\textsuperscript{3-6}

As photosensitive materials, spiropyrans (SP) can undergo reversible conversion between their ring-closed spiropyran form and ring-opened merocyanine (MC) form (Figure 3.1).\textsuperscript{7-10} The SP form is composed of indoline and benzopyran moieties. The two $\pi$-systems are separated by a spiro-carbon, making the absorption in the UV range and the compound colourless. However, in the MC form, the two separate $\pi$-systems become linked by a single extended $\pi$-conjugation, making this isomer strongly coloured (push-pull effect) with an absorption between 550 and 600 nm. The ring-opened MC is a hybrid of a quinoidal resonance and a zwitterionic resonance structure (Figure 3.1).\textsuperscript{10-16} The charge separated zwitterionic form is viewed as the major contributor in polar solvents, while the neutral quinoidal form can be stabilised by non-polar media.\textsuperscript{10-13,16} In non-polar solvent, since the energy gap between the quinoidal form and the excited state of MC is decreased, a red shift in the absorption sometimes can be observed and the solution appears blue.\textsuperscript{16-19} It should be noted that the non-polar solvents can favour the ring-closed SP form.\textsuperscript{20-22} As a result, the zwitterionic and quinoidal forms of the ring-opening structure usually exist as intermediates and thermally convert to the SP form in non-polar solvents.\textsuperscript{16-18}
The MC form has a higher proton affinity than the SP form since MC contains phenoxide group that is capable of protonation. The difference in proton affinity of the two isomers makes it possible to change the SP species into a photoacid by the introduction of a strongly acidic functional group such as sulphonic acid onto it. The acid group can be added either to the indoline or the benzopyran moieties as shown in Figure 3.2. In 1982, Sunamoto et al. introduced a sulphonic acid group to the aromatic ring of the benzopyran unit and they obtained a ring-opened merocyaninesulphonic acid that could reversibly shift pH from weakly to strongly acidic under light illumination (Figure 3.2a and Figure 3.3). In 2011, Liao’s group prepared an indoline-substituted merocyaninesulphonic acid by introducing a propyl sulphonate group to the nitrogen of the indoline moiety (Figure 3.2b). They used this compound as a photoacid to initiate an esterification reaction as well as alter the state of a pH sensitive polymer upon light irradiation. In 2013, another type of indoline-substituted merocyaninesulphonic acid was synthesised by Kojima’s group by attaching the sulphonic acid group to the aromatic ring of the indoline moiety (Figure 3.2c). They found that this compound existed in the ring-opened state while its deprotonated product existed as the ring-closed SP form.
In aqueous solution, the reported merocyaninesulphonic acids exist as the ring-opened merocyanine form (MCH\(^+\)SO\(_3\)\(^{-}\)) with the sulphonic acid as a sulphonate and the phenoxide group protonated to give a weak acid.\(^{3,5,6,23-27}\) Upon visible light irradiation, MCH\(^+\)SO\(_3\)\(^{-}\) acts as a strong acid, with the compound isomerised to the ring-closed spiropyransulphonate (SPSO\(_3\)\(^{-}\)) and the phenolic proton released.\(^{5,23-27}\) The resulting SPSO\(_3\)\(^{-}\) can convert back to MCH\(^+\)SO\(_3\)\(^{-}\) in the dark, increasing the pH as shown in Figure 3.3.

\[
\begin{align*}
\text{MCH}^+\text{SO}_3^- + \text{H}_2\text{O} & \xrightarrow{\text{Light}} \text{MCH}^+\text{SO}_3^- + \text{MCSO}_3^- + \text{H}^+ \\
& \xrightarrow{\text{Dark}} \text{SPSO}_3^- + \text{H}^+ \\
\text{Solid} & \Rightarrow \text{(High pH)} & \text{SPSO}_3^- & \Rightarrow \text{(Low pH)}
\end{align*}
\]

**Figure 3.3** pH change generated by photoisomerisation of merocyaninesulphonic acid in water.

It has been reported that spiropyrans can undergo hydrolysis under aqueous conditions (Figure 3.4), but the rate of hydrolysis is relatively slow in acidic solution.\(^{28-31}\) As a result, these merocyaninesulphonic acids are relatively stable in the aqueous solution due to their acidic nature.

![Figure 3.4 Hydrolysis of spiropyran species in the presence of H\(_2\)O.\(^{28-31}\)](image)

Based on the reversible photoacidic nature of merocyaninesulphonic acids, a number of applications have been developed in the areas of biological and materials science, for example, to catalyse chemical reactions,\(^{5,32}\) to kill multidrug-resistant bacteria,\(^{25}\) to control the release of fragrant molecules,\(^{27}\) to construct a supramolecular hydrogel in three dimensions,\(^{26}\) to optically control a microbial fuel cell,\(^{23}\) or even to manipulate the movement of organic droplets.\(^{24}\) In 2014, Florea *et al.* created a pH gradient in aqueous solution with light illumination using a merocyaninesulphonic acid as a photoacid in water, thus moving a lipophilic droplet as a result of a surface tension change from the pH gradient.\(^{24}\) In this chapter, a variety of merocyaninesulphonic acids that have potential application in light-induced droplet motion systems were synthesised and characterised. The
properties of these merocyaninesulphonic acids such as photochromism, stability, acidity and solubility could be varied by changing the position of the sulphonic acid group or using different functional groups. Different merocyaninesulphonic acids with an indoline substitution or a phenol substitution were prepared to vary the properties of the MCs. Electron-donating groups like methoxy and electron-withdrawing group like nitro were used to vary the pH range and acidity. Organic solvent solubilizing groups like long alkyl chains and water solubilizing groups like sodium sulphonates were introduced to vary the solubility.

3.2 Synthesis and characterisation of merocyaninesulphonic acids

3.2.1 Synthesis of merocyaninesulphonic acids

The reported classic method to synthesise merocyaninesulphonic acids is the condensation of methylene indoline bases or their precursors with o-hydroxy benzaldehydes (Figure 3.5).\textsuperscript{7,9,33} To simplify the synthetic process, the precursors of the methylene bases were directly used to react with o-hydroxy aromatic aldehydes and the sulphonic acid groups were introduced either to the methylene base precursors or to the o-hydroxy benzaldehydes. The synthesis of the methylene base precursors could be derived from phenylhydrazine derivatives that were
commercially available or readily prepared from aniline derivatives. \(\text{o-Hydroxy benzaldehyde derivatives are usually obtained by the addition of functional groups to salicylaldehyde by sulphonation, nitration and other electrophilic reactions}. Four different types of mono-substituted merocyaninesulphonic acids were synthesised in this work.

For the first type, the sulphonic acid group is connected to the nitrogen of the indoline moiety through an alkyl chain.\(^5\)\(^,\)\(^6\) The sulphonic acid group was introduced by the reaction of the indole derivative with 1,3-propanesultone as indicated in Figure 3.6. \(\text{MC}_1\text{H}^+\text{SO}_3^–\), \(\text{MC}_2\text{H}^+\text{SO}_3^–\), \(\text{MC}_3\text{H}^+\text{SO}_3^–\), \(\text{MC}_4\text{H}^+\text{SO}_3^–\) with different functional groups on the aromatic ring of the indoline part or the phenol part were synthesised as shown in Figure 3.5 and described in Chapter 2. All the compounds were soluble in water from \(10^{-3}\) - \(10^{-4}\) M and in polar organic solvents such as dimethyl sulphoxide (DMSO) but not in less polar solvents like chloroform.

For the second type, the sulphonic acid group is on the aromatic ring of the indoline moiety.\(^6\)\(^,\)\(^3\)\(^4\) The sulphonic acid group was introduced using the starting material \(p\)-hydrazinobenzenesulphonic acid (Figure 3.7). The resulting merocyaninesulphonic acid \(\text{MC}_3\text{H}^+\text{SO}_3^–\) had very poor solubility in water.

**Figure 3.6** Synthesis of mono-substituted merocyaninesulphonic acids \(\text{MC}_1\text{H}^+\text{SO}_3^–\), \(\text{MC}_2\text{H}^+\text{SO}_3^–\), \(\text{MC}_3\text{H}^+\text{SO}_3^–\), and \(\text{MC}_4\text{H}^+\text{SO}_3^–\)

**Figure 3.7** Synthesis of merocyaninesulphonic acid \(\text{MC}_3\text{H}^+\text{SO}_3^–\).
For the third type, the sulphonic acid group is attached on the phenol moiety. The sulphonic acid group was introduced through the sulphonation of salicylaldehyde.\textsuperscript{3,24} MC\textsubscript{6}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−} with three methoxy groups on the indoline component and MC\textsubscript{7}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−} with a long alkyl chain on the indoline moiety were synthesised (Figure 3.8). Because of the long alkyl chain, MC\textsubscript{7}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−} was slightly soluble in organic solvents like chloroform and DMSO but nearly insoluble in water. MC\textsubscript{6}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−} had similar water and organic solubility to the first type.

![Figure 3.8](image-url)

Figure 3.8 Synthesis of mono-substituted merocyaninesulphonic acids MC\textsubscript{6}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−} and MC\textsubscript{7}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−}.

The solubility of the previous three types of merocyaninesulphonic acids in water was relatively low. As has been reported, the introduction of one or more sulphonate solubilizing groups is an efficient strategy to improve the water solubility of spiropyran species.\textsuperscript{31} In light of the previous work, a sodium sulphonate group was introduced to merocyaninesulphonic acid to increase its solubility in water. Figure 3.9 shows the synthetic route for this sodium sulphonate-substituted merocyaninesulphonic acid (MC\textsubscript{8}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−}) beginning with phenylhydrazine hydrochloride. The sulphonic acid group and sodium sulphonate group largely increased the solubility in water and the concentration of its aqueous solution could be greater than 0.2 M.
3.2.2 Characterisation of merocyaninesulphonic acids

All the merocyaninesulphonic acids were characterised by nuclear magnetic resonance (NMR), ultraviolet-visible (UV/Vis) and Fourier transform infrared (FT-IR) spectroscopy, and Electrospray ionisation mass spectrometry (ESI-MS).

The photoinduced reversible isomerisation between $\text{MCH}^+\text{SO}_3^-$ and $\text{SPSO}_3\text{H}$ was initially studied in organic solvent – DMSO (Figure 3.10a) using UV/Vis spectroscopy. Freshly prepared DMSO solutions of these merocyaninesulphonic acids appeared yellow, with a characteristic absorption between 400 and 450 nm (Figure 3.10b), indicating that they were in the protonated merocyanine ($\text{MCH}^+$) form. In addition, the absorption of MC at 560 nm was also observed in the spectra of the three nitro-substituted merocyaninesulphonic acids (Figure 3.10a), which is probably because the electron-withdrawing NO$_2$ makes the phenolic hydroxyl proton more acidic and easily donated to any acceptor in the environment thus forming a small amount of MC.

Under illumination by 365 nm light for 10-30 s, these peaks disappeared and the solutions became colourless (Figure 3.10c), suggesting that the $\text{MCH}^+$ (or MC) was isomerised to SP (Figure 3.10a). A feature absorption at 300 to 350 nm corresponding to the $\pi-\pi^*$ electronic excitation of the benzopyran part was observed in the UV/Vis spectra of SP.

For compounds $\text{MC}_3\text{H}^+\text{SO}_3^-$, $\text{MC}_4\text{H}^+\text{SO}_3^-$ and $\text{MC}_5\text{H}^+\text{SO}_3^-$, which have a nitro group on the phenol moiety (Figure 3.6-3.7), this lower energy absorption of the corresponding SP form was at around 350 nm while for other merocyaninesulphonic acids without a nitro group, the SP absorption was around 300 nm (Figure 3.10c). If the resulting colourless solution was kept in the
dark from several hours to several days, depending on the substituents, the SP form converted back to MCH$^+$ as expected.$^3$

\[
\text{MCH}^+\text{SO}_3^- \leftrightarrow 365 \text{ nm light} \quad \text{SPSO}_3\text{H}
\]

(yellow) \quad \text{dark} \quad \text{(colourless)}

**Figure 3.10** (a) Photoinduced reversible isomerisation between MCH$^+$SO$_3^-$ and SPSO$_3$H. UV/Vis spectra of merocyaninesulphonic acids MC$_1$H$^+$SO$_3^-$ (black), MC$_2$H$^+$SO$_3^-$ (red), MC$_3$H$^+$SO$_3^-$ (blue), MC$_4$H$^+$SO$_3^-$ (olive), MC$_5$H$^+$SO$_3^-$ (green), MC$_6$H$^+$SO$_3^-$ (cyan), MC$_7$H$^+$SO$_3^-$ (magenta), and MC$_8$H$^+$SO$_3^-$ (purple) in DMSO ($3 \times 10^{-3}$ M): (b) just prepared and then (c) illuminated by 365 nm light for 10-30 s.

In aqueous solution, the effect of the nitro group on the aromatic ring on the UV/Vis absorption of freshly prepared merocyaninesulphonic acids is further demonstrated. As discussed before and illustrated in Figure 3.3, the aqueous solution of merocyaninesulphonic acids is an equilibrium mixture of MCH$^+$ and MC. For those merocyaninesulphonic acids with no NO$_2$, the compound was weakly acidic and the equilibrium was towards MCH$^+$. Correspondingly, the characteristic absorption for MCH$^+$ was observed between 400 and 450 nm, while the absorption for MC at around 500 nm was relatively weak or even not seen (Figure 3.11a). However, the addition of the electron-withdrawing NO$_2$ at the para position of OH on the aromatic ring largely increased the acidity, increasing proton dissociation. As a result, the equilibrium was driven towards MC and the strong absorption at around 500 nm was seen (Figure 3.11a).
Upon irradiation by 365 nm light for 5-30 s, both the MCH\(^+\) and MC peaks dramatically decreased or nearly disappeared (Figure 3.11b), indicating the isomerisation of MCH\(^+\) to SP.\(^5\) Similar to the UV/Vis spectra in DMSO, the compounds with aromatic nitro group have absorptions around 350 nm, while those with no nitro group at around 300 nm. The resulting SP form could convert back to MCH\(^+\) in the dark after at most a few hours, a shorter conversion time than for DMSO.

**Figure 3.11** UV/Vis spectra of merocyaninesulphonic acids MC\(_3\)H\(^+\)SO\(_3\)\(^-\) (black), MC\(_4\)H\(^+\)SO\(_3\)\(^-\) (red), MC\(_5\)H\(^+\)SO\(_3\)\(^-\) (blue), MC\(_6\)H\(^+\)SO\(_3\)\(^-\) (olive), MC\(_7\)H\(^+\)SO\(_3\)\(^-\) (green), MC\(_8\)H\(^+\)SO\(_3\)\(^-\) (magenta), and MC\(_9\)H\(^+\)SO\(_3\)\(^-\) (purple) in water: (a) just prepared and then (b) illuminated by 365 nm light for 10-30 s. A saturated solution was used for MC\(_5\)H\(^+\)SO\(_3\)\(^-\) due to its poor solubility. For the other merocyaninesulphonic acids, the concentration was 3×10\(^{-5}\) M.

As most of the merocyaninesulphonic acids had relatively good solubility in DMSO (>10\(^{-2}\) M), deuterated DMSO (DMSO-\(d_6\)) was used as the NMR solvent for characterisation. All the merocyaninesulphonic acids showed similar NMR spectra. The singlet between 1.7-1.8 ppm for the six protons of gem-dimethyl group indicated a ring-opened MC structure (two distinct methyl signals are observed for spiropyrans due to their loss of symmetry). The presence of the MC was further supported by the doublets at around 8.4-8.6 ppm and 7.6-8.1 ppm with a coupling constant of around 16.5 Hz, indicative of a trans ethylenic bond. It should be noted that, although E and Z are recommended by International Union of Pure and Applied Chemistry (IUPAC) to describe the conformation of double bonds, trans and cis are usually used in spiropyran/merocyanine compounds because of their
clarity. For merocyaninesulphonic acids with no NO₂ group, a singlet at around 11 ppm for the phenolic hydroxyl group was observed, suggesting that the proton on the sulphonic acid group had dissociated during synthesis and attached to the more nucleophilic phenolate ion. While for those compounds with a NO₂, this signal cannot be seen at around 11 ppm, undoubtedly due to their relatively greater acidity and resultant signal broadening.³⁷,³⁸ It should be noted that an amount of the ring-closed SP form (1-50 mol%) was observed in most of the spectra, likely generated by the photoinduced ring closure or by the contact of the MCH⁺SO₃⁻ with the basic glass wall, which will be discussed in Section 3.2.4.

Two typical examples of the ¹H NMR spectra of these merocyaninesulphonic acids are assigned in detail below (Figure 3.12). The ¹H NMR spectrum of MC₆H⁺SO₃⁻ is shown in Figure 3.12a (blue labels). The six proton singlet of the gem-dimethyl groups is at 1.78 ppm. The two doublets for the trans ethylenic bond are found at 8.42 (blue H₄) and 7.65 (blue H₃) ppm with a coupling constant of 16.5 Hz, assigned with reference to previously reported spectra.¹⁴,³⁹,⁴⁰ The slightly broadened singlet for the phenolic hydroxyl group is at 11.19 ppm. All the other alkyl and aromatic protons were assigned according to their integrations and couplings.

The presence of the SP form (14 mol%) (red labels) was evidenced by the two distinct methyl signals at 1.27 and 1.11 ppm, and the two doublets at 7.03 and 5.69 ppm that have a coupling constant of 10.2 Hz for a cis ethylenic bond, typical of spiropyrans. All the other alkyl and aromatic SP protons were easily assigned from their integrations and couplings.

For MC₃H⁺SO₃⁻, which has a nitro group, the singlet for the two geminal methyl groups was at 1.80 ppm and the two doublets for the trans ethylenic bond were found at 8.50 and 8.08 ppm, with a coupling constant of 16.5 Hz (Figure 3.12b, blue labels). The amount of its SP form, as indicated in Figure 3.12b (red labels), is less than 1 mol%.
Figure 3.12 $^1$H NMR spectra of (a) MC$_6$H$^+$SO$_3^-$ and (b) MC$_3$H$^+$SO$_3^-$ in DMSO-$d_6$. The blue labels are for MCH$^+$ signals and the red labels for the SP form.
The FT-IR spectra of representative merocyaninesulphonic acids are shown in Figure 3.13, MC$_2$H$^+$SO$_3^-$ and MC$_4$H$^+$SO$_3^-$ without nitro groups and MC$_3$H$^+$SO$_3^-$ and MC$_6$H$^+$SO$_3^-$ with nitro groups. The feature peaks at around 1600, 1530 and 1470 cm$^{-1}$ resulting from the delocalised π-system, 1300 and 1230 cm$^{-1}$ resulting from O–H bending and C–O stretching of phenol, and 1030 cm$^{-1}$ for sulphonate salt, were found in the spectra of all the compounds. The characteristic peaks for the aromatic NO$_2$ appear to be at around 1540 and 1340 cm$^{-1}$ given that these vibrations were only observed in the spectra of MC$_3$H$^+$SO$_3^-$ and MC$_6$H$^+$SO$_3^-$.\(^{41-44}\)

![Figure 3.13 FT-IR spectra of merocyaninesulphonic acids MC$_2$H$^+$SO$_3^-$, MC$_4$H$^+$SO$_3^-$, MC$_3$H$^+$SO$_3^-$ and MC$_6$H$^+$SO$_3^-$ between 1000 and 1700 cm$^{-1}$.](image)

Since compounds MC$_2$H$^+$SO$_3^-$, MC$_4$H$^+$SO$_3^-$, MC$_6$H$^+$SO$_3^-$ and MC$_8$H$^+$SO$_3^-$ have not been reported before, they were also characterised by high resolution ESI-MS and their structures further confirmed (Table 3.1).

**Table 3.1** High resolution mass analysis for merocyaninesulphonic acids.

<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MC$_2$H$^+$SO$_3^-$</td>
<td>C$<em>{22}$H$</em>{24}$NO$_5$S</td>
<td>414.1375</td>
<td>414.1369</td>
</tr>
<tr>
<td>MC$_4$H$^+$SO$_3^-$</td>
<td>C$<em>{22}$H$</em>{24}$N$_2$O$_7$S</td>
<td>459.1226</td>
<td>459.1242</td>
</tr>
<tr>
<td>MC$_6$H$^+$SO$_3^-$</td>
<td>C$<em>{22}$H$</em>{24}$NO$_7$S</td>
<td>446.1273</td>
<td>446.1278</td>
</tr>
<tr>
<td>MC$_8$H$^+$SO$_3^-$</td>
<td>C$<em>{29}$H$</em>{38}$NO$_4$S</td>
<td>496.2522</td>
<td>496.2534</td>
</tr>
<tr>
<td>MC$_6$H$^+$SO$_3^-$</td>
<td>C$<em>{21}$H$</em>{21}$NNaO$_7$S$_2$</td>
<td>486.0662</td>
<td>486.0663</td>
</tr>
</tbody>
</table>
3.2.3 Photoacidic behaviour of merocyaninesulphonic acids

As photoacids, these merocyaninesulphonic acids are able to adjust pH of their aqueous solution upon light irradiation (Figure 3.3). Since the sulphonic acid group has a much lower pKₐ than the phenol group, the isomerisation between the MC and SP forms in water is accompanied by a pH change.³⁵,²⁴,⁴⁵ Where possible, the merocyaninesulphonic acids were fully dissolved in water and the pH of the aqueous solutions measured immediately, following irradiation of the aqueous solution until no change in pH was observed and then after the solution had been kept in the dark and attained a stable pH (Figure 3.3).

As is shown in Table 3.2, the aqueous solutions of these compounds are weakly acidic with pHs in the range of 4.7 to 6.1. The pH was able to be decreased under 365 nm light illumination by 0.3 to 1.5 pH units. The most effective compounds are MC₁H⁺SO₃⁻ (1.2 pH units) and MC₈H⁺SO₃⁻ (1.5 pH units). Shi et al. had demonstrated a 2.2 pH unit change for a 6×10⁻⁴ M solution of MC₁H⁺SO₃⁻ and a 1.6 pH unit change has been reported by Florea and co-workers for an unsubstituted merocyaninesulphonic acid (P937, Table 3.3). If the illuminated solution was kept in dark, the pH was able to decrease to the initial value (Table 3.2). In the weakly acidic MC form, a nitro group para to OH had a significant effect on the pH, leading to the pH values of MC₃H⁺SO₃⁻ and MC₄H⁺SO₃⁻ being lower than those of MC₁H⁺SO₃⁻ and MC₇H⁺SO₃⁻ with no NO₂ groups. However, in the strongly acidic SP form after light illumination, the substituent effect on pH was not obvious, while concentration played a more important role. As a result, the lowest pH (3.3) was obtained by illumination of MC₈H⁺SO₃⁻, which had the higher concentration (1 mM). The solubilities of MC₅H⁺SO₃⁻ and MC₇H⁺SO₃⁻ in water are so poor that they cannot be used as photoacids in aqueous solution.

The pKₐ of each solution was calculated and is also shown in Table 3.2. The pKₐ values of compounds MC₁H⁺SO₃⁻ and MC₃H⁺SO₃⁻ have been reported previously as 7.8 and 6.4, respectively (Table 3.3). The values obtained here are in good agreement given that the degree of dissociation of the MCH⁺SO₃⁻ is dependent on the degree of photo and thermal isomerisation of the merocyanine. Merocyaninesulphonic acids with a nitro group have a lower pKₐ, indicating their stronger acidity.
Table 3.2 pH change of the aqueous solution of merocyaninesulphonic acids with certain concentration under 365 nm light illumination.

<table>
<thead>
<tr>
<th>Merocyanine-sulphonic acids</th>
<th>Concentration in water/M</th>
<th>Just prepared (MC form)</th>
<th>Illuminated by 365 nm light (SP form)</th>
<th>Kept in dark after 365 nm light illumination (MC form)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>pH</td>
<td>pKa</td>
<td>pH</td>
</tr>
<tr>
<td>$MC_1H^+SO_3^-$</td>
<td>$1.5 \times 10^{-4}$</td>
<td>5.7</td>
<td>7.5</td>
<td>4.5</td>
</tr>
<tr>
<td>$MC_2H^+SO_3^-$</td>
<td>$0.5 \times 10^{-4}$</td>
<td>5.9</td>
<td>7.5</td>
<td>5.0</td>
</tr>
<tr>
<td>$MC_3H^+SO_3^-$</td>
<td>$2.0 \times 10^{-4}$</td>
<td>4.7</td>
<td>5.7</td>
<td>4.3</td>
</tr>
<tr>
<td>$MC_4H^+SO_3^-$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>5.2</td>
<td>6.4</td>
<td>4.6</td>
</tr>
<tr>
<td>$MC_6H^+SO_3^-$</td>
<td>$0.5 \times 10^{-4}$</td>
<td>6.1</td>
<td>8.0</td>
<td>5.8</td>
</tr>
<tr>
<td>$MC_8H^+SO_3^-$</td>
<td>$1.0 \times 10^{-3}$</td>
<td>4.8</td>
<td>6.5</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Table 3.3 Previously reported pH change of the aqueous solution of merocyaninesulphonic acids under 365 nm light illumination.

<table>
<thead>
<tr>
<th>Merocyanine-sulphonic acids</th>
<th>Concentration in water/M</th>
<th>Just prepared (MC form)</th>
<th>Illuminated by 365 nm light (SP form)</th>
<th>Kept in dark after 365 nm light illumination (MC form)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>pH</td>
<td>pKa</td>
<td>pH</td>
</tr>
<tr>
<td>$MC_1H^+SO_3^-$</td>
<td>$5.9 \times 10^{-4}$</td>
<td>5.5</td>
<td>7.8</td>
<td>3.3</td>
</tr>
<tr>
<td>$MC_2H^+SO_3^-$</td>
<td>$3.7 \times 10^{-4}$</td>
<td>4.9</td>
<td>6.4</td>
<td>3.9</td>
</tr>
<tr>
<td>$P937$</td>
<td>$1.0 \times 10^{-3}$</td>
<td>5.0</td>
<td>7.0</td>
<td>3.4</td>
</tr>
</tbody>
</table>

It is clear from these results that the merocyaninesulphonic acids without nitro substituents afforded the largest pH change on irradiation and could be effectively utilised as photoacids for droplet movement, as previously demonstrated by Florea et al.\textsuperscript{24} Furthermore, solubility also played an important role in their behaviour as photoacids. Poor solubility can largely decrease the capacity to change pH, thus limiting their application in droplet motion systems.

3.2.4 Reaction of merocyaninesulphonic acids with base

The acidic nature of merocyaninesulphonic acids makes them easily deprotonated by base. It has been reported for protonated merocyanines that the deprotonation of
the phenolic hydroxyl group generates a MC intermediate with a purple or blue colour (Figure 3.14) depending on the substituents.\textsuperscript{10,19,40} The resulting MC typically converts to the colourless SP form in a short time (Figure 3.14).\textsuperscript{10,46,47} Previous work has shown that electron-withdrawing substituents such as the NO\textsubscript{2} group \textit{para} to O\textsuperscript{−} were able to stabilise the MC form.\textsuperscript{15,48}

\[
\begin{align*}
\text{MCH}^+\text{SO}_3^- & \quad \text{Base} \quad \left[ \text{MCSO}_3^- \right] \quad \rightarrow \quad \text{SPSO}_3^- \\
(\text{yellow}) & \quad \text{(purple/blue)} & \quad \text{(colourless)}
\end{align*}
\]

\textbf{Figure 3.14} Conversion of merocyaninesulphonic acids to the SP form via a coloured MC intermediate in the presence of base.

Here, DMSO was used as the solvent to investigate the deprotonation reaction since most of the merocyaninesulphonic acids had relatively high solubility in this aprotic polar solvent. Triethylamine (TEA), which is soluble in DMSO, was used as the base. The addition of TEA (1.2 equiv.) into the DMSO solution of the merocyaninesulphonic acids led to the instantaneous formation of a highly coloured intermediate whose further reactivity depended on the merocyaninesulphonic acid used. Typically, the coloured MCH\textsuperscript{+} solutions became colourless after seconds or minutes to hours. The rapid disappearance of the intermediate absorbance presented problems in the UV/Vis spectroscopic measurements, which usually needed around one minute or more to measure a spectrum. Thus, fast decolouration of some unstable intermediates afforded weak UV/Vis absorptions. The UV/Vis spectra of all eight merocyaninesulphonic acid DMSO solutions immediately after treatment with TEA are shown in Figure 3.15a.

The substituent \textit{para} to the phenoxide O\textsuperscript{−} had a significant effect on the stability and the UV/Vis absorption of the MC intermediate. For merocyaninesulphonic acids \textit{MC}_{1}\text{H}^+\text{SO}_3\text{−}, \textit{MC}_{2}\text{H}^+\text{SO}_3\text{−}, \textit{MC}_{6}\text{H}^+\text{SO}_3\text{−} and \textit{MC}_{7}\text{H}^+\text{SO}_3\text{−} with no NO\textsubscript{2} group at the \textit{para} position, large red shifts compared to the MCH\textsuperscript{+} forms (Figure 3.10) were observed in the UV/Vis spectra (Figure 3.15a). The resulting
absorptions were around 600 nm and the intermediates appeared intensely blue (Figure 3.15a inset), similar to that reported by Kaljn et al.\textsuperscript{19} The intermediates were not stable and disappeared within minutes as is illustrated for \( \text{MC}_2\text{H}^+\text{SO}_3^- \) (Figure 3.15b).

In contrast, for merocyaninesulphonic acids \( \text{MC}_3\text{H}^+\text{SO}_3^- \), \( \text{MC}_4\text{H}^+\text{SO}_3^- \) and \( \text{MC}_5\text{H}^+\text{SO}_3^- \) all of which have a \( \text{NO}_2 \) substituent, the base-generated purple intermediate was relatively stable. Their UV/Vis spectra showed strong absorptions at around 560 nm (Figure 3.15a).\textsuperscript{16} \( \text{MC}_4\text{H}^+\text{SO}_3^- \) produced the most stable intermediate whose characteristic peak at 560 nm only decreased slightly in intensity after 60 min (Figure 3.15c).

![Figure 3.15](image_url)

**Figure 3.15** (a) UV/Vis spectra of merocyaninesulphonic acids \( \text{MC}_1\text{H}^+\text{SO}_3^- \) (black), \( \text{MC}_2\text{H}^+\text{SO}_3^- \) (red), \( \text{MC}_3\text{H}^+\text{SO}_3^- \) (blue), \( \text{MC}_4\text{H}^+\text{SO}_3^- \) (olive), \( \text{MC}_5\text{H}^+\text{SO}_3^- \) (green), \( \text{MC}_6\text{H}^+\text{SO}_3^- \) (cyan), \( \text{MC}_7\text{H}^+\text{SO}_3^- \) (magenta) and \( \text{MC}_8\text{H}^+\text{SO}_3^- \) (purple) in DMSO (\( 3\times10^{-5} \) M) after the solution was treated with 1.2 equivalent of TEA. (b) UV/Vis spectra of MC intermediate generated by treating \( \text{MC}_3\text{H}^+\text{SO}_3^- \) with TEA in DMSO. The UV/Vis spectroscopy was recorded every minute after addition of TEA. (c) UV/Vis spectra of MC intermediate generated by treating \( \text{MC}_4\text{H}^+\text{SO}_3^- \) with TEA in DMSO. The UV/Vis spectroscopy was recorded every three minutes after addition of TEA.
$^1$H NMR spectroscopy was used to attempt to investigate the deprotonation process. However, since it took at least 5 min for the data collection in the $^1$H NMR experiment, the unstable MC intermediates likely converted to the SP form during this time. The attempts to record spectra at lower temperature were also unsuccessful of inconclusive. For merocyaninesulphonic acids with no nitro group, only the SP form was detected after addition of TEA (1.2 equiv.) as shown for MC$_6$H$^+$SO$_3^-$ in Figure 3.16a. The signals coincided with those of the minor SP isomer observed in the $^1$H NMR spectrum of MC$_6$H$^+$SO$_3^-$ itself as illustrated in Figure 3.12a, except for the Et$_3$NH$^+$ signals at 1.2, 3.3 and 8.8 ppm.\textsuperscript{37}

For merocyaninesulphonic acids with a nitro group, the MC intermediate could be analysed. For MC$_3$H$^+$SO$_3^-$, MC$_4$H$^+$SO$_3^-$ and MC$_5$H$^+$SO$_3^-$ that have a nitro group, the MC intermediate was relatively stable and detectable by NMR in the deprotonation process. The $^1$H NMR spectra of MC$_3$H$^+$SO$_3^-$ and MC$_5$H$^+$SO$_3^-$ after addition of TEA (1.2 equiv.) was a mixture of the MC intermediate and the ring-closed SP form. For MC$_4$H$^+$SO$_3^-$, however, the intermediate was relatively stable and almost no SPSO$_3^-$ was detected in about 10 min after addition of 1.2 equiv. of TEA. In the $^1$H NMR spectrum of the intermediate, a singlet for the six methyl protons at 1.74 ppm was observed, further proving that the intermediate is an MC species (Figure 3.16b). The chemical shifts of the two protons on the double bond were so close that the peak looked like a singlet (Figure 3.16b). This MC intermediate was stabilised not only by the NO$_2$ group on the phenol part but also by the methoxy group on the indoline part.
Figure 3.16 $^1$H NMR spectra of (a) MC$_6$H$^+$SO$_3^-$ and (b) MC$_4$H$^+$SO$_3^-$ approximately 10 min after addition of TEA (1.2 equiv.) in DMSO-$d_6$.

While this work was being undertaken, Klajn’s group used MC$_1$H$^+$SO$_3^-$ with a flexible coordination cage to create a stabilised encapsulated MC form of the merocyaninesulphonic acid.$^{19}$ They got an intense blue colour resulting from the caged MC in aqueous solution with a characteristic absorption at ~592 nm in the UV/Vis spectrum. They were also able to obtain a crystal structure of the caged MC.

In our case, similar blue species with a UV/Vis absorption at 600 nm were observed following the deprotonation of the merocyaninesulphonic acids without nitro groups in DMSO, although these intermediates were clearly not stable in DMSO and reacted rapidly to form the SP derivatives. In contrast, the MC intermediates generated by the deprotonation of merocyaninesulphonic acids with an electron-withdrawing nitro group appeared purple with a UV/Vis absorption at around 560 nm, indicating that resulting MC was stabilised by the polar solvent DMSO. Consequently, the resulting zwitterionic MCs were relatively stable, consistent with the experimental results.
As discussed earlier, the ring-opened MC is a hybrid of a quinoidal resonance structure and a zwitterionic resonance structure (Figure 3.1) and the contribution of each resonance form and resulting MC stability is determined by the surrounding media. As previously demonstrated, the thermal reversion of MC to the SP form involves two steps: rotation of the central bond C=C or C=C bond of MC (indicated by red circles, Figure 3.17) and a following ring-closure to form SP.\(^9,13,16,17,49-51\) For merocyaninesulphonic acids with no nitro group as in our case, the rapid reaction of the trans MC formed suggested that ring closure to the SP form occurred by way of the quinoidal form as in Figure 3.17a. For merocyaninesulphonic acids with a nitro group, since the electron-withdrawing NO\(_2\) stabilised the zwitterionic form of the MC intermediate generated by deprotonation, requiring the much higher energy transformation from trans to cis to generate the ring-closed SP (Figure 3.17b).

**Figure 3.17** The thermal reversion of the (a) quinoidal and (b) zwitterionic MC intermediates to SP by the rotation of the central bond indicated by red circles and the following ring closure reaction.

It has been reported that the isomerisation of the central bond dominates the total process in polar solvent since a solvent effect was observed for the thermal reversion.\(^{13,17}\) Since rotation of the central C=C (zwitterionic MC) to complete the trans to cis isomerisation was associated with a much higher barrier (~60 kcal/mol higher) than that of the C=C (quinoidal MC), the reversion of the zwitterionic MC to SP should be slower.\(^{17}\) In other words, the zwitterionic MC with a NO\(_2\) was more stable than the quinoidal MC with no NO\(_2\).

As was demonstrated before, the merocyaninesulphonic acids could be easily deprotonated due to their high sensitivity to the base. While preparing the DMSO
solution of merocyaninesulphonic acids, slight blue or purple colour could be observed close to the glass wall as soon as the solution was loaded to a glass vial and faded in a short time. This was likely because of the slightly basic property of the glass, which could deprotonate merocyaninesulphonic acids to generate the SP form via the coloured intermediate. This could also explain the existence of a slight amount of the SP form in the 1H NMR spectra of merocyaninesulphonic acids.

3.2.5 Merocyaninesulphonic acid based sensor

The high sensitivity of MC₄H⁺SO₃⁻ to base and the dramatic colour change in this deprotonation process made this merocyaninesulphonic acid a potential material for sensing volatile bases. Spiropyran-based sensors for gaseous acids including HCl, CH₃COOH, HCOOH and CF₃COOH detecting have been widely investigated. However, such sensors for dry gaseous bases have scarcely been reported. Therefore, incorporation of the merocyaninesulphonic acid into a polymer substrate was investigated for this purpose.

Polydimethylsiloxane (PDMS) was chosen as the substrate material due to its low cost and high tolerance to most volatile compounds. Moreover, the colour change could be easily observed because of the optical property of PDMS. We developed a gaseous base sensor by embedding MC₄H⁺SO₃⁻ and 4-dodecylbenzenesulphonic acid (DBSA) into PDMS. DBSA was used to stabilise the ring-opened structure of MC₄H⁺SO₃⁻ since this MCH⁺ was so sensitive to base that it could be partly deprotonated in PDMS before contacting with gaseous base. The MC₄H⁺SO₃⁻/DBSA-PDMS sensor was then used to detect the vapours of triethylamine and ammonia. As is shown in the UV spectra, the sensor appeared yellow with a characteristic absorption at 477 nm after preparation (Figure 3.18). Exposure of the MC₄H⁺SO₃⁻/DBSA-PDMS sensor to the vapour of ammonia water (Figure 3.18a) or triethylamine (Figure 3.18b) gradually changed the yellow colour to dark purple. The absorption at 477 nm was also gradually shifted to 567 nm and a new absorption at 398 nm was generated (Figure 3.18b). As is shown in the UV/Vis spectra, it took 10-20 s for the sensor to respond to the gaseous base to change the colour from yellow to purple. This was probably because the basic
gas needed to go through the PDMS and react with DBSA before it deprotonated $\text{MC}_4\text{H}^+\text{SO}_3^-\text{to generate the purple MC intermediate.}$

Figure 3.18 UV/Vis spectra of $\text{MC}_4\text{H}^+\text{SO}_3^-/\text{DBSA-PDMS}$ sensor exposed in the vapour of (a) ammonia water and (b) triethylamine. The size of the sensor is 2×1×0.1 cm. 2 mL of NH$_3$•H$_2$O or Et$_3$N was added into a 20 mL vial. Then after 5 min, the sensor was placed on the top of the vial to start the test.

In order to further investigate the colour change of the sensor, we used dry ammonia gas to treat the sensor directly. The colour changed from yellow to purple immediately on contact with the gas (Figure 3.19). Since nearly no water was contained in the dry ammonia gas, the colour change is from the direct acid-base reaction of merocyanine sulphonic acid with ammonia and no water is involved in this process. This $\text{MC}_4\text{H}^+\text{SO}_3^-/\text{DBSA-PDMS}$ sensor provided a simple method to detect gaseous NH$_3$ by visible colour change, which could have potential application in the industry as well as in daily life to monitor gas hazard, although further improvement is still needed.$^{55,56}$

Figure 3.19 Colour change of $\text{MC}_4\text{H}^+\text{SO}_3^-/\text{DBSA-PDMS}$ sensor exposed in dry ammonia gas. The size of the sensor is 2×1×0.1 cm.
3.3 Conclusion

In this chapter, a series of merocyaninesulphonic acids were synthesised and characterised. Most of these merocyaninesulphonic acids could act as photoacids to reversibly change pH. They could also be deprotonated by gaseous base such as triethylamine and ammonia to generate spiropyran and a purple or blue intermediate MC was observed during the deprotonation process. For merocyaninesulphonic acids with no nitro groups on the phenol moiety, the intermediate MC was blue and disappeared in minutes. While for those merocyaninesulphonic acids bearing a nitro group, the intermediate was purple and relatively stable.

Based on this, a basic gas sensor was developed by embedding a merocyaninesulphonic acid with a nitro group \((\text{MC}_4\text{H}^+\text{SO}_3^-)\) and 4-dodecylbenzenesulphonic acid into PDMS. Among all the merocyaninesulphonic acids, \(\text{MC}_7\text{H}^+\text{SO}_3^-\) has a good solubility in chloroform, while \(\text{MC}_8\text{H}^+\text{SO}_3^-\) has a high solubility in water, making it possible to construct oil-in-water or water-in-oil droplet motion systems.

3.4 References


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Chapter 4  Photocontrolled movement of organic droplets containing spiropyran

4.1  Introduction

The motion of droplets manipulated by tension gradients has been used to emulate the transport process in nature, for example, chemotaxis and phototaxis. By creating a tension gradient in the environment, the droplet can move towards the high surface/interfacial tension area due to the Marangoni effect. One example is the work of Lagzi in 2010, where an organic droplet moved to the exit of a maze on water by surface tension gradients generated by pH gradients.\textsuperscript{1} The velocity of the movement was up to 10 mm s\textsuperscript{-1}. However, the control of such motion is limited. For example, the droplet can only move forwards but cannot move back since the direction of the gradient is hard to change once it has been generated. In 2014, Florea \textit{et al.} used a photoactive spiropyran sulphonic acid in the aqueous solution in special channels to generate surface tension gradients by light to move organic droplets placed in the channels.\textsuperscript{2} In this case, the motion resulted from the surface tension change controlled by light and the droplet was able to move backwards or forwards on water with a speed of 4 mm s\textsuperscript{-1}, but the control was still limited since the motion was driven by the change in the environment. If photoactive materials could be used in the droplet, the photoinduced movement could be initiated by the change in the droplet itself. As discussed in the Introduction (Section 1.4.2.1), this was achieved by Suzuki \textit{et al.} who demonstrated that the photogeneration of a oleate surfactant in a droplet led to droplet movement under water.\textsuperscript{3} However, while good control of the motion could be achieved, the reported speed of the movement was just 0.006 mm s\textsuperscript{-1}, thousands of times slower than that in the works of Lagzi and Florea. Clearly, a larger Marangoni effect is needed as a result of the photoactivation of the droplet.

Inspired by the novel work of Florea and co-workers in which the droplet was moved on an aqueous solution containing a water soluble spiropyran sulphonic acid by photoinduced pH change,\textsuperscript{2} it was proposed that an organic soluble spiropyran
could be used in the organic droplet to generate a sufficient surface tension or interfacial tension (IFT) change to move a droplet on or under water using only light. This would potentially provide complete control of droplet movement.

4.2 Photochemistry of SPCH$_2$CH$_2$OH

The spiropyran derivative used was an ethanol substituted spiropyran (SPCH$_2$CH$_2$OH), which is commercially available. SPCH$_2$CH$_2$OH is soluble in organic solvents but insoluble in water. It can undergo photoinduced conversion between the ring-closed SP form and the ring-opened MC form upon light irradiation (Figure 4.1). In the presence of active protons provided by strong acid like trifluoroacetic acid, hydrochloric acid, sulphonic acid, the MC form can be easily protonated to form MCH$^+$, which can be converted to the SP form upon visible light irradiation via the SPH$^+$ intermediate.

![Figure 4.1](image)

Figure 4.1 Photo and pH induced conversion between the SP, MC and MCH$^+$ forms of SPCH$_2$CH$_2$OH.

Prior to using the spiropyran for droplet experiments, it was characterised by nuclear magnetic resonance (NMR) and ultraviolet-visible (UV/Vis) spectroscopy. Upon dissolving in dichloromethane (DCM), the solution of SPCH$_2$CH$_2$OH appeared purple and then became colourless within 15 min. This colourless isomer was the SP form as shown by its NMR spectra. As is shown in the proton NMR ($^1$H NMR) spectrum, two distinct singlets for the six methyl protons were observed at 1.20 and 1.29 ppm as well as two groups of multiplets at 3.86-3.68 and 3.52-3.28
ppm for the two pairs of methylene protons, respectively, due to the asymmetric structure of this compound. The coupling constant for the two olefinic protons was 10.4 Hz indicating the \textit{cis} structure of this double bond. All the protons and carbons were further assigned by carbon-13 NMR (\textsuperscript{13}C NMR) and two-dimensional NMR (2D NMR) spectroscopy including correlation (COSY), heteronuclear single-quantum correlation (HSQC) and heteronuclear multiple-bond correlation (HMBC) spectroscopy (see Section 2.2.2). The results were consistent with reported values where available.\textsuperscript{5} The existence of only the SP form in the solution indicated that the ring-closed form of \textit{SPCH\textsubscript{2}CH\textsubscript{2}OH} was more thermally stable than the ring-opened MC form in chloroform at room temperature as shown by Raymo \textit{et al.} for acetonitrile.\textsuperscript{5}

It has been reported that the MC form has a feature absorption at 560 to 600 nm in its UV/Vis spectrum due to its extended conjugated \pi-electronic system.\textsuperscript{4-6,13,14} However, the UV/Vis spectrum of a 15 min aged DCM solution of \textit{SPCH\textsubscript{2}CH\textsubscript{2}OH} showed no absorption above 400 nm, further confirming the absence of the MC form (Figure 4.2b). Following 365 nm light illumination, the colourless solution of \textit{SPCH\textsubscript{2}CH\textsubscript{2}OH} became purple with a characteristic absorption at 578 nm due to the formation of the MC isomer, \textit{MCCH\textsubscript{2}CH\textsubscript{2}OH} (Figure 4.2b). However, no signals for \textit{MCCH\textsubscript{2}CH\textsubscript{2}OH} could be seen in the corresponding \textsuperscript{1}H NMR spectrum (Figure 4.2a), which resulted from the rapid conversion of the generated MC form back to the SP form in the time that it took to undertake the NMR measurement.\textsuperscript{5} Irradiation of the purple UV/Vis solution containing \textit{MCCH\textsubscript{2}CH\textsubscript{2}OH} with visible light led to the disappearance of the peak at 578 nm in 20 s (Figure 4.2b), suggesting complete conversion of the MC form into SP. The LED-based visible light source was not particularly well focused for droplet work. Therefore, the effect of a 405 nm hand held laser that had a higher intensity and consistent focus was also examined, despite the apparent low absorption of \textit{MCCH\textsubscript{2}CH\textsubscript{2}OH} at 405 nm. Nonetheless, the photoisomerisation of \textit{MCCH\textsubscript{2}CH\textsubscript{2}OH} to \textit{SPCH\textsubscript{2}CH\textsubscript{2}OH} appeared to be as effective with 405 nm light as with visible light (Figure 4.2b).
Figure 4.2 (a) $^1$H NMR spectra of SPCH$_2$CH$_2$OH in CDCl$_3$ after preparation (red line), followed by illumination under 365 nm light for 30 min (blue line). The concentration of SPCH$_2$CH$_2$OH is 0.025 M. (b) UV/Vis spectra of a 15 min aged DCM solution of SPCH$_2$CH$_2$OH (black line) after irradiation at 365 nm for 20 seconds (red line) showing the characteristic absorption of MCCH$_2$CH$_2$OH at 578 nm, followed by irradiation with 405 nm or visible light for 20 seconds (blue line). The concentration is 5×10$^{-5}$ M.

Since the photoisomerisation between MC and SP forms causes a significant change in the hydrophilic/hydrophobic nature of the substance,\textsuperscript{15,16} the surface-activity of spiropyran species at organic/water interface is also sensitive to light.\textsuperscript{17-19} The merocyanine moiety has been reported to be able to decrease the IFT of an organic/water interface.\textsuperscript{17} Therefore, an examination of the effect on IFT by SPCH$_2$CH$_2$OH was undertaken using the well-established pendant drop method (see Section 2.3.4.1). A droplet of 0.01 M SPCH$_2$CH$_2$OH in CHCl$_3$ was generated under DI water and illuminated by 365 nm light as well as by 365 nm and 405 nm
light alternatively, while measuring the IFT, in order to determine whether there was a consistent IFT effect from the photoisomerisation. As is shown in Figure 4.3a, upon 365 nm light irradiation, the IFT of \text{SPCH}_2\text{CH}_2\text{OH}/\text{CHCl}_3 in water decreased from 27 mN m$^{-1}$ to 20 mN m$^{-1}$ with the generation of the MC form at the organic/water interface.

![IFT measurement by the pendant drop method for a SPCH$_2$CH$_2$OH/CHCl$_3$ droplet (0.01 M) in DI water (a) with or without 365 nm light illumination (black and red line respectively), or (b) alternatively illuminated by 365 nm light and 405 nm light. The curves were smoothed by adjacent averaging.](image)

When the droplet was alternatively illuminated by 365 nm light and 405 nm light for 20 second periods, the IFT decreased under 365 nm light and then increased under 405 nm light as expected, although there was never sufficient irradiation time for maximum IFT change in either direction. This resulted ultimately in an overall IFT decreased from 27 mN m$^{-1}$ to 22 mN m$^{-1}$ (Figure 4.3b) over 12 cycles. This was likely due to the incomplete conversion of MC to SP using the 405 nm light but a higher SP to MC conversion by the 365 nm light, leading to less and less SP over time. Nonetheless, this ability to change IFT under light illumination suggested that the spiropyran species could be useful for droplet movement.
4.3 Photocontrolled droplet motion systems based on spiropyran and surfactant

Reported droplet motion systems have usually been composed of organic droplets and aqueous solution.\textsuperscript{20,21} Because interfacial tension plays a crucial role in droplet motion, a surfactant either in the droplet or in the external environment has been an inevitable part in most of these reported systems.\textsuperscript{20,22} Therefore, the use of surfactant was used for the initial studies in this work.

4.3.1 Initial investigation

Droplets have been typically made of a fatty acid or derivative, or ionic liquid, which may be dissolved in a water-insoluble organic solvents.\textsuperscript{1,2,20,21,23,24} In order to dissolve the photoactive species $\text{SPCH}_2\text{CH}_2\text{OH}$, organic solvents were used to construct the droplet, with a mixture of 1,2-dichloroethane (DCE)/toluene used to ensure the droplet floated on the aqueous phase. The fatty acid 2-hexyldecanoic acid (HDA) was also added to the droplet, since it had been previously used for organic droplets.\textsuperscript{1,2} Most importantly, HDA is slightly acidic and it might have protonated $\text{SPCH}_2\text{CH}_2\text{OH}$ assisting the photoisomerisation. In the aqueous phase, a surfactant has typically been used to reduce surface tension,\textsuperscript{21} so sodium dodecylbenzenesulphonate (SDBS) was chosen as the surfactant since it has a relatively good solubility in both water and the organic solvents.

As an initial attempt to move an organic droplet, a solution was created from $\text{SPCH}_2\text{CH}_2\text{OH}$ (0.04 M) and HDA (0.04 M), in DCE/toluene (1:2, v/v). A 2 $\mu$L droplet of this solution was added to an aqueous solution containing SDBS (5 mM) in a glass Petri dish (5 cm) and the droplet floated on the aqueous solution. It was necessary to use a light source that could be focused on the droplet and provide enough energy for the photoisomerization. Therefore, the same 365 nm light was used as for the UV/Vis experiments since the beam focus could be adjusted. When the $\text{SPCH}_2\text{CH}_2\text{OH}$/HDA droplet was irradiated with this focussed 365 nm light, it was found to move away from the light as can be seen in Figure 4.4 and in Movie
4.1. The illuminated part of the colourless \textit{SPCH}_2\textit{CH}_2\textit{OH}/HDA droplet became purple-red immediately upon 365 nm light irradiation and the colour covered all the droplet in a short time, indicating the generation of \textit{MCCH}_2\textit{CH}_2\textit{OH} (Figure 4.1). At the same time, the droplet moved away from the light source with a speed of around 1 mm s$^{-1}$. While the droplet was moving, a red fluorescent plume trailing the droplet was observed (Figure 4.4b). By changing the direction of illumination, the motion direction also changed.

![Figure 4.4](image)

Figure 4.4 (a) Illustration of the movement away from 365 nm light of a \textit{SPCH}_2\textit{CH}_2\textit{OH}/HDA droplet on the surface of a surfactant solution. (b) Image of the position of a \textit{SPCH}_2\textit{CH}_2\textit{OH}/HDA droplet at t = 43 s from Movie 4.1 while it was moving away from 365 nm light. The position of this droplet at t = 38 s is indicated by a red circle. The illumination direction is indicated by the purple arrow. The red fluorescent plume trailing the droplet along the illuminated path is shown.

4.3.1.1 The concentration of surfactant

In the initial experiments, the concentration of SDBS used was 5 mM, which was above its critical micelle concentration 1 (CMC1, around 1.5 mM) and below its critical micelle concentration 2 (CMC2, around 7 mM).

For the freshly prepared surfactant solution with a concentration of 5 mM, the solution was clear and movement of the \textit{SPCH}_2\textit{CH}_2\textit{OH}/HDA droplet away from 365 nm light readily occurred. However, this surfactant solution was found to be unstable and became cloudy in a day or more after preparation. If the concentration of SDBS was increased to 7 mM, which was close to CMC2, the behaviour of the \textit{SPCH}_2\textit{CH}_2\textit{OH}/HDA droplet under light illumination was not affected. Most

*All movies associated with this thesis are in the associated electronic supplementary information (ESI).
importantly, the resulting surfactant solution was quite stable and still clear after several months or more. If the concentration was much higher than 7 mM, the solution appeared milky and partly blocked the light, which hindered movement. As a result, the concentration of SDBS used in the following experiments in this thesis was 7 mM.

4.3.1.2 The effect of water hardness on droplet formation

In the early droplet motion experiments, it was fortunate that tap water had been used to prepare the surfactant solution. An SPCH$_2$CH$_2$OH/HDA droplet made from DCE/toluene (1:2, v/v) floated on the aqueous solution with most of the droplet immersed into water and the droplet/air interface was small (Figure 4.5a-b). Furthermore, the underwater part of the droplet appeared spherical (Figure 4.5b). However, if tap water was replaced by deionised water (DI water), most of the droplet appeared to be quite flat on the surface of the surfactant solution increasing the droplet/air interface and making it difficult to obtain a spherical droplet (Figure 4.5c-d). As a result, the droplet motion was significantly affected, with slow or no movement, and little control under light illumination. The difference between tap water and DI water was clearly the ions present. DI water contains few ions while tap water contains a range of ions such as Ca$^{2+}$, Mg$^{2+}$, Na$^+$, Cl$^-$ suggesting that ions probably played an important role in droplet formation on water.

Figure 4.5 (a) Top view and (b) lateral view of a SPCH$_2$CH$_2$OH/HDA droplet on the surface of SDBS aqueous solution prepared with tap water. (c) Top view and (d) lateral view of a SPCH$_2$CH$_2$OH/HDA droplet on the surface of SDBS aqueous solution (7 mM) prepared with DI water.

To investigate the effect of ions, known amounts of CaCl$_2$, MgCl$_2$ or NaCl were added to DI water to prepare the surfactant solution. The results showed that spherical droplets could be formed with concentrations of CaCl$_2$ in the surfactant solution made from DI water of 0.4 mM or higher or of 0.5 mM or higher
concentration of MgCl₂. However, the presence of NaCl proved not to work even when the concentration was increased to 10 mM. So droplet formation was related to the dissolved amount of CaCl₂ and MgCl₂, or water hardness. Water hardness of the local tap water was 38-45 mg CaCO₃/L (Table 4.1), equal to 0.38-0.45 mM, which is similar to the result obtained for CaCl₂ and MgCl₂.

**Table 4.1** Water analysis data of local (Illawarra) tap water from the local government.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Units</th>
<th>ADWG* Health</th>
<th>ADWG* Aesthetic</th>
<th>Illawarra 10th - 90th percentile range</th>
</tr>
</thead>
<tbody>
<tr>
<td>True colour</td>
<td>TCU or HU</td>
<td>na</td>
<td>15</td>
<td>&lt;2</td>
</tr>
<tr>
<td>Turbidity</td>
<td>NTU</td>
<td>na</td>
<td>4</td>
<td>0.1 - 0.2</td>
</tr>
<tr>
<td>Total dissolved solids</td>
<td>mg/L</td>
<td>na</td>
<td>600</td>
<td>78 – 93</td>
</tr>
<tr>
<td>pH</td>
<td>pH units</td>
<td>na</td>
<td>6.5 - 8.5</td>
<td>7.5 - 8.0</td>
</tr>
<tr>
<td>Conductivity</td>
<td>mS/cm</td>
<td>na</td>
<td>na</td>
<td>15 – 14</td>
</tr>
<tr>
<td>Total hardness</td>
<td>mg CaCO₃/L</td>
<td>na</td>
<td>200</td>
<td>38 – 45</td>
</tr>
<tr>
<td>Calcium hardness</td>
<td>mg CaCO₃/L</td>
<td>na</td>
<td>na</td>
<td>29 – 34</td>
</tr>
<tr>
<td>Magnesium hardness</td>
<td>mg CaCO₃/L</td>
<td>na</td>
<td>na</td>
<td>8 – 11</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>mg CaCO₃/L</td>
<td>na</td>
<td>na</td>
<td>25 – 28</td>
</tr>
<tr>
<td>Temperature</td>
<td>degrees C</td>
<td>na</td>
<td>na</td>
<td>14 – 23</td>
</tr>
<tr>
<td>Dissolved oxygen</td>
<td>% saturation</td>
<td>na</td>
<td>&gt;89%</td>
<td>101 – 112</td>
</tr>
</tbody>
</table>

Legend: na = no published health or aesthetic guideline value. *ADWG = Australian Drinking Water Guidelines 2011

It has been reported that ionic strength affects the micellisation of anionic surfactant and that CaCl₂ leads to compact aggregates with enhanced structural rigidity. This likely contributed to the formation and stabilisation of spherical droplets. Furthermore, for SPCH₂CH₂OH/HDA droplets, they hardly moved without CaCl₂ in the aqueous solution prepared with DI water. Therefore, DI water containing 0.4 mM CaCl₂ was used instead of tap water as a standard condition for many of the following experiments in this thesis.

4.3.1.3 Revisiting droplet motion

During the course of these studies into the use of CaCl₂ in DI water, it was observed that, after the droplet moved away from 365 nm light (Figure 4.6, Movie 4.2), the resulting red droplet containing MCCH₂CH₂OH could be moved with 405 nm light. A 405 nm laser was used to illuminate the resulting purple-red droplet since this light had been used to convert MC to SP (Figure 4.2b) for the UV/Vis studies. The illuminated part of the droplet became colourless, which spread to all the
droplet, indicating the conversion from the MC form to the SP form. At the same time, the droplet moved towards 405 nm light (Figure 4.6, Movie 4.3).

![Figure 4.6](image)

**Figure 4.6** Illustration of the movement away from 365 nm light of a SPCH₂CH₂OH/HDA droplet on the surface of SDBS aqueous solution (7 mM) containing 0.4 mM CaCl₂ (left) and the movement towards 405 nm light of the resulting MCCH₂CH₂OH/HDA droplet (right). The red fluorescent plume trailing the droplet along the illuminated path is shown.

### 4.3.2 Exploration of key factors controlling droplet movement

In order to optimise and extend the droplet motion system as well as to gain an insight into the mechanism, a study of the key factors related to the photoinduced movement was needed. Spiropyran is the only photoactive material in the system, so its role in controlling the movement with light needed to be investigated. Since the spiropyran was soluble in a variety of organic solvents, the application of other solvents could be examined. By adjusting the density of the droplet, movement under water could be realised. The use of HDA was inspired by previous work, so its role in this movement was not clear. Whether it could protonate SPCH₂CH₂OH or not needed to be confirmed. Furthermore, the effect of other acids on the motion instead of HDA could also be studied.

#### 4.3.2.1 The role of spiropyran

The crucial role of spiropyran in the motion was confirmed by the fact that no movement was observed under light illumination without SPCH₂CH₂OH in the organic droplet. To find out whether this movement could be generated by other SPs, another organic soluble spiropyran (SPCH₃) (Figure 4.7) was synthesised as a replacement for SPCH₂CH₂OH. SPCH₃ was readily prepared by the reaction of
1,3,3-trimethyl-2-methyleneindoline and 2-hydroxy-5-nitrobenzaldehyde in the presence of organic base like piperidine (Figure 4.7a).

This simple synthesis presented the opportunity to investigate the effect of nitro groups on the phenol ring on the motion. It is well-known that the presence of nitro groups on the SP strongly impact on the ring opening kinetics of the SP. Thus, \( \text{SP(NO}_2\text{)}_2 \) was also synthesised by the reaction of 9,9,9a-trimethyl-2,3,9,9a-tetrahydro-oxazolo[3,2-a]indole and 3,5-dinitro-2-hydroxy benzaldehyde in ethanol at room temperature (Figure 4.7b). However, its poor solubility in the droplet solvents meant that this compound could not be used in the droplet motion systems.

\[ \text{SPCH}_3 + \text{organic base, ethanol, reflux} \rightarrow \text{SPCH}_3 \]

\[ \text{SP(NO}_2\text{)}_2 + \text{ethanol, r.t.} \rightarrow \text{SP(NO}_2\text{)}_2 \]

Figure 4.7 Structure and synthesis of \( \text{SPCH}_3 \) and \( \text{SP(NO}_2\text{)}_2 \).

Replacement of \( \text{SPCH}_3\text{CH}_2\text{OH} \) with \( \text{SPCH}_3 \) gave a droplet that, under identical conditions, moved in a similar way to that of the \( \text{SPCH}_3\text{CH}_2\text{OH} \) droplet, further confirming the photoisomerisation as being the cause of droplet movement.

4.3.2.2 The range of organic solvents

The density of the droplet could be changed by adjusting the ratio of DCE and toluene. In the initial experiment, the ratio of DCE and toluene was 1:2 (v/v) and the droplet floated on water. However, if the ratio of DCE and toluene was 1:1 or pure DCE was used, the droplet sunk to the bottom and the motion under light illumination still occurred. Again, irradiation of the underwater droplet with 365 nm light led to droplet colouration and movement away from the light.
(Movie 4.4). Subsequent 405 nm light irradiation of the deep red underwater droplet gave movement towards the light as previously (Movie 4.5).

Apart from DCE and toluene, other organic solvents, which were able to dissolve \textit{SPCH$_2$CH$_2$OH} and had poor solubility in water, for example, dichloromethane, chloroform, nitrobenzene, and chlorobenzene could also be used in the system. Surprisingly, butanol could be used together with DCE even though it has moderate solubility in water. This was attributed to the presence of surfactant on the surface of the droplet, preventing the loss of solvent from the droplet into the aqueous phase.

4.3.2.3 The role of 2-hexyldecanoic acid

HDA is a fatty acid commonly used in droplet experiments, which not only helped the formation of the organic droplet on water, but also became a better surfactant by deprotonation to promote the movement of droplets.$^{2,32,33}$ Since the ring-opened \textit{MCCH$_2$CH$_2$OH} generated by isomerisation of \textit{SPCH$_2$CH$_2$OH} bears a phenolate group, it had the potential to receive the proton from HDA, thus deprotonating it to make it into a better surfactant. However, no reaction was observed by adding HDA to the \textit{SPCH$_2$CH$_2$OH} solution followed by 365 nm light illumination according to the NMR spectra (Figure 4.8a). This was further confirmed by the absence of the feature absorption for MCH$^+$ at around 430 nm in the UV/Vis spectrum of the 365 nm light illuminated \textit{SPCH$_2$CH$_2$OH}/HDA solution (Figure 4.8b).

Given that in other droplet systems, HDA had caused droplet movement through deprotonation$^1$ and, since this was not likely to happen in this droplet, it was believed that HDA was probably not essential for the movement. This was confirmed by investigating an \textit{SPCH$_2$CH$_2$OH} droplet that did not contain HDA. The movement of this droplet under 365 nm light illumination was nearly identical to that with HDA. However, there appeared to be a larger plume from the droplet without HDA suggesting that the surfactant HDA might have helped to hold the photoactive material in the droplet and reduce its release into water. As a consequence, the \textit{SPCH$_2$CH$_2$OH}/HDA droplet could be simplified in later experiments to just \textit{SPCH$_2$CH$_2$OH} in organic solvents in the presence of SDBS.
Figure 4.8 (a) $^1$H NMR spectra of SPCH$_2$CH$_2$OH/HDA (1:1, mole/mole) before (red line) and after (blue line) 365 nm light illumination showing no change on the signals for the protons of spiropyran. The concentration of SPCH$_2$CH$_2$OH is 0.025 M. (b) UV/Vis spectra of a 15 min aged solution of SPCH$_2$CH$_2$OH/HDA (1:1, mol/mol) in DCM (black line) after irradiation under 365 nm for 20 seconds (red line) showing the characteristic absorption of MC at 575 nm, followed by irradiation with 405 nm or visible light for 20 seconds (blue line). The concentration of SPCH$_2$CH$_2$OH is 5×10$^{-5}$ M.

4.3.2.4 Optimisation of SPCH$_2$CH$_2$OH droplet

As has been discussed before, since HDA is not necessary for the droplet motion, the SPCH$_2$CH$_2$OH/HDA droplet content could be simplified to just SPCH$_2$CH$_2$OH. A droplet composed of SPCH$_2$CH$_2$OH in organic solvents was able to move away from 365 nm light and then towards 405 nm light in the aqueous solution containing 7 mM of SDBS and 0.4 mM of CaCl$_2$ (Figure 4.9, Movie 4.6). No significant ejection of plume from the droplet could be seen on 405 nm light irradiation likely due to the poor fluorescence of the colourless SP. Using this simplified system, the effect of acid in the aqueous phase could be investigated.
4.3.2.5 The effect of the acid in the aqueous solution

In order to study the effect of an external acid on the droplet motion, the aqueous medium was acidified and the light-controlled movement of SPCH\textsubscript{2}CH\textsubscript{2}OH/DCE droplets under water was investigated. It was speculated that acid might affect the photokinetics of the SP isomerisation and therefore the droplet speed. The addition of three acids at the same concentration as the SPCH\textsubscript{2}CH\textsubscript{2}OH in the droplet (0.1 M), hydrochloric (HCl), methanesulphonic (CH\textsubscript{3}SO\textsubscript{3}H) and oxalic ((COOH)\textsubscript{2}) acids, were investigated.

Prior to these experiments, the need to use both acid and CaCl\textsubscript{2} in the aqueous medium was investigated. It was found for underwater movement in the presence of acid that CaCl\textsubscript{2} could be omitted from the aqueous phase without any effect on the movement, and all of the following acid experiments for underwater movement were undertaken without CaCl\textsubscript{2} in the aqueous medium. It should be noted, however, that for the movement on water, CaCl\textsubscript{2} was still needed even though acid was added to the aqueous solution because CaCl\textsubscript{2} was essential for droplet formation on water.

Typically, for the movement of the SPCH\textsubscript{2}CH\textsubscript{2}OH droplet in SDBS (7 mM) and HCl (0.1 M) aqueous solution, the maximum speed away from 365 nm light was 13.4 mm s\textsuperscript{-1} (Table 4.2, Movie 4.7). However, the maximum velocity towards 405 nm light was just 3.7 mm s\textsuperscript{-1}. The total moving distance was up to 2232 mm including 1692 mm driven by 365 nm light and 540 mm attracted by 405 nm light. With the other acids, CH\textsubscript{3}SO\textsubscript{3}H (Movie 4.8a-b) and (COOH)\textsubscript{2} (Movie 4.9), similar speeds and distances could be obtained (Table 4.2). The fastest movement
(14.9 mm s\(^{-1}\)) was obtained by moving a \textbf{SPCH\textsubscript{2}CH\textsubscript{2}OH} droplet away from 365 nm light in SDBS (7 mM) and (COOH)\textsubscript{2} (0.1 M) aqueous solution.

\textbf{Table 4.2} Motion data of \textbf{SPCH\textsubscript{2}CH\textsubscript{2}OH} droplet in DI water containing SDBS (7 mM) and acid (0.1 M) under light illumination.

<table>
<thead>
<tr>
<th>Droplet</th>
<th>Aqueous solution</th>
<th>Motion under 365 nm light</th>
<th>Motion under 405 nm light</th>
<th>Total moving distance /mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>AVG speed /mm s(^{-1})</td>
<td>Maximum speed /mm s(^{-1})</td>
<td>moving distance /mm</td>
</tr>
<tr>
<td>SPCH\textsubscript{2}CH\textsubscript{2}OH/DCE</td>
<td>SDBS + HCl + H\textsubscript{2}O</td>
<td>3.5</td>
<td>13.4</td>
<td>1692</td>
</tr>
<tr>
<td>SPCH\textsubscript{2}CH\textsubscript{2}OH/DCE</td>
<td>SDBS + CH\textsubscript{3}SO\textsubscript{3} + H\textsubscript{2}O</td>
<td>3.3</td>
<td>12.0</td>
<td>1737</td>
</tr>
<tr>
<td>SPCH\textsubscript{2}CH\textsubscript{2}OH/DCE</td>
<td>SDBS + Oxalic acid + H\textsubscript{2}O</td>
<td>3.1</td>
<td>14.9</td>
<td>1757</td>
</tr>
</tbody>
</table>

The effect of acid on the droplets was determined by UV/Vis spectroscopy. As illustrated in Figure 4.1, it was expected that acid would assist the opening of the SP to MC, resulting in the formation of MCH\(^+\), which can clearly be seen by the new absorption in the UV/Vis spectrum at ~430 nm. Droplets placed in the appropriate aqueous solution were illuminated by 365 nm light typically passing through the aqueous media for 3 minutes, then a fixed amount of the droplet was obtained and diluted with chloroform and the UV/Vis spectrum obtained. The UV/Vis spectrum of the \textbf{SPCH\textsubscript{2}CH\textsubscript{2}OH}/DCE droplet under SDBS (7 mM) and HCl (0.1 M) aqueous solution that had been illuminated by 365 nm light for 3 min showed the generation of MCH\(^+\) (Figure 4.10, black line). If the concentration of HCl was decreased to 0.001 M, less MCH\(^+\) was formed together with a small amount of MC under the same conditions (Figure 4.10, red line), suggesting a slower rate of protonation. As a consequence, the speed and moving distance also decreased when less acid was used. If SDBS solution (7 mM) was used without HCl, a large amount of MC was generated with nearly no MCH\(^+\) after 3 min illumination of 365 nm light (Figure 4.10, blue line), and the \textbf{SPCH\textsubscript{2}CH\textsubscript{2}OH}/DCE droplet moved slowly. These results show that acid enhanced the movement.

Additionally, if the same droplet was kept in HCl solution (0.1 M) without any surfactant under 365 nm light illumination for 3 min, almost no MCH\(^+\) was formed and much less MC (Figure 4.10, olive line), although a larger amount of material (plume) appeared to be ejected into the aqueous medium. The formation of the
small amount of MC in the droplet was surprising. However, since the light was shining through the water and the ejected material, this may have affected the amount of light entering the droplet and therefore the amount of MC formed. Repetition of the same experiment but shining the light through the glass wall of the container onto a droplet stuck to the wall resulted in the formation of much more MC in the droplet (Figure 4.10, green line), similar to that for the droplet containing SDBS without HCl in the aqueous phase (Figure 4.10, blue line). This result supported the theory that the presence of MC/MCH⁺ in the water affected the amount of light entering the droplet. It should be noted that repeating the experiment without either SDBS or HCl resulted in a much larger amount of MC in the droplet (Figure 4.10, cyan line). It can be concluded, therefore, that both acid and surfactant assist the solubilisation of the photoproducts into the aqueous phase.

**Figure 4.10** UV/Vis spectra of a SPCH₂CH₂OH/DCE droplet (0.1 M) illuminated by 365 nm light for 3 min in the aqueous solution of SDBS (7 mM) and HCl (0.1 M) (black line), SDBS (7 mM) and HCl (1 mM) (red line), SDBS (7 mM) (blue line), HCl (0.1 M) (olive and green lines) and pure water (cyan line). As a control, UV/Vis spectrum of the SPCH₂CH₂OH/DCE droplet kept in dark in the aqueous solution of SDBS (7 mM) and HCl (0.1 M) was also obtained (magenta line). The measurements were conducted by the following procedure: 10 µL of the droplet was loaded into a 2 mL glass vial filled with 1 mL of the aqueous solution. The droplet was irradiated by 365 nm light for 3 min or kept in dark for 3 min. Then 1.5 µL of the droplet was taken by a micropipette and added to 3 mL of chloroform and UV/Vis spectrum of the resulting chloroform solution was recorded immediately.
4.3.2.6 Placing acid into the $\text{SPCH}_2\text{CH}_2\text{OH}$ droplet

Since acids in the aqueous phase were able to promote the motion of $\text{SPCH}_2\text{CH}_2\text{OH}$ droplets, their use in the droplet was then investigated. With this in mind, a DCE droplet of $\text{SPCH}_2\text{CH}_2\text{OH}$ (0.1 M) containing $\text{CH}_3\text{SO}_3\text{H}$ (0.1 M) but no surfactant was prepared. On illumination of this droplet for 44 s (Figure 4.11 and Movie 4.10), it barely moved although a large amount of red fluorescent material was released from the droplet (Figure 4.11c). Presumably, as concluded above, the very strong water soluble acid assisted the conversion SP to MCH$^+$ during illumination as evidenced by the yellow droplet colour, resulting in the release of the MCH$^+$ into the aqueous phase.

![Figure 4.11](image)

**Figure 4.11** Illustrations of the behaviour of a freshly made $\text{SPCH}_2\text{CH}_2\text{OH}/\text{CH}_3\text{SO}_3\text{H}$ droplet in the aqueous solution of SDBS (7 mM) under 365 nm light illumination. (a) The yellow droplet before light illumination ($t = 0$ s). (b) The droplet started to move upon 365 light illumination with the release of red florescent material. (c) The droplet stopped moving after illuminated by 365 nm light for around 40 s and it was surrounded by the released material. The illumination direction is indicated by the purple arrow. All the photos were taken from Movie 4.10.

Then a weak acid, acetic acid ($\text{CH}_3\text{COOH}$), was used instead of $\text{CH}_3\text{SO}_3\text{H}$. The $\text{SPCH}_2\text{CH}_2\text{OH}/\text{CH}_3\text{COOH}$ droplet was able to move away from 365 nm light with a speed up to 4.1 mm s$^{-1}$ and then move towards 405 nm light with a speed up to 5.4 mm s$^{-1}$ (Figure 4.12, Table 4.3 and Movie 4.11). However, the total moving distance was relatively short (110 mm), which was likely due to the loss of $\text{CH}_3\text{COOH}$ into water due to its solubility (miscible with water). The effect of the water solubility of the acids in the photocontrolled motion of the acid-contained droplet was further confirmed by the replacement of $\text{CH}_3\text{COOH}$ with benzoic acid ($\text{C}_6\text{H}_5\text{COOH}$) that was also a weak acid but slightly soluble in water (3.4 g L$^{-1}$). The velocity of the movement of did not change much, but the moving distance
was increased to 586 mm (Table 4.3, Movie 4.12). In order to further reduce the solubility of acid in water, lipoic acid with a solubility of 0.24 g L\(^{-1}\) was used and the moving distance of SPCH\(_2\)CH\(_2\)OH/lipoic acid droplet in SDBS solution under light illumination was up to 1334 mm ((Table 4.3, Movie 4.13). Surprisingly, if octanoic acid (C\(_7\)H\(_{15}\)COOH) with a solubility of 6.8 g L\(^{-1}\) was used, the total moving distance of SPCH\(_2\)CH\(_2\)OH droplet containing this acid was up to 2817 mm. The maximum speed was also increased to 10.7 mm s\(^{-1}\) under 365 nm light and 7.2 mm s\(^{-1}\) under 405 nm light, respectively (Table 4.3, Movie 4.14). However, if the acid used in the droplet was too weak or the solubility was too poor, like HDA, whose solubility in water was around 3×10\(^{-5}\) g L\(^{-1}\), it did not affect the motion of the SPCH\(_2\)CH\(_2\)OH droplet in SDBS aqueous solution.

**Table 4.3** Motion data of SPCH\(_2\)CH\(_2\)OH/acid droplet in DI water containing SDBS (7 mM) under 365 nm/405 nm light illumination. For C\(_6\)H\(_5\)COOH, lipoic acid and C\(_7\)H\(_{15}\)COOH, the amount used was 1 equivalent. While for CH\(_3\)COOH, 10 equivalent was used due to its good solubility in the aqueous phase.

<table>
<thead>
<tr>
<th>Droplet</th>
<th>Aqueous solution</th>
<th>Motion under 365 nm light</th>
<th>Motion under 405 nm light</th>
<th>Total moving distance /mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>AVG speed /mm s(^{-1})</td>
<td>Maximum speed /mm s(^{-1})</td>
<td>moving distance /mm</td>
</tr>
<tr>
<td>SPCH(_2)CH(_2)OH/CH(_3)COOH/DCE</td>
<td>SDBS + H(_2)O</td>
<td>1.4</td>
<td>4.1</td>
<td>70</td>
</tr>
<tr>
<td>SPCH(_2)CH(_2)OH/C(_6)H(_5)COOH/DCE</td>
<td>SDBS + H(_2)O</td>
<td>1.6</td>
<td>4.9</td>
<td>312</td>
</tr>
<tr>
<td>SPCH(_2)CH(_2)OH/lipoic acid/DCE</td>
<td>SDBS + H(_2)O</td>
<td>1.8</td>
<td>5.1</td>
<td>770</td>
</tr>
<tr>
<td>SPCH(_2)CH(_2)OH/C(<em>7)H(</em>{15})COOH/DCE</td>
<td>SDBS + H(_2)O</td>
<td>3.7</td>
<td>10.7</td>
<td>1848</td>
</tr>
</tbody>
</table>
So it could be concluded that acid in the $\text{SPCH}_2\text{CH}_2\text{OH}$ droplet promoted the photoinduced movement in the aqueous solution of SDBS by enhancing the photoisomerisation of spiropyran with the generation of $\text{MCH}^+$, which was released into the aqueous phase. The acidity and solubility of the acid used in the droplet were important in this process. A strong acid appeared to promote the release of MC/$\text{MCH}^+$, trapping the droplet in the released materials in the aqueous solution. The acid should not be too soluble, or it would escaped from the droplet in a short time making the motion not last long. Consequently, organic acids with a $\text{pK}_a$ around 4.5, and soluble in organic solvents but slightly soluble in water, were found to be the most effective for droplet movement.

4.3.2.7 Placing acid and surfactant into the $\text{SPCH}_2\text{CH}_2\text{OH}$ droplet

In order to realise the motion in pure water, thus decreasing the dependence of the droplet on the characteristics of the aqueous phase and making the motion more versatile, the motion system of $\text{SPCH}_2\text{CH}_2\text{OH}/\text{C}_7\text{H}_{15}\text{COOH}/\text{DCE}$ droplet in SDBS aqueous solution was further modified by using SDBS in the droplet. Based on this, a 2 $\mu$L droplet composed of $\text{SPCH}_2\text{CH}_2\text{OH}$ (0.1 M), SDBS (0.02 M) and $\text{C}_7\text{H}_{15}\text{COOH}$ (1 M) in chloroform was created. Chloroform was chosen as the solvent since all the materials especially SDBS had good solubility in this solvent. The droplet moved away from 365 nm light in DI water (Figure 4.13). The droplet was found not stable on contacting with the water surface, so it should be carefully generated under water.

![Figure 4.13](image)

**Figure 4.13** (a) Illustration of the movement away from light of a $\text{SPCH}_2\text{CH}_2\text{OH}$/acid/surfactant droplet in DI water following irradiation with 365 nm. (b) Image of the position of a $\text{SPCH}_2\text{CH}_2\text{OH}$/acid/surfactant droplet at $t = 16.9$ s from Movie 4.15 while it was moving away from 365 nm light. The position of this droplet at $t = 7.4$ s is indicated by a red circle. The illumination direction is from right side of the image.
The distance moved was around 52 mm and the velocity was up to 8 mm s\(^{-1}\) (Table 4.4, Movie 4.15). It should be noted that the resulting droplet got stuck on the glass surface and did not move upon 405 nm light illumination even though it had the tendency to move towards the 405 nm light source; washing the glass with piranha solution did not prevent the droplet sticking to the glass.

### Table 4.4 Motion data of \(\text{SPCH}_2\text{CH}_2\text{OH}/\text{acid/surfactant droplet in pure DI water under 365 nm/405 nm light illumination.}\)

<table>
<thead>
<tr>
<th>Droplet</th>
<th>Aqueous solution</th>
<th>Motion under 365 nm light</th>
<th>Motion under 405 nm light</th>
<th>Total moving distance /mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{SPCH}_2\text{CH}_2\text{OH}/\text{C}_7\text{H}_1\text{COOH/SDBS/CHCl}_3)</td>
<td>H(_2)O</td>
<td>AVG speed /mm s(^{-1})</td>
<td>Maximum speed /mm s(^{-1})</td>
<td>AVG speed /mm s(^{-1})</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.6</td>
<td>8.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Since the concentration of SDBS (0.02 M) in the droplet was too high to form a droplet for a pendant drop IFT measurement, the droplet was diluted to 1/10 to test the IFT. The result showed that the IFT of \(\text{SPCH}_2\text{CH}_2\text{OH}/\text{SDBS/C}_7\text{H}_1\text{COOH/CHCl}_3\) increased by around 5 mN/m under 365 nm light illumination and then recovered under 405 nm light (black line, Figure 4.14), which is opposite to the IFT change of \(\text{SPCH}_2\text{CH}_2\text{OH/CHCl}_3\) droplet without surfactant and acid (Figure 4.3b).
To investigate the role of SDBS and acid in the IFT change, further IFT measurements for \( \text{SPCH}_2\text{CH}_2\text{OH/C}_7\text{H}_{15}\text{COOH/CHCl}_3 \) and \( \text{SPCH}_2\text{CH}_2\text{OH/SDBS/CHCl}_3 \) droplets were carried out. The \( \text{SPCH}_2\text{CH}_2\text{OH/C}_7\text{H}_{15}\text{COOH/CHCl}_3 \) droplet (without surfactant) had an opposite trend in the photoinduced IFT change (red line, Figure 4.14) to the surfactant-containing droplet (black line, Figure 4.14) but a similar trend to that of the \( \text{SPCH}_2\text{CH}_2\text{OH/CHCl}_3 \) droplet (Figure 4.3b), albeit significantly reduced. In contrast, the \( \text{SPCH}_2\text{CH}_2\text{OH/SDBS/CHCl}_3 \) droplet without acid was not sensitive to light illumination. Clearly, both surfactant and octanoic acid are crucial to the increased IFT change but reasons for this are not clear yet.

### 4.4 Photocontrolled surfactant-free droplet motion system based on spiropyran

Maass \textit{et al.} have demonstrated that as long as a sufficient IFT change is created, droplet motion can be generated.\textsuperscript{35} Since SPs have the capacity to change IFT independently as shown in Figure 4.3, photocontrolled surfactant-free motion of a droplet should be able to be achieved using SP solely. However, isothermal photoactivated droplet motion without surfactant has not been reported.

A photoactive droplet (2 \( \mu \)L) containing only \( \text{SPCH}_2\text{CH}_2\text{OH} \) (0.1 M) in DCE/toluene (1:1, v/v) was created. Surprisingly, this droplet moved \textbf{towards} the 365 nm light source along the light beam in DI water with a red fluorescent plume trailing the droplet as illustrated in Figure 4.15 and can be seen in Movie 4.16. This movement was only possible once the problem of \( \text{SPCH}_2\text{CH}_2\text{OH} \) droplets sticking on the glass surface was solved by treating the glass surface with piranha solution (98% \( \text{H}_2\text{SO}_4/30\% \text{H}_2\text{O}_2 = 3:1, \text{v/v} \)).

This change in droplet movement direction appeared to correlate with the change in IFT. If the IFT decreased on 365 nm illumination (Figure 4.3), the surfactant-free droplet moved towards the light whereas if the IFT increased on 365 nm illumination (black line, Figure 4.15), the surfactant-containing droplet moved away from the light.
Figure 4.15 (a) Illustration of the movement towards 365 nm light of a SPCH$_2$CH$_2$OH droplet in DI water. (b) The red fluorescent plume trailing the droplet along the illuminated path is shown. The illumination direction is indicated by the purple arrow. This photo was taken from Movie 4.16.

At first, pure DCE was used as the droplet solvent. For a DCE droplet of SPCH$_2$CH$_2$OH (0.1 M), the movement under 365 nm light in DI water was found to be relatively slow and the droplet got stuck easily. A mixture of DCE and toluene (1:1, v/v) which had a lower density than DCE, was then used. For a 2 µL (1.6 mm diameter) DCE/toluene droplet of SPCH$_2$CH$_2$OH, the motion speed was up to 3.3 mm s$^{-1}$ (Table 4.5). The droplet moved for just 24 mm and still stuck easily to the glass. The size range of droplets that could be moved was from 0.2 mm (0.004 µL) to 7.8 mm (~200 µL) in diameter. Droplets above or below those limits easily got stuck on the glass surface. The lowest concentration of the photoactive component to ensure motion was 0.01 M. A 2 µL droplet with that concentration of SPCH$_2$CH$_2$OH moved slowly for only 3 mm and then stopped. It should be noted that the droplet did not move unless the glass was treated with piranha solution. After 365 nm light illumination, however, the droplet did not move away from 405 nm light even though 405 nm light was able to increase the IFT by the generation of SP (Figure 4.3b). It was probably because the droplet stuck to the hydrophilic surface after it is covered by the hydrophilic MC form.

Table 4.5 Motion data of SPCH$_2$CH$_2$OH droplet in pure DI water under 365 nm/405 nm light illumination

<table>
<thead>
<tr>
<th>Droplet</th>
<th>Aqueous solution</th>
<th>Motion under 365 nm light</th>
<th>Motion under 405 nm light</th>
<th>Total moving distance /mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AVG speed /mm s$^{-1}$</td>
<td>Maximum speed /mm s$^{-1}$</td>
<td>moving distance /mm</td>
<td>AVG speed /mm s$^{-1}$</td>
</tr>
<tr>
<td>SPCH$_2$CH$_2$OH/DCE/PhCH$_3$</td>
<td>H$_2$O</td>
<td>1.2</td>
<td>3.3</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Attempts to move these droplets on water were not successful since there was no surfactant in the aqueous solution to stabilise the organic droplet at the water/air interface. Consequently, this droplet could only move under DI water.

Movement of the droplet through the water was investigated by adjusting the solvent mixture. Thus, 3D droplet movement was achieved by changing the droplet density to be similar to water using DCE/toluene (1:1.7, v/v) (Figure 4.16, Movie 4.17). The movement was somewhat limited and the droplet moved up towards light for just 2 mm. However, the maximum velocity was up to 3 mm s$^{-1}$ and the average speed was around 1.5 mm s$^{-1}$.

![Figure 4.16](image)

**Figure 4.16** 3D movement of a 0.72 µL DCE/toluene (1:1.7, v/v) droplet of $\text{SPCH}_2\text{CH}_2\text{OH}$ (0.1 M) up towards 365 nm light in DI water. All the photos were taken from Movie 4.17. The illumination direction was from the top. The light in the initial ($t = 0$ s) photo is from an extra background light used to enable the video capture.

This ability to move the droplet off the glass surface clearly demonstrated that the generation of the motion was independent of the surface that the droplet was in contact with. It has been reported for droplets on a solid surface that they were able to move as long as there was a difference in the advancing and receding contact angles generated by an IFT change.$^{37-41}$

The generation of the plumes from the droplet in pure water presented the opportunity to characterise them without the impact from the surfactant, $\text{CaCl}_2$ or acid. This was done by fluorescence and mass spectral analysis of an extracted water sample following droplet movement. The fluorescence emission at 650 nm (Figure 4.17a) under 365 nm light illumination indicated that the plume compound was in the MC form,$^{4,14,42}$ which was further supported by the matrix-assisted laser
desorption/ionisation time-of-flight mass spectrometry (MALDI-TOF MS) spectrum with a molecular ion peak (M+H) at 353 (Figure 4.17b).

![Image](image_url)

**Figure 4.17** (a) Fluorescence emission spectra of the plume generated by (a) moving SPCH$_2$CH$_2$OH organic droplets in DI water. (b) MALDI-TOF MS spectrum for the plume generated by moving SPCH$_2$CH$_2$OH (MW = 352) organic droplets in DI water.

To further investigate the effect of surfactant on changing the motion direction upon 365 nm light, the motion of the SPCH$_2$CH$_2$OH droplet under an aqueous solution containing different concentrations of SDBS was investigated. To simplify the system, CaCl$_2$ and acid were not used even though they would have enhanced the motion.

When the concentration of SDBS was 1.2 mM (lower than CMC1), the SPCH$_2$CH$_2$OH droplet still moved towards 365 nm light, but the motion speed and motion distance were significantly reduced, 0.5 mm s$^{-1}$ and 3 mm, respectively (Movie 4.18). When the concentration of SDBS was increased to 1.5 mM (CMC1), the SPCH$_2$CH$_2$OH droplet still moved towards 365 nm light with a slow speed and for a short distance immediately after it was placed in the aqueous phase (Movie 4.19). However, if the droplet was kept in the aqueous solution of SDBS (1.5 mM) for 20 min before light illumination, it moved away from 365 nm light (Movie 4.20), with a velocity of 0.8 mm s$^{-1}$ and distance of around 5 mm. When the concentration of SDBS was further increased to 2.2 mM or higher, the SPCH$_2$CH$_2$OH droplet was able to move away from 365 nm light as soon as it was placed in the aqueous phase (Movie 4.21) and there was no need to wait for 20 min but no improvement in velocity and moving distance was observed.
Figure 4.18 IFT measured by the pendant drop method for (a) \( \text{SPCH}_2\text{CH}_2\text{OH}/\text{DCE} \) droplet (0.1 M) in DI water containing SDBS (2.2 mM) without 405 nm light illumination (red line) and with 405 nm light illumination from 20 s (black line), (b) pure DCE droplet (0.1 M) in DI water containing SDBS (2.2 mM) without 365 nm light illumination, (c) \( \text{SPCH}_2\text{CH}_2\text{OH}/\text{DCE} \) droplet (0.1 M) in DI water without 365 nm light illumination (red line) and with 365 nm light illumination from 20 s (black line), and (d) pure DCE droplet in DI water without 365 nm light illumination. All the curves were smoothed by adjacent averaging of 20 points.

In order to find out why this variation in movement occurred, IFT measurements of \( \text{SPCH}_2\text{CH}_2\text{OH}/\text{DCE} \) (0.1 M) droplets were carried out. For a droplet in 2.2 mM SDBS solution, the IFT of \( \text{SPCH}_2\text{CH}_2\text{OH}/\text{DCE} \) in the surfactant solution decreased from 8.9 to 8.1 mN m\(^{-1}\) within 20 s after its generation (red line, Figure 4.18a) without illumination, which is likely due to the absorption of surfactant onto the droplet surface. Upon 365 nm light irradiation (after 20 s), a sharp increase in IFT (around 2 mN m\(^{-1}\)) was observed (black line, Figure 4.18a). It should be noted that the IFT of pure DCE (4.4 mN m\(^{-1}\)) (Figure 4.18b) in the aqueous solution of SDBS (2.2 mM) is affected over 20 s in a similar way to that of the \( \text{SPCH}_2\text{CH}_2\text{OH}/\text{DCE} \) droplet, further indicating the absorption of surfactant on the droplet surface. As a contrast, the IFT of \( \text{SPCH}_2\text{CH}_2\text{OH}/\text{DCE} \) (0.1 M) in
DI water was also measured. In the absence of 365 nm light illumination, the IFT value of SPCH$_2$CH$_2$OH/DCE in DI water is 24.4 mN m$^{-1}$ (Figure 4.18c), which is close to that of pure DCE in water (26.2 mN m$^{-1}$) (Figure 4.18d), suggesting that SPCH$_2$CH$_2$OH did not have a surfactant-like effect on the droplet. A decrease in IFT (7 mN m$^{-1}$) was observed by illuminating SPCH$_2$CH$_2$OH/DCE droplet in water with 365 nm light (Figure 4.18c). The results showed that the presence of surfactant in the aqueous phase has reversed the trend of IFT change under 365 nm light illumination, thus changing the motion direction. As long as light illumination increases IFT, the photoactive droplet moves away from light source. While if light illumination decreases IFT, the photoactive droplet moves towards light.

4.5 Mechanism

It has been reported that Marangoni flow, initiated by an IFT gradient, plays a crucial role in droplet motion through an immiscible liquid.\textsuperscript{32,43-45} As long as an IFT gradient is created on the droplet surface, a Marangoni flow is generated and directed from the area of low IFT to the area of high IFT (blue lines, Figure 4.19).\textsuperscript{32,43-45} At the same time, an internal convection is also formed to create a positive feedback loop (red lines, Figure 4.19).\textsuperscript{32,45} The droplet moves in the opposite direction to the Marangoni flow and the same direction as the internal convection.\textsuperscript{32,45}

![Image](image_url)

**Figure 4.19** Illustration of a droplet moving by Marangoni flow. The flow field outside and inside the droplet is indicated by the blue and red lines, respectively. The motion direction is the same as the internal flow through the droplet (red line).\textsuperscript{46}
Chemical reaction at the interface between the droplet and its surrounding medium has been widely used to induce droplet motion through the accumulation and release of the chemical products, which affect the interfacial energy, leading to a local IFT change and generating a corresponding Marangoni flow. As has been observed in the experiments above, the droplet motion has been caused by a photoinduced chemical reaction, the photoisomerisation between SPCH$_2$CH$_2$OH and MCCH$_2$CH$_2$OH, which was able to generate an IFT change and a corresponding Marangoni flow. However, the photoactive droplets under light irradiation behaved differently with or without surfactant, the photoinduced chemical reaction may have changed the IFT in two different ways based on the presence or absence of surfactant.

4.5.1 Droplet motion with surfactant

In most reported droplet motion systems related to surfactant, the IFT gradient originated from the imbalanced distribution of surfactant on the droplet surface as a result of the gain or loss of surfactant. For the experiments above in the presence of surfactant whether in the droplet or the aqueous medium (Section 4.3), the photoisomerisation likely affected the distribution of surfactant on the droplet surface. This imbalanced distribution was likely generated by the significant change in the isomer polarity of the SP and MC forms leading to a change in surfactant surface distribution and possible merocyanine surface coverage. It should be noted that even though the photoisomerisation between SP and MC was accompanied by an IFT change, the behaviour of SDBS at the organic/water interface dominated the IFT change since it is much more surface active. This was confirmed by the IFT measurements of DCE droplet in DI water (26.2 mN m$^{-1}$), SPCH$_2$CH$_2$OH/DCE droplet in DI water (24.4 mN m$^{-1}$) and DCE droplet in DI water containing 2.2 mM of SDBS (4.4 mN m$^{-1}$) (see Figure 4.18).

4.5.1.1 Motion away from the 365 nm light source

As has been discussed before, SPCH$_2$CH$_2$OH droplets were able to move away from 365 nm light in the presence of surfactant either in the aqueous phase or in the
droplet. In order to confirm whether Marangoni flows were significant in the photoactivated droplet motion, larger (10 μL) \( \text{SPCH}_2\text{CH}_2\text{OH} \)/HDA/DCE droplets were studied. For these photoactive droplets, there is an obvious colour change under 365 nm light irradiation because of the formation of red MC (Figure 4.20, Movie 4.22). The Marangoni convection is evident from the dark red material flow inside the droplet. The direction of the internal flow is away from 365 nm light through the droplet (Figure 4.20b-c, Movie 4.22). The droplet moves in the same direction as the internal flow.\(^{35,44,45,48,50,51}\) It should be noted that this experiment was undertaken before HDA was found not necessary for the movement, so HDA was still used in the droplet and it had no effect on the result.

![Figure 4.20](image)

**Figure 4.20** (a) Photo of a 10 μL transparent yellow \( \text{SPCH}_2\text{CH}_2\text{OH} \)/HDA droplet under aqueous solution containing SDBS and CaCl\(_2\), (b) immediately after (< 1 s) irradiation (365 nm) and before movement showing the start of the Marangoni convection of red merocyanine material moving down the centre of the droplet, (c) irradiation (365 nm) 3 s after movement showing the evolution of the convection current back around the droplet. (d) Detailed evaluation of the red convective flow inside a \( \text{SPCH}_2\text{CH}_2\text{OH} \) droplet in aqueous SDBS/CaCl\(_2\) solution under 365 nm light illumination. The illumination direction is indicated by the purple arrow.
After simplifying \( \text{SPCH}_2\text{CH}_2\text{OH}/\text{HDA}/\text{DCE} \) droplet to \( \text{SPCH}_2\text{CH}_2\text{OH}/\text{DCE} \), a more detailed investigation of the red convective flow was carried out using a \( \text{SPCH}_2\text{CH}_2\text{OH}/\text{DCE} \) droplet (Figure 4.20d, Movie 4.23). Upon 365 nm light irradiation, red MC starts to form in the illuminated area and then flows to the non-illuminated side through the centre part of the droplet (Figure 4.20d, \( t = 0.0-1.0 \) s). After the flow reaches the non-illuminated side, it grows and then circulates back to the illuminated area, making the flow a closed loop (Figure 4.20d, \( t = 1.2-2.1 \) s). The flow can be seen (Figure 4.20d, \( t = 2.2-3.8 \) s) until the droplet is deep red (Figure 4.20d, \( t = 7.0 \) s). The release of red fluorescent material from the illuminated part of the droplet into the aqueous solution can be clearly seen from \( t = 2.0-7.0 \) s (Figure 4.20d).

Carbon particles were also used to visualise the Marangoni flow on the droplet surface. As is shown in Figure 4.21, a \( \text{SPCH}_2\text{CH}_2\text{OH}/\text{SDBS/C}_7\text{H}_{15}\text{COOH}/\text{CHCl}_3 \) droplet (10 µL) was used to move through micron-sized carbon particles in DI water under 365 nm light illumination. As long as the carbon particles were close enough to the droplet, the particles moved with a fast flow towards 365 nm light in the direction of IFT increase, in accordance with the Marangoni flow (Movie 4.24). The velocity of the flow estimated from the movement of carbon particles was up to 40 mm s\(^{-1}\), which is 20 times higher than the speed of the droplet (2 mm s\(^{-1}\)) (Figure 4.21).

![Figure 4.21](image)

**Figure 4.21** Movement of micro-scale carbon particles (indicated by red and blue circles) on the surface of a \( \text{SPCH}_2\text{CH}_2\text{OH}/\text{SDBS/C}_7\text{H}_{15}\text{COOH}/\text{CHCl}_3 \) (10 µL) droplet upon 365 nm light illumination in DI water. As observed in Movie 4.24 from 4.36 s to 4.53 s, the droplet moved away from 365 nm light with a distance of about 0.3 mm, while the carbon particles moved towards light on the droplet-water interface with a distance of about 7 mm during the same time period.

If smaller carbon particles (sub-micron) were used, the flow in the bulk water phase surrounding the droplet could be observed (Figure 4.22, Movie 4.25). Once the
droplet entered the suspension of carbon powder under 365 nm light illumination, the droplet appeared to get stuck although there was a clear Marangoni flow around the droplet as evidenced by the movement of the carbon particles (Figure 4.22b-d and Movie 4.25).

**Figure 4.22** Movement of nanoscale carbon particles in DI water surrounding a SPCH$_2$CH$_2$OH/SDBS/C$_2$H$_5$COOH/CHCl$_3$ droplet (10 µL) upon 365 nm light illumination. The illumination direction is indicated by the purple arrow. The carbon particles moved towards 365 nm light on the droplet-water interface and continued moving in the bulk solution. The carbon suspension was transferred from the illuminated side to the non-illuminated side in the bulk solution.

Consequently, it can be concluded that, upon 365 nm light irradiation, SP was converted to the zwitterionic MC close to the droplet/water interface in the illuminated area (Figure 4.23a), thus decreasing the amount of surfactant SDBS and resulting in an increase in IFT (high $\gamma$) in the same area (Figure 4.23). This generated an internal Marangoni convection flow, directed towards the non-illuminated area through the droplet and then back to the illuminated area (red arrows, Figure 4.23b). The droplet moved in the same direction as the internal flow, which is away from light (Figure 4.23b).$^{35,44,45,48,50,51}$ The droplet likely stopped moving after the accumulation of MC on the droplet surface. The existence of acid either in the droplet or in the aqueous phase could have accelerated the photoconversion from SP to MC thus promoting the motion.

**Figure 4.23** (a) IFT increase generated by the photoconversion from the SP to the MC form which affects the distribution of the surfactant SDBS on the droplet surface. (b) Illustration of a droplet moving away from 365 nm light by Marangoni flow (blue arrows) in the presence of surfactant as a result of the photoisomerisation generating a Marangoni internal convection (red arrows).
4.5.1.2 Motion towards the 405 nm light source

The SPCH$_2$CH$_2$OH/HDA/DCE droplet became dark red after movement away from the 365 nm light due to the formation of MCCH$_2$CH$_2$OH. The resulting MCCH$_2$CH$_2$OH/HDA/DCE droplet was able to move towards 405 nm light. In order to observe the Marangoni flow, the dark red MCCH$_2$CH$_2$OH/HDA/DCE droplet (10 μL) (Figure 4.24a) was further illuminated by a 405 nm laser. For these MCCH$_2$CH$_2$OH droplets, there is an obvious colour change under 405 nm light irradiation because of the formation of transparent yellow SPCH$_2$CH$_2$OH (Figure 4.24b-c and Movie 4.26). Upon 405 nm light irradiation, the droplet surface becomes transparent yellow and the transparent yellow flows to the non-illuminated area (blue arrows, Figure 4.24b and Movie 4.26). The flow returns back to the illuminated area through the centre of the droplet (black arrows, Figure 4.24c and Movie 4.26). The droplet moves in the same direction as the internal flow, which is towards the light source.

![Figure 4.24](image)

**Figure 4.24** (a) Photo of a 10 μL MCCH$_2$CH$_2$OH/HDA droplet generated by illumination of a SPCH$_2$CH$_2$OH/HDA droplet with 365 nm light under an aqueous solution of SDBS/CaCl$_2$. (b) MCCH$_2$CH$_2$OH/HDA droplet immediately on irradiation (405 nm) and before movement showing the start of the Marangoni convection current of transparent yellow flowing towards the non-illuminated side along the droplet surface indicated by the blue arrow. (c) Irradiated MCCH$_2$CH$_2$OH/HDA droplet during movement showing the evolution of the convection current back through the droplet indicated by the white arrow.

As a consequence, it can be concluded that, upon 405 nm light irradiation, the zwitterionic MC was converted to SP (Figure 4.25a) close to the droplet/water interface in the illuminated area, thus increasing the amount of surfactant SDBS and resulting in an decrease in IFT (low γ) in the same area (Figure 4.25). This generated an internal Marangoni convection flow, directed towards the non-illuminated area through the droplet surface and then back to the illuminated
area through the droplet (Figure 4.25b). The droplet moved in the same direction as the internal flow, which is towards light (Figure 4.25a). The droplet stopped moving after all the MC was converted to SP, which was indicated by the decolouration of the dark red droplet.

Figure 4.25 (a) IFT increase generated by the photoconversion from MCCH$_2$CH$_2$OH to SPCH$_2$CH$_2$OH which affects the distribution of the surfactant SDBS on the droplet surface. (b) Illustration of a droplet moving towards 405 nm light by Marangoni flow in the presence of surfactant as a result of the photoisomerisation generating a Marangoni internal convection (red arrows).

4.5.2 Droplet motion without surfactant

Without any surfactant in the droplet or aqueous medium (Section 4.4), the photoisomerisation still led to a change in IFT (Figure 4.3 and 4.18c). Surprisingly, this direct approach to IFT change resulted in droplet motion towards 365 nm light, opposite to the 365 nm light-induced motion in the presence surfactant.

Without surfactant, the photoisomerisation between SP and MC determined the IFT change at the droplet/water interface. As has been measured before, the MC form has a lower IFT than the SP form at an organic/water interface (Figure 4.3). As a result, 365 nm light illumination decreased the IFT on the droplet surface by converting SPCH$_2$CH$_2$OH (high $\gamma$) to MCCH$_2$CH$_2$OH (low $\gamma$) (Figure 4.26a), thus initiating Marangoni stress directed towards the high IFT area (non-illuminated area), causing droplet movement towards the light (Figure 4.26b). While the droplet was moving, material was released into the water phase to form the red-fluorescent plume trailing the droplet, which was characterised as MCCH$_2$CH$_2$OH. The MC species, which failed to be released into water, accumulated on the droplet surface. It has been demonstrated that the accumulation of the surface active product on the droplet surface obstructs the movement.$^{32}$
release of \textbf{MCCH\textsubscript{2}CH\textsubscript{2}OH} into the water phase was relatively slow due to its poor solubility, while its generation under 365 nm light was fast. As a consequence, the products accumulated on the droplet surface in a short time, limiting the motion to a short distance (24 mm).

![Figure 4.26](image)

\textbf{Figure 4.26} (a) Photoconversion of \textit{SPCH\textsubscript{2}CH\textsubscript{2}OH} to \textit{MCCH\textsubscript{2}CH\textsubscript{2}OH} with accompanying IFT decrease. (b) Illustration of a \textit{SPCH\textsubscript{2}CH\textsubscript{2}OH} droplet moving towards 365 nm light by Marangoni flow (blue arrows) in DI water without surfactant as a result of the photoisomerisation generating a Marangoni internal convection (red arrows).

\section*{4.6 Summary}

In this chapter, a series of photoactive droplets based on \textit{SPCH\textsubscript{2}CH\textsubscript{2}OH} have been developed. These droplets were able to move away from or towards the light source on or under the aqueous solution, depending on the composition of the organic droplet and the aqueous solution as well as the wavelength of light. In the presence of surfactant, the \textit{SPCH\textsubscript{2}CH\textsubscript{2}OH} droplet moved away from 365 nm light and then towards 405 nm light. Acid and CaCl\textsubscript{2} were able to promote the motion. However, without surfactant, the \textit{SPCH\textsubscript{2}CH\textsubscript{2}OH} droplet moved towards 365 nm light under DI water. The Marangoni flow originated by IFT change due to the photoisomerisation between SP and MC playing a crucial role in the movement. In all these droplet motion systems, the droplet was observed to move in the same direction as the internal convective flow through the centre of the droplet, from high IFT to low IFT. Since the photoactive materials were used in the droplet and the motion was controlled by the photoinduced change within the droplet itself, total control of the droplet motion and direction could be achieved. Similarly, in phototaxis systems, the organism also moves towards or away from stimulus of light by changing itself rather than the environment. Our system provides a simple approach to emulate the phototaxis behaviour in nature.\textsuperscript{52}
4.7 References


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(27) Data taken from 2016 water analysis report provided by Sydney Water.


(36) Larger droplets tended to lose their spherical shape such that their diameter does not accurately indicate their volume.


Chapter 5  Photocontrolled movement of organic droplets containing a protonated merocyanine/surfactant salt

5.1  Introduction

Manipulation of liquid droplets has attracted increasing attention in recent years because of their potential applications in bionics, microfluids, and drug delivery.\textsuperscript{1,2} As one of the simplest methods for droplet manipulation, controlled movement of organic droplets in an aqueous environment based on tension change or Marangoni effects has been widely investigated.\textsuperscript{2,3} In order to achieve controlled motion, a continuous change should be created.

One popular strategy is to create a change in the external environment of the droplet.\textsuperscript{2} Chemical gradients in the aqueous solution surrounding the droplet have been widely used to achieve this goal.\textsuperscript{4-7} However, as has been reported, the droplet can only be moved in limited directions, along or against the gradient.\textsuperscript{4-7} The termination of movement is another problem once the gradients are created. In recent years, better control has been achieved using light with photoactive materials in the aqueous solution; the droplet movement can be started and stopped by light illumination of the solution.\textsuperscript{8,9} However, there still exist limitations, for example, the complex arrangements of the light sources\textsuperscript{8} or the use of specific channels.\textsuperscript{9} Most of the limitations originated from the fact that the droplet motion depends on the external environment.

Another strategy is to create a change in the droplet itself, that is, the active materials are dissolved in the organic droplet rather than the surrounding media. In this case, the movement depends on the change of the droplet itself and is independent of the external environment. This seems to be a more efficient and promising way to realise the total control of droplet motion, even though it has been scarcely reported before.\textsuperscript{10,11} Based on this strategy, a series of photoactive spiropyran-based droplets were developed and an efficient control of their motion by light illumination was realised in the previous chapter. For most droplets, surfactant in the aqueous environment was essential for movement. However, a
CHCl₃ droplet containing SPCH₂CH₂OH, C₇H₁₅COOH and surfactant SDBS was able to move in pure water upon light illumination, even though the distance of movement was short. This discovery of motion in pure water reduced the dependence on the external aqueous medium, but the short distance limited its application. As a result, efficient movement in water without additives needed to be developed, which could largely extend the application of this system.

As has been demonstrated in the previous chapter, the interaction between the surfactant and spiropyran/merocyanine species played an important role in the light-induced IFT change and the corresponding movement of the droplet. The short distance of the movement of the SPCH₂CH₂OH/C₇H₁₅COOH/SDBS/CHCl₃ droplet in DI water was attributed to the fast loss of the water soluble surfactant SDBS from the droplet into water. In order to reduce the release of surfactant and increase its interaction with the photoactive materials, a spiropyran/merocyanine species that could act as a surfactant needed to be created. To achieve this goal, a protonated merocyanine MCH⁺ surfactant salt was prepared by treating SPCH₂CH₂OH with a strongly acidic surfactant.¹¹⁻¹³ This MCH⁺ surfactant salt was then used in the photocontrolled droplet motion systems without surfactant in the aqueous phase.

5.2 Preparation and photochemistry of protonated merocyanine/surfactant salt

The acid-induced ring opening of spiropyrans has been widely investigated and used to generate MCH⁺ salts.¹²⁻²³ As has been reported before, MCH⁺ can be obtained by treating spiropyran with strong acid like trifluoroacetic acid (CF₃COOH), hydrochloric acid (HCl), camphorsulphonic acid, p-toluensulphonic acid and dodecylbenzenesulphonic acid (DBSA) in organic solvents.¹²,¹³,¹⁶⁻²³ In order to generate a MCH⁺ surfactant salt that could be used in our tension change-induced droplet motion systems, DBSA, which is not only a strong acid (pKₐ ~ −2.8)²⁴ but also a good surfactant, was used as the acid to react with SPCH₂CH₂OH.¹²,¹³ The solution of the MCH⁺ surfactant salt (MCH⁺DBS⁻) was obtained by dissolving SPCH₂CH₂OH and DBSA in organic solvents like DCM,
DCE, chloroform and nitrobenzene and keeping the solution in dark overnight (Figure 5.1a).

Ultraviolet-visible (UV/Vis) spectroscopy was used to investigate this protonation process. Upon the addition of 1 mole equivalent of DBSA into the DCM solution of \( \text{SPCH}_2\text{CH}_2\text{OH} \), a feature peak at 427 nm for \( \text{MCH}^+ \) was observed in the UV/Vis spectrum (black line, Figure 5.1b), indicating that the \( \text{MCH}^+\text{DBS}^- \) had started to form (Figure 5.1a). After keeping the mixture in the dark overnight, the absorption at 427 nm reached a maximum (red line, Figure 5.1b). Upon 365 nm, 405 nm or visible light irradiation, \( \text{MCH}^+\text{DBS}^- \), the characteristic absorption at 427 nm almost disappeared (green, blue and cyan lines, Figure 5.1b) and, at least in the case of the visible light irradiation (cyan line, Figure 5.1b), a spectrum consistent with that of \( \text{SPCH}_2\text{CH}_2\text{OH} \) (Figure 4.2b) was generated.

Further investigation of the protonation process of \( \text{SPCH}_2\text{CH}_2\text{OH} \) with DBSA was carried out by proton nuclear magnetic resonance (\( ^1\text{H} \) NMR) spectroscopy. By adding 1 equivalent of DBSA to the deuterated chloroform (CDCl\(_3\)) solution of \( \text{SPCH}_2\text{CH}_2\text{OH} \), the characteristic \( ^1\text{H} \) NMR signals of \( \text{SPCH}_2\text{CH}_2\text{OH} \) (Figure 5.2b) disappeared and were replaced by a new set of signals (Figure 5.2c). After the
mixture of **SPCH\textsubscript{2}CH\textsubscript{2}OH** and DBSA was kept in dark for 12 h at room temperature, a simpler \textsuperscript{1}H NMR spectrum was apparent (Figure 5.2d) attributed to **MCH\textsuperscript{+}DBS\textsuperscript{-}**, confirming the observation in the UV/Vis spectrum (red line, Figure 5.1b).

![Figure 5.2](image)

Figure 5.2 (a) Labelled structure of **SPCH\textsubscript{2}CH\textsubscript{2}OH** (black labels), the SPH\textsuperscript{+} form or the cis MCH\textsuperscript{+} form (red labels), the MCH\textsuperscript{+} form (blue labels) and DBS\textsuperscript{-} (green labels). \textsuperscript{1}H NMR spectra of (b) **SPCH\textsubscript{2}CH\textsubscript{2}OH** (0.025 M) in CDCl\textsubscript{3}, (c) within 5 min after addition of 1 equivalent of DBSA, (d) in dark for 12 h after addition of DBSA and (e) followed by 365 nm light illumination for 30 min. The characteristic signals for **SPCH\textsubscript{2}CH\textsubscript{2}OH**, the SPH\textsuperscript{+} form, the MCH\textsuperscript{+} form and DBS\textsuperscript{-} in the spectra were labelled as black, red, blue and green, respectively.

Similar to that previously observed in Chapter 3 for the \textsuperscript{1}H NMR spectra of protonated merocyanines (Figure 3.12), two doublets can be seen at 8.26 and
8.19 ppm with a coupling constant of 16.4 Hz, for the protons of the *trans* ethylenic bond, and a six proton singlet at 1.83 ppm, for the gem-dimethyl groups (Figure 5.2d). Moreover, the integration ratio of the peaks at 8.26, 8.19 and 1.83 ppm was 1:1:6, consistent with the proton numbers. The doublet at 8.81 ppm and the triplets at 4.72 and 4.96 ppm were assigned to H5, H8' and H9'of MCH·DBS⁻, respectively, according to previous assignments (Figure 3.12). The DBSA used was a mixture of isomers, and its spectrum is shown in Figure 5.2f; the aromatic doublets for the protons (H3 and H5) closest to the alkyl chain at 7.28 and 7.24 ppm, the doublets for the protons (H2 and H6) closest to the sulphonic acid group at 7.81 ppm and the singlet for the sulphonic acid proton at 9.60 ppm can be clearly seen. In the spectrum of MCH·DBS⁻ in Figure 5.2d, the doublets for H3 and H5 of DBS⁻ were observed.

The interpretation of the ¹H NMR spectrum of the freshly prepared material (Figure 5.2c) was more difficult. In the UV/Vis spectrum of the freshly prepared solution, the initial formation of MCH·DBS⁻ (black line, Figure 5.1b) was evident and signals H8'-H11' of MCH·DBS⁻ were clearly evident. However, the H3-H5 signals were shifted and broadened. This suggested that the MCH·DBS⁻ was undergoing a dynamic process into one of more other compounds. Other signals in the spectrum (Figure 5.2c) were found at 6.99, 6.37 and 1.42 ppm, which gave an integral ratio of 1:1:6. These signals seemed to be similar to the SPCH₂CH₂OH signals occurring at 6.67, 5.89, 1.20 and 1.29 ppm (Figure 5.2b). The coupling constant for the double bond H3 peak at 6.37 ppm was 8.6 Hz, confirming that the double bond stayed as the cis conformation. The coalescence of the two singlets at 1.20 and 1.29 ppm for the two distinct methyl groups in the spectrum of SPCH₂CH₂OH to one singlet at 1.42 ppm might either result from the reported acid promoted fast interconversion between the two R and S enantiomers of spiropyran¹⁷,¹⁹,²⁰,²⁵,²⁶ or as a result of the formation of MC species.

To further investigate the photochromism of MCH·DBS⁻, the 12 h old solution of SPCH₂CH₂OH and DBSA was illuminated by 365 nm light for 30 min and this resulted in a near identical spectrum (Figure 5.2e) to that of Figure 5.2c.

It has been reported that, by treating spiropyran with strong acid, two competitive reactions could initially take place, direct protonation of indoline
nitrorgen\textsuperscript{15,16,18,20,27,28} to form SPH\textsuperscript{+} and/or acid-catalysed ring opening of the benzopyran ring to generate \textit{trans} MCH\textsuperscript{+} via \textit{cis} MCH\textsuperscript{+} (Figure 5.3).\textsuperscript{17,22} It has been reported that the SPH\textsuperscript{+} can spontaneously convert to the \textit{trans} MCH\textsuperscript{+}.\textsuperscript{20} The \textit{trans} MCH\textsuperscript{+} was photoactive and able to undergo a ring-closing reaction under light illumination (visible) to yield either \textit{cis} MCH\textsuperscript{+} or a spiropyran species (SP or SPH\textsuperscript{+}) (Figure 5.3).\textsuperscript{18,20,21

Figure 5.3 Photo and pH induced conversion between the SP, SPH\textsuperscript{+}, MC and MCH\textsuperscript{+} forms of SPCH\textsubscript{2}CH\textsubscript{2}OH.

Similarly, in our case, by adding strong acid DBSA to the solution of SPCH\textsubscript{2}CH\textsubscript{2}OH, the protonated species SPH\textsuperscript{+}DBS\textsuperscript{−} (or \textit{cis} MCH\textsuperscript{+}DBS\textsuperscript{−}) and \textit{trans} MCH\textsuperscript{+}DBS\textsuperscript{−} were generated competitively as seen in the 1H NMR spectrum after 5 min (Figure 5.2c), with all SPH\textsuperscript{+}DBS\textsuperscript{−} (or \textit{cis} MCH\textsuperscript{+}DBS\textsuperscript{−}) eventually converted to \textit{trans} MCH\textsuperscript{+}DBS\textsuperscript{−}. Following this, SPH\textsuperscript{+}DBS\textsuperscript{−} (or \textit{cis} MCH\textsuperscript{+}DBS\textsuperscript{−}) could be regenerated by illumination of the \textit{trans} MCH\textsuperscript{+}DBS\textsuperscript{−} solution with 365 nm or visible light (Figure 5.2e).

It should be noted that during the course of this work, Kortekaas \textit{et al.} reported that protonation of spiropyans leads predominantly to \textit{cis} MCH\textsuperscript{+} salts rather than protonated SPs, disagreeing with earlier work concerning the formation of SPH\textsuperscript{+} salts.\textsuperscript{22}

To further investigate this protonation process of spiropyran by DBSA, other spiropyans like SPCH\textsubscript{3} with a methyl group connected to the nitrogen of the indoline moiety and SP(NO\textsubscript{2})\textsubscript{2}, with two nitro groups on the aromatic ring, were reacted with DBSA (Figure 5.4).
Figure 5.4 Conversion between the spiropyran, protonated spiropyran and protonated merocyanine forms of SPCH$_3$ and SP(NO$_2$)$_2$ in the presence of DBSA.

By adding 1 equivalent of DBSA to the CDCl$_3$ solution of SPCH$_3$, only a single species was generated with a broadened doublet at 6.28 ppm likely for a cis ethylenic proton in the $^1$H NMR spectrum (Figure 5.5, purple line), broadened singlet at 3.25 ppm for N-methyl protons and a singlet at 1.47 ppm for the gem-dimethyl protons. These broaden singlets suggest an equilibrium process between two species. The signals at 8.07 and 8.06 ppm were similar to those in the spectrum of SPCH$_3$ at 8.00 and 8.03 ppm (Figure 5.5, black line), supporting the assignment of this species as protonated SPCH$_3$, SPCH$_3$H$^+$DBS$^-$ (Figure 5.5).

Signals for the rest of the aromatic protons as well as the second ethylenic proton were in the range of 7.45 to 7.10 ppm (Figure 5.5, purple line). Doublets at 7.60, 7.13 and 7.09 for DBS$^-$ were also seen (Figure 5.5, purple line). Interestingly, by decreasing the amount of DBSA, all the signals in the $^1$H NMR spectrum shifted upfield (Figure 5.5, green, blue and red lines) towards the corresponding signals in the spectrum of SPCH$_3$ (Figure 5.5, black line) and the broadened signals became sharper. This suggested that the equilibrium process lay in favour of the SPCH$_3$ at lower DBSA concentration. Compared to the N-ethanol group in SPCH$_2$CH$_2$OH, the N-methyl group in SPCH$_3$ was less sterically bulky, making the nitrogen easier to be protonated. Therefore, the generation of SPCH$_3$H$^+$DBS$^-$ could have been dynamically faster. However, given that all the above NMR signals were similar to those assigned by Kortekaas et al. for a cis protonated merocyanine, $^{13}$C NMR spectra of SPCH$_3$ and SPCH$_3$H$^+$DBS$^-$ were obtained to attempt to distinguish between the protonated SP and MC.
Figure 5.5 $^1$H NMR spectra of a 5 min old CDCl$_3$ solution of SPCH$_3$ (0.025 M) and of DBSA with a mole ratio of 1:1 (purple line), 2:1 (green line), 4:1 (blue line) and 10:1 (red line). The spectrum of SPCH$_3$ in CDCl$_3$ (0.025 M) was also listed as a comparison (black).

In the work of Kortekaas et al., the signal for the cis ethylenic carbon of the cis MCH$^+$ salt was observed at ~190 ppm in the $^{13}$C NMR spectrum. However, in our case, no signals were observed above 162 ppm in the $^{13}$C NMR of the protonated SPCH$_3$ (Figure 5.6, red spectrum), confirming that this protonated intermediate was not cis MCH$^+$ and therefore likely to be the N-protonated SPCH$_3$H$^+$DBS$^-$.

Figure 5.6 $^{13}$C NMR spectra of SPCH$_3$ (0.025 M) (blue line) in CDCl$_3$ and within 5 min after addition of 1 equivalent of DBSA (red line).
After keeping the $\text{SPCH}_3\text{H}^+\text{DBS}^-$ solution in the dark for 36 h at room temperature, $\text{SPCH}_3\text{H}^+\text{DBS}^-$ was converted to the MCH$^+$ form ($\text{MCCH}_3\text{H}^+\text{DBS}^-$) along with a small amount of $\text{SPCH}_3$, indicated by the two doublets at 8.33 and 7.90 ppm for the trans ethylenic bond, the singlets at 4.22 and 1.80 ppm for the N-methyl and the gem-dimethyl groups, respectively (Figure 5.7b). A downfield shift (0.18 ppm) of the two aromatic protons next to the sulphonate group of DBS$^-$ was observed. Irradiation of $\text{SPCH}_3\text{H}^+\text{DBS}^-$ solution with 365 nm light for 30 min led to 50% reconversion of $\text{MCCH}_3\text{H}^+\text{DBS}^-$ to $\text{SPCH}_3\text{H}^+\text{DBS}^-$ as indicated by the $^1\text{H}$ NMR spectrum in Figure 5.7c.

In contrast, treating $\text{SP(NO}_2)_2$ with DBSA in CDCl$_3$ gave no signals in the $^1\text{H}$ NMR spectrum for the SPH$^+$ form after 5 min. Instead, only the MCH$^+$ form ($\text{MC(NO}_2)_2\text{H}^+\text{DBS}^-$) was detected (Figure 5.8c). This can be explained by the two electron-withdrawing nitro groups that could stabilise the ring-opened structure, thus promoting the acid-induced ring opening process and leading to the fast generation of $\text{MC(NO}_2)_2\text{H}^+\text{DBS}^-$. By illuminating the $\text{MC(NO}_2)_2\text{H}^+\text{DBS}^-$
solution with 365 nm light, \( \text{SP(NO}_2\text{)}_2 \) was partly reformed (Figure 5.8d) with no \( \text{SP(NO}_2\text{)}_2\text{H}^+\text{DBS}^- \) detected, supporting the rapid interconversion.

Finally, since \( \text{MCH}^+\text{DBS}^- \) was the only product found in the NMR spectrum by keeping the mixture of \( \text{SPCH}_2\text{CH}_2\text{OH} \) and DBSA in the dark for 12 h, an attempt was made to isolate the \( \text{MCH}^+\text{DBS}^- \). By mixing \( \text{SPCH}_2\text{CH}_2\text{OH} \) and DBSA (1:1, mol/mol) in toluene and keeping the mixture in the dark for more than 24 h, a yellow precipitate was obtained (Figure 5.9a), which was confirmed as \( \text{MCH}^+\text{DBS}^- \). The UV and NMR spectra of this product showed no difference from those of the 12 h old solution of SP and DBSA (Figure 5.9b-c).

This solid \( \text{MCH}^+\text{DBS}^- \) could be used to construct photoactive droplets. However, since this compound was not isolated until the end of this project, the droplets used for the bulk of this work were prepared by keeping the organic solution of \( \text{SPCH}_2\text{CH}_2\text{OH} \) and DBSA in dark for 12 h.
Figure 5.9 (a) Mixture of \( \text{SPCH}_2\text{CH}_2\text{OH} \) and DBSA (1:1.1, mol/mol) in toluene after 51 h in dark. A slightly excessive amount of DBSA was used to increase the conversion rate of \( \text{SPCH}_2\text{CH}_2\text{OH} \) to \( \text{MCH}^+\text{DBS}^- \). The yellow precipitate is \( \text{MCH}^+\text{DBS}^- \). (b) UV/Vis spectra of \( \text{MCH}^+\text{DBS}^- \) (5×10\(^{-5}\) M) in DCM immediately after preparation (black line) followed by 365 nm (red line) or 405 nm light illumination (blue line). (c) \(^1\)H NMR spectrum of \( \text{MCH}^+\text{DBS}^- \) (0.025 M) in CDCl\(_3\). The signals for the \( \text{MCH}^+ \) part and \( \text{DBS}^- \) were labelled as blue and green, respectively.

5.3 Photocontrolled motion of \( \text{MCH}^+\text{DBS}^- \) droplet

5.3.1 Composition of \( \text{MCH}^+\text{DBS}^- \) droplet

The \( \text{MCH}^+\text{DBS}^- \) droplet was composed of a 12 h old organic solution of \( \text{SPCH}_2\text{CH}_2\text{OH} \) (0.1 M) and DBSA (1:1, mol/mol). In addition, \( \text{SPCH}_3 \) and
\(\text{SP(NO}_2\text{)}_2\) also could be used to construct droplets by the reaction with DBSA in the dark for 36 h and 6 h, respectively. The resulting droplets are defined as \(\text{MCH}_3\text{CH}^+\text{DBS}^-\) and \(\text{MC(NO}_2\text{)}_2\text{H}^+\text{DBS}^-\). A wide range of organic solvents could be used to prepare \(\text{MCH}^+\text{DBS}^-\) droplets, including chloroform, dichloromethane, 1,2-dichoroethane, nitrobenzene and 1,2-dichlorobenzene. Importantly, if a droplet was prepared without \(\text{MCH}^+\text{DBS}^-\), no light-induced movement was observed, indicating that the photoactive material was essential for the movement.

It should be noted that this light-induced motion originated from an isothermal effect rather than thermocapillary effect, which was demonstrated by the fact that, if \(\text{MCH}^+\text{DBS}^-\) was replaced by an organic material, 2-[4-(dimethylamino)benzylidene]malononitrile (DMN), that had a similar absorption at around 430 nm to \(\text{MCH}^+\text{DBS}^-\) (Figure 5.10), no droplet motion was observed under 405 nm light illumination.\(^{32-34}\)

![Figure 5.10 UV/Vis spectrum of DMN in DCM (5x10^{-5} M) with a strong absorption at 432 nm.](image)

5.3.2  **Motion in aqueous solution containing surfactant**

5.3.2.1  **Controlled motion of \(\text{MCH}^+\text{DBS}^-\) droplets**

At first, an aqueous solution of surfactant SDBS (7 mM) and \(\text{CaCl}_2\) (0.4 mM) was used as the aqueous medium for droplet motion as previously used for \(\text{SPCH}_2\text{CH}_2\text{OH}\) droplets. The organic droplet was composed of \(\text{MCH}^+\text{DBS}^-\) (0.1 M) in DCE/PhCH\(_3\) (1:2, v/v). In contrast to \(\text{SPCH}_2\text{CH}_2\text{OH}\) droplets, which moved away from 365 nm light on the surface of SDBS and \(\text{CaCl}_2\) solution,
irradiation of a MCH+DBS− droplet on the same aqueous solution resulted in a motion towards 365 nm light (Figure 5.11a, Movie 5.1). Typically, the motion speed for a 2 μL MCH+DBS− droplet was 2.3 mm s⁻¹. The motion direction was changed with the illumination direction of the light.

Underwater movement was achieved as long as pure DCE was used as the droplet solvent (Figure 5.11b, Movie 5.2). Typically, for a MCH+DBS− (0.1 M) droplet made of DCE, it moved towards 365 nm light at a speed of 6.7 mm s⁻¹. It was found that the concentration of MCH+DBS− for the movement could be as low as 0.025 M. An obvious deformation of the droplet upon light irradiation was observed (Figure 5.11c, Movie 5.2).

![Figure 5.11 Illustration of the movement towards light of a MCH+DBS− droplet (a) on the surface of a surfactant solution or (b) under the solution following irradiation with 365 nm or 405 nm light. The red fluorescent plume that can be observed trailing the droplet is shown. (c) Shape change of a 5 μL MCH+DBS−/DCE droplet while it was moving towards 365 nm light. All the pictures was taken from Movie 5.2.](image)

Whether on or under water, the dark yellow MCH+DBS− droplet kept on moving towards 365 nm light until it ran out of “fuel” and the droplet became light yellow. For a DCE/PhCH₃ (1:2, v/v) droplet of MCH+DBS− (0.1 M) after it stopped moving under light illumination, the resulting yellow droplet became orange red if it was
left on the water surface in ambient light for about 20 minutes (Movie 5.3), indicating the formation of the MC species and the loss of acid in the droplet. This orange-red droplet moved away from 365 nm light and then towards 405 nm light (Movie 5.3), which was similar to the behaviour of the DCE/PhCH$_3$ (1:2, v/v) droplet of SPCH$_3$CH$_2$OH on the same solution (Chapter 4, Movie 4.2). This was probably because the majority of the water soluble DBSA (or DBS$^-$) was released from the droplet into the aqueous medium upon light irradiation with only neutral SPCH$_3$CH$_2$OH/MCCH$_2$CH$_2$OH left in the droplet. This will be discussed in section 5.5.1.

5.3.2.2 Self-motion of DBSA droplet

During the course of these MCH$^+$DBS$^-$ droplet experiments in the aqueous solution containing SDBS, slight self-motion was observed after light illumination. If the anionic surfactant SDBS was replaced by a cationic surfactant, cetylpyridinium chloride or cetyltrimethylammonium bromide (CTAB), self-motion occurred in a more significant way, even before light illumination. Typically, by adding a 2 µL DCE droplet of MCH$^+$DBS$^-$ (0.1 M) into the aqueous solution containing CTAB and CaCl$_2$, the MCH$^+$DBS$^-$ droplet immediately moved randomly on the bottom of the Petri dish with an obvious shape change, without light irradiation (Movie 5.4). Since no photoinduced reaction was involved in this process, the self-motion was likely not directly related to MCH$^+$DBS$^-$.

This was further confirmed by loading a droplet containing only DBSA into the same surfactant solution, which also resulted in a self-motion of the droplet (Movie 5.5). However, no locomotion of the DBSA droplet was observed without surfactant in the aqueous solution. These results suggested that the self-motion originated from the interaction between the two different types of surfactants on the droplet surface.

5.3.3 Motion in pure water

In order to avoid the self-motion of MCH$^+$DBS$^-$ droplet, deionised water (DI water) was used as the aqueous medium instead of surfactant solution. The droplet still moved towards the 365 nm or 405 nm light source along the beam and no
self-motion was found before or after light illumination. Tap water or sea water without surfactant also could be used instead of DI water and the photoinduced movement was not affected. The use of fresh water or sea water from natural sources suggested the possibility of emulating the phototaxis behaviour of living organisms in a natural environment.

A limitation was that the droplet could only move under water. As soon as the droplet contacted the water surface, it broke up. This was probably because the droplet was not stable at the water-air interface without surfactant in the aqueous phase.

5.3.3.1 Motion in 2D

The discovery that droplets could be moved in pure water, led to a study of how much the composition of the droplets could be varied. By using either DCE, chloroform or nitrobenzene as the solvent, the density of the MCH^+DBS^- droplet was much higher than that of water. As a result, the MCH^+DBS^- droplet stayed on the container bottom in DI water, as previously demonstrated for a surfactant-containing medium (Figure 5.11b), and it was able to move towards 365 nm or 405 nm light under water (Figure 5.12, Movie 5.6-5.7). A fluorescent plume trailing the droplet could be observed while it was moving towards the light source.

![Figure 5.12](image-url) Illustration of the movement towards light of a MCH^+DBS^- droplet under DI water following irradiation with 365 nm or 405 nm light. The red fluorescent plume that can be observed trailing the droplet is shown.

As can be seen from Table 5.1, the moving distance of a 2 µL MCH^+DBS^- droplet towards 365 nm light was 315 mm (Movie 5.6), higher than that towards 405 nm light (Movie 5.7). However, the average speed was the same, even though the
movement under 405 nm light had a much higher maximum speed, which was up to 15.8 mm/s.

**Table 5.1** Motion data of MCH\(^+\)DBS\(^-\), MCCH\(_3\)H\(^+\)DBS\(^-\) and MC(NO\(_2\))\(_2\)H\(^+\)DBS\(^-\) droplet in DI water under 365 nm/405 nm light illumination

<table>
<thead>
<tr>
<th>Droplet</th>
<th>Mole ratio of SP to DBSA</th>
<th>Distance of motion towards light source /mm</th>
<th>Average velocity /mm s(^{-1})</th>
<th>Maximum velocity /mm s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>365 nm 405 nm</td>
<td>365 nm 405 nm</td>
<td>365 nm 405 nm</td>
</tr>
<tr>
<td>MCH(^+)DBS(^-)</td>
<td>1:1</td>
<td>315 236</td>
<td>7.4 7.4</td>
<td>15.8 10</td>
</tr>
<tr>
<td>MCCH(_3)H(^+)DBS(^-)</td>
<td>1:1</td>
<td>44 45</td>
<td>4.7 6.3</td>
<td>6.3 12.5</td>
</tr>
<tr>
<td>MC(NO(_2))(_2)H(^+)DBS(^-)</td>
<td>1:1</td>
<td>45 283</td>
<td>0.4 5.8</td>
<td>0.9 8.5</td>
</tr>
<tr>
<td>MC(NO(_2))(_2)H(^+)DBS(^-)</td>
<td>1:2</td>
<td>277 678</td>
<td>3.1 9.8</td>
<td>6.4 15.4</td>
</tr>
</tbody>
</table>

For this 2D movement under DI water, nitrobenzene droplets composed of MCH\(_3\)CH\(^+\)DBS\(^-\) or MC(NO\(_2\))\(_2\)H\(^+\)DBS\(^-\) were also tried and both droplets moved towards 365 nm or 405 nm light source. For MCCH\(_3\)H\(^+\)DBS\(^-\) droplets (2 \(\mu\)L, 0.1 M), the length of movement under 365 nm light illumination (Movie 5.8) and 405 nm light illumination (Movie 5.9) was similar, both less than 50 mm, which was quite short. The average velocity was 6.3 mm/s under 405 nm light, slightly higher than that under 365 nm light. The movement under 405 nm light had a higher maximum speed, which was double than that under 365 nm light.

In contrast, the performance of MC(NO\(_2\))\(_2\)H\(^+\)DBS\(^-\) droplet under 405 nm light (Movie 5.10) was much better than that under 365 nm light (Movie 5.11). For a 2 \(\mu\)L MC(NO\(_2\))\(_2\)H\(^+\)DBS\(^-\) droplet (0.1 M, SP(NO\(_2\))\(_2\):DBSA = 1:1, mol/mol), movement was as far as 283 mm with an average speed of 5.8 mm/s under 405 nm light, and 45 mm with an average speed of 0.4 mm/s under 365 nm light. If the initial ratio of SP(NO\(_2\))\(_2\) (0.1 M) and DBSA was 1:2, the moving distance under 405 nm was 678 mm and the average speed was 9.8 mm/s (Movie 5.12). The maximum speed was up to 15.4 mm/s. The velocity and distance of movement under 365 nm light were also increased (Movie 5.13) compared with the MC(NO\(_2\))\(_2\)H\(^+\)DBS\(^-\) droplet with less DBSA (SP(NO\(_2\))\(_2\):DBSA = 1:1).

As has been demonstrated before, protonation of SP(NO\(_2\))\(_2\) with DBSA to generate MC(NO\(_2\))\(_2\)H\(^+\)DBS\(^-\) was relatively fast (Figure 5.8). As a result, the excess DBSA
that existed in the $\text{MC(NO}_2\text{)}_2\text{H}^+\text{DBS}^-\text{ droplet (SP(NO}_2\text{)}_2\text{DBSA = 1:2)}$ was able to protonate the (SP(NO$_2$)$_2$ and regenerate $\text{MC(NO}_2\text{)}_2\text{H}^+\text{DBS}^-\text{ immediately following irradiation of } \text{MC(NO}_2\text{)}_2\text{H}^+\text{DBS}^-\text{. In this way, the consumption of the photoactive } \text{MC(NO}_2\text{)}_2\text{H}^+\text{DBS}^-\text{ was reduced, resulting in the } \text{MC(NO}_2\text{)}_2\text{H}^+\text{DBS}^-\text{ droplet with excess DBSA moving further and faster.}

These results demonstrated that a variety of spiropyrans could be used to prepare MCH$^+$/surfactant salts and therefore construct photoactive droplets, which were able to move towards the light source in DI water. Enlightened by this, the droplet motion system could be easily extended by using a variety of spiropyrans.

Droplet movement in aqueous solutions with different pHs was also investigated. By moving MCH$^+\text{DBS}^-$ droplets in water with different pHs, obtained by the addition of specific amounts of HCl or NaOH, it was found that the pH tolerance of this droplet motion system was relatively high, from pH –0.3 to 11.0.

Other solvents with high densities like chloroform and 1,2-dichloroethane can also be used. It should be noted that the droplet got stuck easily on the glass surface if it was not properly cleaned. So all the glassware used, including the glass Petri dishes and glass slides, were treated with piranha solution.

5.3.3.2 Motion in 3D

The high stability of the MCH$^+\text{DBS}^-$ droplet under water opened the way for droplet movement in three dimensions (3D) by adjusting the density of the droplet to match that of water. Since Young et al. reported the 3D movement of small bubbles in pure liquids by the thermocapillary effect in 1959, efforts have been made to achieve total control over 3D movement.$^{35,36}$ In Young’s work, the bubbles could only be held stationary or driven downwards in the vertical direction.$^{12}$ In 1999, Hadland demonstrated similar thermocapillary migration but in the horizontal direction in reduced gravity.$^{36}$ However, the special condition creating reduced gravity, made its application difficult. In these reported cases of moving bubbles or droplets in 3D by the thermocapillary effect, a special cell had to be used to generate the proper temperature gradient and the motion direction could not be changed once the temperature gradient was generated.$^{35,36}$ These limitations make
challenging to achieve free control over the movement of droplets in liquid in 3D. In this current work, by simply using a portable light source like a laser pointer, the droplet containing MCH DBS could be moved in any desired direction in DI water. In this way, totally controlled 3D movement was achieved.

By using a mixture of nitrobenzene and toluene (1:1.9, v/v) to prepare the solution of MCH DBS, the resulting droplet had a similar density to water. This 2 µL droplet (1.56 mm in diameter) was moved up from the bottom of a 100×100×100 mm tank filled with DI water and then accurately into a narrow necked vial (6.25 mm diameter) mounted on the side of the tank by two 405 nm laser pointers fixed in the vertical direction and the horizontal direction respectively as shown in Figure 5.13 and Movie 5.14, in order to demonstrate the control of the movement. The speed for upward movement was 7.4 mm s⁻¹, while that for horizontal movement was 3.9 mm s⁻¹. The high accuracy of this light-guided 3D movement opens up an efficient way for directed transport in microfluidics.

Figure 5.13 Light-induced movement of a MCH DBS droplet (2 µL, indicated by white arrow) in a water tank filled with DI water: moving upwards (left), moving in horizontal direction (middle) and entering the narrow mouth of a vial mounted on the side of the tank (right). The droplet moved towards 405 nm light all the time and the illumination direction was indicated by a schematic of the laser.

Further investigation of the upward movement was carried out by using a video camera. As was demonstrated by the sequence of photos (Figure 5.14, Movie 5.15), the larger 10 µL MCH DBS droplet appeared spherical before light illumination and a deformation was observed at T = 62 ms upon light irradiation, due to the initial attachment of the droplet to the glass surface. However, after the droplet had left the bottom and continued moving up, the lower half of the spherical droplet was observed to be significantly compressed compared to the upper half (T = 134-
391 ms). This could be explained by the release of surfactant DBSA through the droplet/water interface of the non-illuminated area, below the lower half of the droplet. This compressed shape lasted for a short time even after the light was switched off (Figure 5.14b, T = 409 ms). Additionally, large and fast currents were observed clearly within the droplet while it was moving up (Figure 5.14b, T = 134-409 ms), due to the internal Marangoni convection flow that caused the droplet movement.

![Figure 5.14](image)

**Figure 5.14** Light-induced upward motion of a MCH-DBS^- droplet (10 µL): (a) schematic for the droplet motion experiment, (b) Sequence of photographs of the upward motion upon 405 nm light irradiation. The droplet appeared spherical at first (T= 0 ms). Then under 405 nm light illumination, the droplet left the bottom with an obvious deformation at T = 62 ms and moved up towards with a fusiform shape (T = 134-391 ms). Fast convective flows within the droplet were observed along with the upward movement. After the irradiation was removed (T = 409 ms), the droplet stopped moving up and became spherical again (T = 951 ms).

### 5.4 Characterisation of the system

The photoisomerisation of MCH-DBS^- and the generation and release of DBSA were found to be crucial to the controlled movement of MCH-DBS^- droplet. NMR spectroscopy as well as interfacial tension (IFT) and pH measurements were used to characterise this system.

#### 5.4.1 NMR spectroscopy

^1H NMR spectroscopy was used to show the composition change of the droplet and the aqueous solution with light illumination. A 0.1 M solution of MCH-DBS^-
(1:1, mol/mol) in CDCl$_3$ (100 µL) prepared from SPCH$_2$CH$_2$OH and DBSA (1:1, mol/mol) was either kept in the dark or illuminated by 365 nm light for 15 min, and the $^1$H NMR spectra of the organic and aqueous phases were then obtained, and the spectra are shown in Figure 5.15. As can be seen, after the MCH$^+$DBS$^-$ solution was kept under D$_2$O in the dark for 15 min, the ratio of MCH$^+$ and DBS$^-$ was still 1:1 (Figure 5.15a) and no signals for DBSA were detected in the aqueous phase (Figure 5.15c), indicating that MCH$^+$DBS was relatively stable at the CDCl$_3$/D$_2$O interface in the dark. However, if the MCH$^+$DBS$^-$/CDCl$_3$ solution under D$_2$O was irradiated by 365 nm light for 15 min, generation of spiropyran species in the organic layer were observed (Figure 5.15b). The two doublets at 6.80 and 6.96 ppm for SPCH$_2$CH$_2$OH were overlapped by other broadened signals (Figure 5.15b), which were likely from SPH$^+$DBS$^-$, as discussed in the previous section, suggesting that the spiropyran species were a mixture of SPCH$_2$CH$_2$OH and SPH$^+$DBS$^-$. This was further confirmed by the broadened doublet at 5.96 ppm (Figure 5.15b), which was assigned to the coalescence of the SPCH$_2$CH$_2$OH and SPH$^+$DBS$^-$ ethylenic protons (H3). The overlap of the signals of SPCH$_2$CH$_2$OH and SPH$^+$DBS$^-$ further confirmed their similarity in conformation. It should be noted that, compared to the spectrum of pure SPCH$_2$CH$_2$OH in CDCl$_3$ (Figure 5.2b), the downfield shift of the signals between 7.3 and 5.9 ppm for SPCH$_2$CH$_2$OH in this mixture was observed (Figure 5.15b), attributed to the presence in equilibrium of SPH$^+$DBS$^-$. Since the peaks for the two aromatic protons next to the sulphonate group in DBS$^-$ were seen between 7.87 and 7.75 ppm (Figure 5.15b), the ratio of the merocyanine/spiropyran species (including MCH$^+$, SPCH$_2$CH$_2$OH and the SPH$^+$ form) and DBS$^-$ after light illumination was calculated to be around 1.5:1 by integration, indicating the loss of DBSA (or DBS$^-$) from CDCl$_3$ into D$_2$O (Figure 5.15b). This was further confirmed by the $^1$H NMR spectrum of the aqueous layer after MCH$^+$DBS$^-$/CDCl$_3$ solution under D$_2$O was illuminated by 365 nm light for 15 min, which showed the signals for DBSA (Figure 5.15d).
Figure 5.15 Release of DBSA from the CDCl₃ solution of MCH⁺DBS⁻ (0.1 M) into D₂O investigated by ¹H NMR spectra. (a) Partial NMR of the CDCl₃ layer after the MCH⁺DBS⁻/CDCl₃ solution was kept under D₂O (1 mL) in a 2 mL glass vial in dark for 15 min. The CDCl₃ solution was diluted to 0.025 M with CDCl₃ prior to NMR measurement. (b) Partial NMR of the CDCl₃ layer after the MCH⁺DBS⁻/CDCl₃ solution under D₂O (1 mL) in a 2 mL glass vial was illuminated by 365 nm light for 15 min. The CDCl₃ solution was diluted to 0.025 M with CDCl₃ prior to NMR measurement. (c) Partial NMR of the D₂O layer after the MCH⁺DBS⁻/CDCl₃ solution was kept under D₂O (1 mL) in a 2 mL glass vial in dark for 15 min. (d) Partial NMR of the D₂O layer after the MCH⁺DBS⁻/CDCl₃ solution under D₂O (1 mL) in a 2 mL glass vial was illuminated by 365 nm light for 15 min.
It could be concluded that, as is shown in Figure 5.16, as soon as $\text{SPH}^+\text{DBS}^-\,$ generated at the CdCl$_3$/D$_2$O interface by photoinduced conversion of $\text{MCH}^+\text{DBS}^-\,$ under 365 nm light, the proton in $\text{SPH}^+$ was captured by H$_2$O and $\text{DBS}^-$ was therefore release into the water phase together with the proton, due to the relatively high solubility of DBSA in water; $\text{SPCH}_2\text{CH}_3\text{OH}$ remained in the droplet since it was nearly insoluble in water, consistent with the $^1$H NMR result (Figure 5.15b,d).

![Figure 5.16](image)

**Figure 5.16** Photoconversion of $\text{MCH}^+\text{DBS}^-$ to $\text{SPH}^+\text{DBS}^-$ under light illumination and the following hydrolysis of $\text{SPH}^+\text{DBS}^-$ in the presence of water to generate $\text{SPCH}_2\text{CH}_3\text{OH}$ and DBSA.

### 5.4.2 IFT measurements

#### 5.4.2.1 IFT measurements of $\text{MCH}^+\text{DBS}^-$ droplets

Because of the crucial role that IFT change played in droplet motion, the IFT measurements were carried out on a goniometer using the pendant drop method. However, at the concentration of 0.1 M, which was used for droplet motion, the $\text{MCH}^+\text{DBS}^-$/nitrobenzene droplet easily escaped from the tip of the needle and continued moving towards the light source, making it difficult to get an accurate value. This was due to the concentration of $\text{MCH}^+\text{DBS}^-$ being so high that too much surfactant (DBSA) was generated upon light irradiation, dramatically decreasing the IFT and making the droplet drop from the needle.

In order to keep the droplet on the needle during IFT measurement, the $\text{MCH}^+\text{DBS}^-$ solution was diluted to $2\times10^{-3}$ M with nitrobenzene. At this concentration, the IFT of the $\text{MCH}^+\text{DBS}^-$ droplet could be successfully measured and was initially 16.4 mN m$^{-1}$, decreasing by 4.2 mN m$^{-1}$ in 3 s upon 365 nm light illumination (Table 5.2). In contrast, the decrease in IFT was relatively small (0.3 mN m$^{-1}$) for an $\text{MCH}^+\text{DBS}^-$ droplet under the same conditions without
365 nm light irradiation, indicating that only a small amount of the free DBS$^-$$^-$ surfactant was generated and released into water.

A nitrobenzene droplet containing only DBSA started with a much lower IFT (8.7 mN m$^{-1}$) than for the MCH$^+$DBS$^-$$^-$ droplet and it decreased by about 1 mN m$^{-1}$ after 3 s with or without light irradiation (Table 5.2). The high solubility of DBSA in water made its release into the water phase a spontaneous process and not subject to light illumination. As a result, light had no effect on the IFT drop of the DBSA droplet.

Table 5.2 IFT of MCH$^+$DBS$^-$/nitrobenzene (2×10$^{-3}$ M) and DBSA/nitrobenzene (2×10$^{-3}$ M) using the pendant drop method in water with or without light illumination.

<table>
<thead>
<tr>
<th>Time</th>
<th>MCH$^+$DBS$^-$(2×10$^{-3}$ M)</th>
<th>DBSA (2×10$^{-3}$ M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0s</td>
<td>16.4 ± 0.1</td>
<td>8.7 ± 0.3</td>
</tr>
<tr>
<td>without 365 nm 3s</td>
<td>16.1 ± 0.1</td>
<td>7.3 ± 0.5</td>
</tr>
<tr>
<td>365 nm 3s</td>
<td>12.2 ± 0.1</td>
<td>7.6 ± 0.6</td>
</tr>
</tbody>
</table>

5.4.2.2 Surface tension measurement of the water phase

The released DBSA decreased the surface tension of the aqueous phase surrounding the droplet as well, which also helped the movement. After light illumination of the MCH$^+$DBS$^-$$^-$ droplet under water, the aqueous phase was collected and the surface tension was measure by pendant drop method in air (Table 5.3). After illumination of a 10 µL MCH$^+$DBS$^-$/nitrobenzene (0.1 M) droplet under water (1 mL) with 365 nm light for 10 min, the surface tension of the aqueous solution measured in air was about 31 mN/m lower than that of the same droplet experiment done without illumination (dark, Table 5.3). Under 405 nm light for 5 min, the surface tension decrease of the aqueous solution was about the same as for 365 nm (32 mN/m).

Table 5.3 Surface tension of the aqueous solution with or without light illumination.$^{[a]}$

<table>
<thead>
<tr>
<th>Condition</th>
<th>Time</th>
<th>AVG γ (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dark</td>
<td>10 min</td>
<td>71.0 ± 0.1</td>
</tr>
<tr>
<td>365nm light</td>
<td>10 min</td>
<td>40.3 ± 0.1</td>
</tr>
<tr>
<td>dark</td>
<td>5 min</td>
<td>71.3 ± 0.1</td>
</tr>
<tr>
<td>405nm light</td>
<td>5 min</td>
<td>39.2 ± 0.1</td>
</tr>
</tbody>
</table>

$^{[a]}$The MCH$^+$DBS$^-$/nitrobenzene (0.1 M) droplet is 10 µL and the aqueous solution is 1 mL.
5.4.3 pH measurement

DBSA is a strong acid and its release from the droplet into DI water upon light illumination can be monitored by pH changes. A standard curve of log[c] vs pH was obtained by measuring the pH values of DBSA aqueous solutions at difference concentrations (Figure 5.17). With this curve, the release of DBSA into the water phase could be readily calculated if pH of the solution was measured.

![Figure 5.17 Log[c] vs pH standard curve for DBSA solution.](image)

In order to perform this experiment, a 10 µL nitrobenzene droplet of DBSA with a concentration of 0.1 M, was placed in a 2 mL vial filled with DI water (1 mL) in the dark. The pH of the aqueous phase decreased from 5.4 to 3.26 in just 10 min (Table 5.4). As calculated from the standard curve in Figure 5.17, 82% of DBSA was released during this time period and this value changed little even after 24 h, suggesting that free DBSA in the droplet was released into the water phase quite fast. For a 10 µL MCH\(^{+}\)DBS\(^{-}\) droplet (0.1 M) under the same conditions, however, only 8.6% DBSA was released in 10 min and this value doubled to 17.9% after 24 h, indicating that MCH\(^{+}\)DBS\(^{-}\) is relatively stable in the dark and the automatic generation of free DBSA is slow (Table 5.4).
Table 5.4 Release of DBSA from a DBSA droplet (0.1 M, 10 µL) or a MCH\(^{+}\)DBS\(^{-}\) droplet (0.1 M, 10 µL) into water (1 mL) in the dark at room temperature.\(^{[a]}\)

<table>
<thead>
<tr>
<th>Time</th>
<th>DBSA droplet</th>
<th>MCH(^{+})DBS droplet</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>Concentration of DBSA in water (mM)(^{[a]})</td>
</tr>
<tr>
<td>10 min</td>
<td>3.25</td>
<td>0.815</td>
</tr>
<tr>
<td>30 min</td>
<td>3.25</td>
<td>0.829</td>
</tr>
<tr>
<td>1 h</td>
<td>3.25</td>
<td>0.829</td>
</tr>
<tr>
<td>2 h</td>
<td>3.25</td>
<td>0.829</td>
</tr>
<tr>
<td>24 h</td>
<td>3.26</td>
<td>0.815</td>
</tr>
</tbody>
</table>

\(^{[a]}\) pH of DI water was measured to be 5.40.

\(^{[b]}\) Concentration of DBSA in water was calculated from the standard curve in Figure 5.17.

\(^{[c]}\) If DBSA was completely released (DBSA released = 100%) from the droplet into the aqueous phase, the theoretical concentration of DBSA in water is 1 mM.

For a 10 µL MCH\(^{+}\)DBS\(^{-}\) droplet (0.1 M) placed under DI water (1 mL) in the dark for 10 min, irradiation with 365 nm light was able to release 76.4% of DBSA into the water phase in 10 min. If 405 nm light was used instead of 365 nm light, 77.6% of DBSA was released from the MCH\(^{+}\)DBS\(^{-}\) droplet in 5 min (Table 5.5). Light illumination converted MCH\(^{+}\)DBS\(^{-}\) into the SP form and free DBSA in a short time, thus making the release similar to that of a droplet containing DBSA.

Table 5.5 Release of DBSA from a 10 min dark aged MCH\(^{+}\)DBS\(^{-}\) droplet (0.1 M, 10 µL) into water (1 mL) before and after 365 nm or 405 nm light illumination at room temperature.\(^{[a]}\)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>pH</th>
<th>Concentration of DBSA in water/mM(^{[b]})</th>
<th>DBSA released(^{[c]})</th>
</tr>
</thead>
<tbody>
<tr>
<td>dark (10 min)</td>
<td>4.55</td>
<td>0.104</td>
<td>9.9%</td>
</tr>
<tr>
<td>365 nm light (10 min)</td>
<td>3.30</td>
<td>0.764</td>
<td>76.4%</td>
</tr>
<tr>
<td>405 nm light (5 min)</td>
<td>3.29</td>
<td>0.776</td>
<td>77.6%</td>
</tr>
</tbody>
</table>

\(^{[a]}\) pH of DI water was measured to be 5.40.

\(^{[b]}\) Concentration of DBSA in water was calculated from the standard curve in Figure 5.17.

\(^{[c]}\) If DBSA was completely released (DBSA released = 100%) from the droplet into the aqueous phase, the theoretical concentration of DBSA in water is 1 mM.
In order to visualise the pH change of the aqueous solution around the droplet, a pH indicator, the sodium salt of bromophenol blue (BPB), was used to indicate the release of DBSA. The aqueous solution of BPB appears purple at pH above 4.6 and yellow at pH below 3.0. When a MCH\(^{+}\)DBS\(^{-}\) droplet was moved with light in the aqueous solution of BPB, the release of strongly acidic DBSA changed the pH of the water phase surrounding the droplet to below 3.0, which was able to be visualised by the yellow colour (Movie 5.16). As is indicated by the yellow colour in Figure 5.18, DBSA was released into water from the non-illuminated side of the droplet, in accordance with the result from the 3D experiment where an obvious deformation was observed on the non-illuminated side of the upward moving droplet due to DBSA release.

![Figure 5.18](image)

**Figure 5.18** Light-induced release of DBSA from a MCH\(^{+}\)DBS\(^{-}\) droplet (2 µL, 0.1 M) indicated by the pH indicator BPB (0.002 wt.%) in water: (a) The aqueous solution was purple and almost no yellow colour was observed around the droplet without 405 nm light illumination; (b) under 405 nm light illumination (indicated by white broad arrow), a plume of DBSA with yellow colour was observed in the aqueous solution around the non-illuminated side of the droplet; (c) the low pH trajectory was visualised by the yellow colour following the light-induced movement.
5.5 Mechanism

5.5.1 Marangoni effect

As demonstrated previously by Maass et al. and other researchers, and discussed for SPCH₂CH₂OH droplets in Section 4.5 (Chapter 4), the Marangoni effect initiated by IFT change plays an important role in droplet motion driven by chemical or photochemical reactions.³⁻³⁹ Light (365 nm or 405 nm) irradiation of the MCH⁺DBS⁻ droplet converted MCH⁺DBS⁻ to SPH⁺DBS⁻, which underwent deprotonation to give SPCH₂CH₂OH and the surfactant DBSA. As a result, the IFT of the illuminated area decreased (Figure 5.19). The Marangoni external flow on the droplet surface directed to the area of high IFT (non-illuminated part), formed on the droplet surface (Figure 5.19).³⁻³⁹ The resulting DBSA in the illuminated area was transferred along with the flow on the droplet surface to the non-illuminated area and then released into water (Figure 5.19). The direction of the internal convective flow was towards the illuminated area. The droplet moved in the same direction as the internal convection, towards the light source. The droplet stopped moving when the “fuel”, MCH⁺DBS⁻, ran out or its concentration became too low to provide sufficient IFT change. This mechanism is similar to that of the photocontrolled motion of SPCH₂CH₂OH droplets in DI water, which also moved towards the 365 nm light source. The difference between them is the source of IFT decrease. For the SPCH₂CH₂OH droplet, isomerisation of SPCH₂CH₂OH to MCCH₂CH₂OH under 365 nm light is accompanied by an IFT decrease since the MC form is more surface active than the SP form. No surfactant is involved in this process. However, when it comes to MCH⁺DBS⁻ droplet, photoconversion of MCH⁺DBS⁻ and the following generation of DBSA dominants IFT decrease. As can be seen from Table 5.2, the change in IFT is 4.2 mN m⁻¹ for a MCH⁺DBS⁻ droplet irradiated for 3 s at 365 nm in DI water. In contrast, the change in IFT for a SPCH₂CH₂OH droplet irradiated for ~3 s at 365 nm in DI water is <2 mN m⁻¹ (Figure 4.18). In the latter case, the concentration of SPCH₂CH₂OH was 50 times greater making the IFT differences between the 2 systems likely much greater just double. Therefore, the IFT decrease on MCH⁺DBS⁻ droplets would be dominated by the generation of DBSA rather than the conformation change between the merocyanine and the spiropyran species.
Figure 5.19 (a) IFT decrease generated by the photoconversion from $\text{MCH}^+\text{DBS}^-$ to $\text{SPH}^+\text{DBS}^-$ and the following deprotonation at the droplet/water interface with the formation of surfactant DBSA. (b) Illustration of a droplet moving towards 365 or 405 nm light by Marangoni flow (blue arrows) in DI water as a result of the photoisomerisation and the following formation of surfactant DBSA generating a Marangoni internal convection (red arrows).

Carbon powder was used to show the flows both on the surface of $\text{MCH}^+\text{DBS}^-$ droplets and in the aqueous phase under light illumination. Upon light 365 nm light irradiation, the carbon powder (in micrometre scale) on the droplet surface was pushed to the non-illuminated area (Figure 5.20, Movie 5.17), indicating that the direction of the Marangoni flow on the droplet surface is towards the non-illuminated area. The droplet moved in the opposite direction, which was towards the illumination direction.

Figure 5.20 Movement of carbon particles on the surface of a $\text{MCH}^+\text{DBS}^-$ droplet (2 µL, 0.1 M) as well as in the water phase with or without 365 nm light illumination. (a) The particles were dispersed on the droplet surface at first. (b) Then under 365 nm light illumination (indicated by white arrow), all the particles moved to the non-illuminated side while the droplet moved towards the light source. (c) When the illumination direction was changed, the particles remained at the non-
5.5.2 Estimation of interfacial tension change

As has been demonstrated by Maass et al., the IFT gradient (\(\nabla \gamma\)) for swimming droplets with a radius \(R\) driven by chemical reactions can be estimated.\(^3,40\) For our photodriven MCH\(^+\)DBS\(^-\) droplet, the velocity of droplet motion (\(v\)) and that of the Marangoni surface flow can be viewed as in the same order of magnitude, even though the latter is faster than the former. In this case, \(4\pi R^2 v \nabla \gamma\) can be used to present the energy dissipation generated by the interfacial flow, which should equal to the dissipation from viscous friction \(F_v v\), that is, \(4\pi R^2 v \nabla \gamma = F_v v\).\(^3,40\) Thus \(F_v = 4\pi R^2 \nabla \gamma\) (1)

where \(F_v\) is the Stokes drag force for a small soft sphere moving through a fluid as described in Equation (2).\(^3\)

\[ F_v = 5\pi R \eta v \quad (2) \]

where \(\eta\) is the viscosity of water surrounding the droplet which is \(10^{-3}\) Pa s.

From Equations (1) and (2), the IFT gradient \(\nabla \gamma\) can be calculated as

\[ \nabla \gamma = \frac{5\eta v}{4R} \quad (3) \]

The IFT change (\(\Delta \gamma\)) across the droplet length (2R) can be estimated as

\[ \Delta \gamma = 2R \nabla \gamma = \frac{5\eta v}{2} \quad (4) \]

It can be estimated from Equation (4) that the theoretically IFT change needed to achieve a droplet velocity of 15.8 mm s\(^{-1}\) in our case is \(\Delta \gamma \approx 0.04\) mN m\(^{-1}\), which is much smaller than the measured value (4.2 mN m\(^{-1}\) from Table 5.2).

5.5.3 Measurement of the force generated by interfacial tension change

In order to gain some insight into the magnitude of forces required to drive the droplet motion, measurement of the forces associated with the initial motion was explored. When the droplet moves up under light illumination in DI water, four forces are involved, that is, gravity (\(G\)), buoyancy (\(F_b\)), viscous force (\(F_v\)) and the
driving force provided by light-induced IFT change ($F_i$) (Figure 5.21). If the droplet moves up at a steady speed, the four forces are in balance, that is,

$$F_i + F_b = G + F_v$$  

(5)

![Figure 5.21](image_url) Force analysis for a MCH+DBS− droplet moving up in DI water under light illumination.

The equation for the force of gravity is

$$G = m_d \, g = \rho_d \, V_d \, g = \frac{4}{3} \pi R^3 \, \rho_d \, g$$  

(6)

where $m_d$ is the mass of the droplet, $R$ is the droplet radius, $\rho_d$ is the density of the droplet, $V_d$ is the volume of the droplet and $g$ is gravitational acceleration with a value of 9.8 m s$^{-2}$.

If the droplet is immersed in water, the buoyant force can be calculated using Equation (7).

$$F_b = \rho_w \, V_d \, g = \frac{4}{3} \pi R^3 \, \rho_w \, g$$  

(7)

where $\rho_w$ is the density of DI water, which is 0.9982 g/mL.

From Equations (2), (5), (6) and (7), the driving force provided by IFT change can be written as

$$F_i = G + F_v - F_b = \frac{4}{3} \pi R^3 \, (\rho_d - \rho_w) \, g + 5 \pi \eta v$$  

(8)
In an optimised condition, if the droplet suspends in water under light illumination, that is, \( v = 0 \), Equation (8) can be simplified as

\[
F_l = \frac{4}{3} \pi R^3 (\rho_d - \rho_w) g 
\]  

(9)

To measure the driving force, a series of MCH\(^{+}\)DBS\(^{-}\) droplets with certain volumes were prepared and moved up in a cuvette filled with DI water by a 405 nm light laser. The droplets are composed of MCH\(^{+}\)DBS\(^{-}\) (0.1 M) in the mixed solvent of nitrobenzene and toluene (1:1.6, v/v) with a density of 1.023 g/mL. The power of this 405 nm laser pointer was 2.7 mW measured by a digital optical power and energy meter (PM100D, Thorlabs) equipped with a sim photodiode power sensor (S103C, Thorlabs). The size of the laser beam was around 2.5×1.5 mm.

It was found that a droplet with a diameter of 1.03 mm (\( R = 0.515 \) mm) was able to be suspended in DI water under irradiation of the 405 nm laser (2.7 mW) for 60 s until the fuel ran out (Movie 5.18). In this optimised case, the driving force provided by light-induced IFT change (\( F_l \)) could be readily calculated by Equation (9), giving 0.14 \( \mu \)N. This is similar to the 0.1 \( \mu \)N force estimated by Faris and his coworkers to move a somewhat smaller droplet (0.1 mm diameter) at about the same speed (3 mm s\(^{-1}\)).\(^{41}\)

### 5.6 Summary

In this chapter, a photoactive MCH\(^{+}\)DBS\(^{-}\) salt was prepared by protonating spiropyran with a strongly acidic surfactant DBSA. MCH\(^{+}\)DBS\(^{-}\) could undergo photoisomerisation to regenerate spiropyran species. Movement of organic droplets containing MCH\(^{+}\)DBS\(^{-}\) in DI water was realised. The MCH\(^{+}\)DBS\(^{-}\) droplet was able to move towards the light source (365nm, 405 nm or visible light) as a result of a light-induced isothermal decrease in interfacial tension (Marangoni flow), which originated from the photoconversion from MCH\(^{+}\)DBS\(^{-}\) to SPH\(^{+}\)DBS\(^{-}\) and the following generation of DBSA at the organic/water interface. The droplet could be produced from a range of solvents and and moved in 2D or 3D under water with a velocity of up to 15.8 mm s\(^{-1}\) and a distance of up to 678 mm towards the
irradiation source. Droplet motion could be achieved in a wide range of acidic solutions from pH ~0.3 to 11.0. Mechanistic studies showed that the Marangoni flow, initiated by a IFT decrease resulting from the photoinduced generation of the surfactant DBSA, played a crucial role in the light-controlled movement. The force provided by light illumination was measured by moving the droplet up towards the light source in 3D, which was in the order of nN to µN in our case. The demonstrated controllability, high velocity and relatively long distance of movement hold the promise of developing advanced droplet motion systems for cargo transport, drug delivery and biological emulation.

5.7 References


Chapter 6 Moving photoactive water droplets containing merocyanine-sulphonic acid in fatty alcohols

6.1 Introduction

Moving water droplets through another immiscible liquid in a controlled fashion provides an alternative way to emulate the biological transport and motion processes in Nature.\textsuperscript{1-3} In recent years, many different types of active drops have been developed to perform life-like processes like chemotaxis\textsuperscript{4,5} and phototaxis\textsuperscript{6,7}, as well as intelligent tasks such as maze solving.\textsuperscript{8} The droplet motion in these cases depends on Marangoni flow, which is generated by tension gradients as a result of the external stimulus including chemicals, temperature, electric field and light.\textsuperscript{1,2,9,10} In previous chapters, a series of photoactive organic droplets were developed and moved in water with light. These organic droplets were able to be “pulled” or “pushed” by light on or under water in 2 or 3 dimensions and used as cargo to transport chemical species to perform reactions at a desired location.

However, since the majority of chemical and biological reactions relate to life activities take place in water, it is of significance to develop a reverse system, moving water droplets in organic phases. It has been reported that water droplets separated by an organic medium are ideal platforms to investigate biological processes,\textsuperscript{3} for example, antibody formation of single cells,\textsuperscript{11} activity of individual enzyme molecules\textsuperscript{12} and the polymerase chain reaction.\textsuperscript{13} The ability to move water droplets in organic media makes it possible to perform these complex tasks in a transport process, thus making the droplet capable of bioprocesses In 2005, Faris and co-workers moved a water droplet containing an enzyme to another droplet under 1-decanol by light to complete enzymatic reactions.\textsuperscript{14} In their work, the droplet was moved away from light due to photoinduced thermal heating producing interfacial tension (IFT) gradients. A complicated laser heating system was applied to keep the laser beam just across the trailing edge of the droplet all the time.\textsuperscript{14}

In previous chapters (Chapters 4 and 5), the manipulation of organic droplets in water (oil-in-water) with light was realised by using organic soluble
spiropyrans/merocyanines in the droplet. By using the same, or similar principles, photocontrolled motion of water droplets in organic media (water-in-oil) could potentially be realised if a water soluble spiropyran/merocyanine species was used. Since the photoactive material would be placed in the droplet, the light-induced movement would be based on the change of droplet rather than the environment and, therefore, better control of the motion would be realised with no need of the complicated photothermal control than had been used previously by Faris et al.\textsuperscript{14}

6.2 Photochromism of sodium sulphonate-substituted merocyaninesulphonic acid

In Chapter 3, a variety of merocyaninesulphonic acids were synthesised and characterised. Most of these merocyaninesulphonic acids had a relatively low solubility (< 1 mM) in water, which limited their application in droplet motion systems. However, as discussed in Chapter 3 and previously reported by Moldenhauer et al.,\textsuperscript{15} the introduction of a sodium sulphonate substitution increased the solubility to 0.2 M, making it possible to construct droplet motion systems. The photochromic properties of this sodium sulphonate-substituted merocyaninesulphonic acid (MC\textsubscript{8}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−}) in water were described in Chapter 3 but will be reviewed here for clarity. The \textsuperscript{1}H NMR spectra in both DMSO and water are discussed in detail below along with IFT measurements.

This sulphonic acid merocyanine, MC\textsubscript{8}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−}, can undergo reversible photoismerisation between the ring-opened MC and ring-closed SP forms (Figure 6.1a), which can be seen in the change in the UV/Vis spectra (Figure 6.1b). The compound was in the ring-opened form upon dissolving in water with a characteristic absorption at 432 nm for protonated merocyanine (MCH\textsuperscript{+}). Under 365 nm or 405 nm light illumination, it converted to the ring-closed spiropyran (SP\textsubscript{8}SO\textsubscript{3}H) with absorptions at 226 and 300 nm (Figure 6.1b).\textsuperscript{7,16,17} The resulting SP isomerised back to MC\textsubscript{8}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−} within 2 h in dark (Figure 6.1b).
Figure 6.1 (a) Photoinduced conversion between the MC and SP forms of $\text{MC}_8\text{H}^+\text{SO}_3^-$. (b) UV/Vis spectra of the freshly prepared aqueous solution of $\text{MC}_8\text{H}^+\text{SO}_3^- (3\times10^{-5} \text{ M})$ showing the initial characteristic absorption of $\text{MCH}^+$ at 432 nm (black line), followed by irradiation with 365 nm or 405 nm light for 5 seconds (red line), and then in the dark for 2 h.

Due to the high solubility of $\text{MC}_8\text{H}^+\text{SO}_3^-$ in dimethyl sulphoxide (DMSO) or water, its NMR spectrum in deuterated DMSO (DMSO-$d_6$) or deuterated water (D$_2$O) was obtained (Figure 6.2). Upon dissolving in DMSO-$d_6$, it existed in the ring-opened protonated merocyanine form, which was evidenced by the singlet at 1.79 ppm for the gem-dimethyl group and the two doublets at 8.54 and 7.91 ppm with a coupling constant of 16.2 Hz for the trans ethylenic bond in the $^1\text{H}$ NMR spectrum (Figure 6.2a). The slightly broadened singlet for the phenolic hydroxyl group at 11.40 ppm indicated that the proton was associated. The $^1\text{H}$ NMR spectrum in D$_2$O was similar, even though most aromatic proton signals overlapped between 7.6-8.0 ppm (Figure 6.2b, red line). The singlet for the gem-dimethyl group at 1.79 ppm was observed, indicating the ring-opened structure. The singlet for the phenolic hydroxyl group was not seen, due to H-D exchange. Upon 405 nm light irradiation, the ring-opened
structure partly isomerised to the ring-closed SP form, as evidenced by the newly generated signals (*) for spiropyran in Figure 6.2b (blue line).

Figure 6.2 (a) $^1$H NMR spectra of $\text{MC}_8\text{H}^+\text{SO}_3^-$ in DMSO-$d_6$ (0.025 M). (b) $^1$H NMR spectra of $\text{MC}_8\text{H}^+\text{SO}_3^-$ in D$_2$O after preparation (red line), followed by 405 nm light illumination for 10 min (blue line). The signals for $\text{SP}_8\text{SO}_3\text{H}$ generated by 405 nm light irradiation are indicated by asterisk.
It has been reported that the photoisomerisation between the merocyanine and spiropyran form causes a significant change in the hydrophilic/hydrophobic nature of the substance. As a result, the surface-activity of spiropyran/merocyanine species is also sensitive to light.\textsuperscript{18,19} Pendant drop measurements were undertaken to determine the change in IFT on photoisomerisation. An IFT decrease of around 1.3 mN m\textsuperscript{−1} in 13 s accompanied the 405 nm light illumination of a MC\textsubscript{8}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−}/H\textsubscript{2}O (0.2 M) droplet in hexanol, indicating that the light generated SP\textsubscript{8}SO\textsubscript{3}H had a lower IFT than MC\textsubscript{8}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−} (Figure 6.3a). Almost no change in IFT of MC\textsubscript{8}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−}/H\textsubscript{2}O in hexanol was observed without irradiation over the same time period (Figure 6.3a).

Maass et al. have estimated that changes in IFT of only 1 mN m\textsuperscript{−1} across 100 µm diameter droplets are required for rapid droplet movement. Thus, the IFT change achieved under light illumination is sufficient to generate movement of a droplet. It is worthy of note that the IFT of a water droplet in hexanol was 2.8 mN m\textsuperscript{−1} higher than that of the 0.2 M MC\textsubscript{8}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−}/H\textsubscript{2}O droplet in hexanol indicating that MC\textsubscript{8}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−} itself was a poor surfactant since a surfactant would have a significant effect on the IFT at a much lower concentration.

\textbf{Figure 6.3} IFT measured by the pendant drop method for MC\textsubscript{8}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−}/H\textsubscript{2}O droplet (0.2 M) (a) in 1-hexanol without 405 nm light illumination (red line) and with 405 nm light illumination from 21 s (black line), and (b) in cyclohexanol without 405 nm light illumination (red line) and with 405 nm light illumination from 12 s (black line). Curves in (a) and (b) were smoothed by adjacent averaging of 10 points and 4 points respectively.

Similar IFT measurements were also carried out in cyclohexanol. A smaller IFT decrease of around 0.3 mN m\textsuperscript{−1} (from 1.1 to 0.8 mN m\textsuperscript{−1}) for the MC\textsubscript{8}H\textsuperscript{+}SO\textsubscript{3}\textsuperscript{−}/H\textsubscript{2}O (0.2 M) droplet in cyclohexanol was observed over 4 s of 405 nm light irradiation (Figure 6.3b). The IFT of a pure water droplet in cyclohexanol was 2.63 mN m\textsuperscript{−1},
significantly lower than for hexanol. Therefore, the smaller IFT decrease for the photoactive droplet in cyclohexanol is consistent with the hexanol results.

6.3 Motion in 2D

Based on the ability of $\text{MC}_8\text{H}^+\text{SO}_3^-$ to change IFT under light illumination, we created photoactive water droplets by dissolving this compound in deionised (DI) water (0.2 M). The surrounding organic media tested were fatty alcohols: 1-hexanol, 1-octanol, 1-decanol and cyclohexanol, a class of compounds mostly existing in nature with low toxicity and relatively high boiling points. All the fatty alcohols were saturated with water prior to use to avoid the dissolution of the water droplet. Typically, introduction of a 2 µL (1.6 mm diameter) $\text{MC}_8\text{H}^+\text{SO}_3^-/\text{H}_2\text{O}$ droplet on the bottom of a polystyrene Petri dish filled with hexanol and irradiation of the droplet with a 405 light source from one side led to the droplet moving straight towards the light as depicted in Figure 6.4a-b and Movie 6.1. The droplet moved as far as 52 mm towards 405 nm light with an average velocity of 3.3 mm/s. The maximum velocity could be up to 7 mm/s. The movement stopped immediately when the laser was switched off. The size of the droplets could range from less than 0.1 mm to as large as 4.7 mm (30 µL) in diameter. Above this, the droplets stuck to the plastic surface and were not able to be moved. The concentration of $\text{MC}_8\text{H}^+\text{SO}_3^-$ could be as low as 0.02 M. At this concentration, the distance a 2 µL $\text{MC}_8\text{H}^+\text{SO}_3^-/\text{H}_2\text{O}$ droplet moved very slowly was only 2 mm. Since the droplet moved towards the light beam, the motion direction could be simply controlled by changing the direction of the laser irradiation (Movie 6.2). No light-induced movement was observed if the droplet was prepared without $\text{MC}_8\text{H}^+\text{SO}_3^-$. In order to determine whether this light-induced motion originated from an isothermal (chromocapillary) effect rather than thermocapillary effect, the photoactive $\text{MC}_8\text{H}^+\text{SO}_3^-$ was replaced with a non-photoactive dye, 2-[4-(dimethylamino)benzylidene]malononitrile (DMN), which also had an absorption around 430 nm. No motion of an aqueous DMN droplet was observed using 405 nm light illumination proving the process was purely isothermal and light-driven. It should be noted that in contrast to previous work in which aqueous
droplets move away from the light source by way of a thermocapillary effect in an organic medium,14,23 our photoactive droplets move towards light.

While the droplet was moving, a light blue fluorescent plume was observed trailing the droplet (Figure 6.4b). The plume was characterised by fluorescence spectroscopy and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry. While moving a 2 µL MC₈H⁺SO₃⁻/H₂O droplet in hexanol with 405 nm light, some of the hexanol solution containing the plume was collected and the fluorescent emission was measured with an excitation wavelength of 405 nm. A strong emission centered at 510 nm was observed in the fluorescence spectrum (Figure 6.4c), which was assigned to MCH⁺ according to previous reports,24,25 indicating the release of the photoactive material MC₈H⁺SO₃⁻ to the surrounding medium. This was further confirmed by the negative ion MALDI-TOF MS spectrum of the plume, which showed m/z peaks at 486.2 and 464.3 for [M−H]⁻ and [M−Na]⁻, respectively (Figure 6.4d).

![Figure 6.4](image)

**Figure 6.4** (a) Illustration of the movement towards light of a 2 µL MC₈H⁺SO₃⁻/H₂O droplet under 1-hexanol following irradiation with 365 or 405 nm light. (b) The light blue fluorescent plume that can be observed trailing the moving droplet under 405 nm light illumination. The white arrow indicates the light illumination direction. The picture was taken from Movie 6.1. (c) Fluorescence spectra of the plume generated by moving MC₈H⁺SO₃⁻ droplets in hexanol (excitation wavelength: 405 nm). (d) Negative ion MALDI-TOF MS spectrum for the plume generated by moving MC₈H⁺SO₃⁻ droplets in hexanol.
6.4 Motion in 3D

By using cyclohexanol, whose density is close to water, as the bulk medium, 3D movement of the $\text{MC}_8\text{H}^+\text{SO}_3^-/\text{H}_2\text{O}$ droplet was achieved. A $\text{MC}_8\text{H}^+\text{SO}_3^-/\text{H}_2\text{O}$ droplet (0.58 µL, 0.2 M) with a density of 1.0547 g/mL stayed on at the bottom of a plastic cuvette filled with water saturated cyclohexanol, which had a slightly lower density (0.9624 g/mL) than the droplet. Upon 405 nm light irradiation from the upward direction, the droplet moved towards the light source along the beam as indicated in Figure 6.5 and Movie 6.3. The motion distance was just 2.9 mm and the maximum speed was 3.4 mm/s.

![Image](image_url)

Figure 6.5 (a) Schematic for upward movement of a $\text{MC}_8\text{H}^+\text{SO}_3^-/\text{H}_2\text{O}$ droplet in cyclohexanol generated by 405 nm light illumination. (b) 3D movement of a 0.58 µL $\text{MC}_8\text{H}^+\text{SO}_3^-/\text{H}_2\text{O}$ droplet (0.2 M) up towards 405 nm light in cyclohexanol. All the photos were taken from Movie 6.3.

6.5 Mechanism

As discussed in Sections 4.5 (Chapter 4) and 5.5 (Chapter 5), the Marangoni flow, initiated by an IFT gradient, plays a crucial role in droplet motion through an immiscible liquid. Light illumination decreased the IFT on the droplet surface by converting $\text{MC}_8\text{H}^+\text{SO}_3^-$ (high $\gamma$) to $\text{SP}_8\text{SO}_3\text{H}$ (low $\gamma$), thus initiating Marangoni stress directed towards the high IFT area (non-illuminated area) as well as an internal convection towards the light source through the centre of the droplet to create a positive feedback loop, causing droplet movement in the same direction as the internal convection, towards the light (Figure 6.6a). A high-speed camera was used to capture the photoinduced convective flow within the droplet, which could be visualised because of the precipitated $\text{MC}_8\text{H}^+\text{SO}_3^-$ particles that resulted...
from the high droplet concentration. In order to clearly observe the Marangoni flow, the droplet was kept stationary under light illumination by increasing its size to 5 μL and decreasing the illumination time to seconds. A 405 nm laser was used to irradiate the MC₈H⁺SO₃⁻/H₂O droplet in hexanol from three different directions separately (Figure 6.6b). As can be seen from two of the three videos, the internal Marangoni convection flow was directed towards the point of illumination (low γ) through the droplet (Figure 6.6c-d, Movie 6.4-6.5). In the third case, slight movement of the droplet caused droplet asymmetry, which appears to have affected the Marangoni convection direction (Figure 6.6e, Movie 6.6). Nonetheless, this movie highlights the significant convection flows generated within the droplet on irradiation.

![Figure 6.6](image)

**Figure 6.6** (a) Illustration of the MC₈H⁺SO₃⁻/H₂O droplet movement by Marangoni flow. The flow fields inside and outside the droplet are represented by the red and blue lines, respectively. (b) Schematic of apparatus used to capture internal Marangoni convection in a 5 μL MC₈H⁺SO₃⁻/H₂O droplet under 405 nm light illumination. The camera was fixed in the x direction to take videos when the droplet was illuminated by the 405 nm laser from the x, y or z directions as indicated by the purple arrows. (c) Internal convection indicated by white arrows when the 5 μL MC₈H⁺SO₃⁻/H₂O droplet was illuminated (purple spot) from the x direction. (d) Internal convection indicated by white arrows when droplet was illuminated (purple spot) from the y direction. (e) Internal convection indicated by white arrows when droplet was illuminated (purple spot) from z direction. Movement of the droplet towards the light caused distortion of the Marangoni current. The photographs in (c) to (e) were taken from Movies 6.4, 6.5 and 6.6, respectively.
Given the observed advection of photoisomer during the movement of the \( \text{MC}_8 \text{H}^+\text{SO}_3^-/\text{H}_2\text{O} \) droplet, the question arose as to what contribution this made to the droplet motion. Advection of material from the surface of the droplet clearly occurred as can be seen in the movie of 3D motion (Movie 6.3). However, the speed of the droplets did not appear to be correlated to the size of the resulting droplet plume. Advective transport of a chemical specie from inside a droplet to its surface has been included as part of the modelling of the mechanism of the motion of self-propelled droplets utilizing chemical reactions.\(^{10,27-29}\) This same process likely contributes to the mechanism of movement for the droplets described here.

### 6.6 Calculation of the driving force provided by IFT change

In order to gain some insight into the magnitude of forces required to drive the droplet motion, we undertook to measure the forces associated with the initial motion. The driving force originates from the photoinduced IFT change that occurs following initial light irradiation. The 3D movement of the \( \text{MC}_8 \text{H}^+\text{SO}_3^- \) droplet in cyclohexanol provided a simple model for the force calculation, since the forces involved in this upward movement could be simplified to buoyancy, gravity and the Stokes drag force, along with the photoinduced driving force. Cyclohexanol was used to provide droplet buoyancy.

In the previous Chapter (Section 5.5.3), the \( \text{MCH}^+\text{DBS}^- \) organic droplet with a specific size could be suspended in DI water for 60 s by light irradiation. Since this droplet was in equilibrium, the irradiation force was readily calculated by the difference of gravity and buoyancy based on the droplet size. However, for \( \text{MC}_8 \text{H}^+\text{SO}_3^-/\text{H}_2\text{O} \) droplet in this case, the time and distance of the motion under light illumination were relatively short, making it difficult for the droplet to reach the equilibrium state. As a consequence, the calculation of irradiation force required a more detailed force analysis.

For a \( \text{MC}_8 \text{H}^+\text{SO}_3^-/\text{H}_2\text{O} \) droplet moving up towards 405 nm light source in cyclohexanol, according to Newton’s second law:

\[
\sum F = \frac{dp}{dt}
\]  

(1)
with $F$ the forces applied to the droplet and $p$ the momentum of the droplet of mass $m$ and moving with velocity $v$.

$$p = mv$$

(2)

$$\sum F = F_i + F_b - G - F_v$$

(3)

where $F_i$ is the force provided by light-induced IFT change, $F_b$ is buoyancy, $G$ is gravity and $F_v$ is the Stokes’ drag force (Figure 6.7).

![Figure 6.7 Force analysis for a MC₆H₄SO₃/H₂O droplet moving up in cyclohexanol under light illumination.](image)

According to Equations (1), (2) and (3)

$$F_i = G + F_v - F_b + m \frac{dv}{dt}$$

(4)

The equation for gravity is

$$G = m_d g = \rho_d V_d g$$

(5)

where $m_d$ is the mass of the droplet, $\rho_d$ is the density of the droplet (1.0547 g mL⁻¹), $V_d$ is the volume of the droplet (in m³) and $g$ is gravitational acceleration (9.8 m s⁻²).

If the droplet is immersed in water, the buoyant force can be calculated as follows

$$F_b = \rho_l V_d g$$

(6)

where $\rho_l$ is the density of cyclohexanol (0.9624 g mL⁻¹).
The Stokes drag force \( F_v \), as previously described for a small soft sphere moving through a viscous fluid,\(^9\) is given by

\[
F_v = 5\pi R \eta v
\]

where \( \eta \) is the viscosity of cyclohexanol surrounding the droplet, which is 41.07 mPa s.\(^30\)

From Equations (1) to (7), the force provided by IFT change can be written as

\[
F_i = (\rho_d - \rho_l) V_d g + 5\pi R \eta v + m \frac{dv}{dt}
\]

When \( v = 0 \), the minimum force needed to lift the droplet in cyclohexanol could be obtained

\[
F_{i\text{min}} = G - F_b = (\rho_d - \rho_l) V_d g = \frac{4}{3} \pi R^3 g (\rho_d - \rho_l)
\]

which was the difference between the gravity and buoyancy.

For a \( \text{MC}_{8}\text{H}\text{SO}_{3}\text{H}/\text{H}_{2}\text{O} \) droplet with a volume of 0.58 µL (\( R = 0.52 \) mm) moving up towards 405 nm light under cyclohexanol, the gravity and buoyancy related to the droplet were calculated to be 6.0 and 5.5 µN, respectively. The minimum irradiation force \( (F_{i\text{min}}) \) to lift was 0.52 µN according to Equation (9).

By analysing Movie 6.3 with Tracker 5.0 software, the vertical distance travelled by the droplet was determined (Figure 6.8a). This data was fitted with a polynomial function as shown in Figure 6.8a and differentiated to determine the velocity-time profile (Figure 6.8b). A further polynomial curve fit and differentiation gave the acceleration \( (dv/dt) \) and the corresponding \( mdv/dt \)-time profile (Figure 6.8c) so that Equation (8) could be solved to obtain the irradiation force (in N) as a function of time (Figure 6.8d). As is shown in Figure 6.8c, the values of \( mdv/dt \) were in the range of \(-2\times10^{-8}\) to \(2\times10^{-8}\) N, which was over 25 times less than \( F_{i\text{min}} \), indicating that the contribution of \( mdv/dt \) to \( F_i \) in Equation (8) could be neglected and that \( F_i \) was linear with \( v \) under this condition. As a result, the equations for the \( v \)-t and \( F_i \)-t curves were in the same order, consistent with the force analysis result (Figure 6.8b,d).
Figure 6.8 The (a) y-t, (b) v-t, (c) dv/dt-t and (d) F_i-t curves of a 0.58 µL MCaH⁺SO₃⁻/H₂O droplet moving up towards 405 nm light in cyclohexanol. To omit the effect of initial droplet shape change upon light irradiation, all the experimental data was fitted to the appropriate equation starting at 0.3 s.

Based on the analysis, the equations for the y-t, v-t and F_i-t curves were obtained for the 0.52 mm droplet (Table 6.1). Theoretically, the maximum force could be obtained at \( t = 0 \) s according to the \( F_i-t \) equation (Table 6.1), which was 1.14 µN. However, since there was a significant shape change when the droplet was initially illuminated by light, the equation was obtained from 0.3 s to omit the effect of shape change. As a result, the maximum force calculated at \( t = 0 \) s was not accurate due to the shape change. The irradiation force at \( t = 0.3 \) s was considered to be the maximum force, which was 1.06 µN according to the \( F_i-t \) equation (Table 6.1).

The calculation results showed that the driving force provided by light-induced IFT change was in the range of 1.06 µN, diminishing to around 0.53 µN (calculated according to the equations in Table 6.1) over a few seconds. This is in a similar
order to the 0.1 µN force estimated by Faris and his coworkers to move a somewhat smaller droplet (100 µm diameter) at about the same speed (3 mm s\(^{-1}\)).\(^{23}\)

**Table 6.1** The y-t, v-t and F\(_i\)-t equations obtained by the force analysis for MC₈H⁺SO₃⁻/H₂O droplets with a volume of 0.58 µL moving up towards 405 nm light in cyclohexanol.

<table>
<thead>
<tr>
<th>R/mm</th>
<th>y (mm) – t (s) equation</th>
<th>v (mm s(^{-1})) – t (s) equation</th>
<th>F(_i) (µN) – t (s) equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.52</td>
<td>y = 0.13 + 1.84 t - 0.42 t(^2)</td>
<td>v = 1.84 – 0.84 t</td>
<td>F(_i) = 1.14 – 0.28 t</td>
</tr>
</tbody>
</table>

To further investigate the effect of droplet size on the driving force provided by light-induced IFT change, movies of MC₈H⁺SO₃⁻/H₂O droplets with different sizes moving up towards the 405 nm light source were taken (Movies 6.7-6.10) and the corresponding force analyses were carried out. The gravity, buoyant force and the minimum driving force needed to move these droplets up were calculated and shown in Table 6.2.

**Table 6.2** The gravity, buoyancy and F\(_{\text{min}}\) needed to lift the MC₈H⁺SO₃⁻/H₂O droplets with different sizes under cyclohexanol by light irradiation. The F\(_{\text{min}}\) was calculated according to Equation (9).

<table>
<thead>
<tr>
<th>R/mm</th>
<th>V/µL</th>
<th>G/µN</th>
<th>F(_b)/µN</th>
<th>F(_{\text{min}})/µN</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.32</td>
<td>0.13</td>
<td>1.34</td>
<td>1.23</td>
<td>0.12</td>
</tr>
<tr>
<td>0.41</td>
<td>0.28</td>
<td>2.89</td>
<td>2.64</td>
<td>0.25</td>
</tr>
<tr>
<td>0.52</td>
<td>0.58</td>
<td>5.99</td>
<td>5.47</td>
<td>0.52</td>
</tr>
<tr>
<td>0.60</td>
<td>0.90</td>
<td>9.30</td>
<td>8.49</td>
<td>0.81</td>
</tr>
<tr>
<td>0.71</td>
<td>1.50</td>
<td>15.50</td>
<td>14.15</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Using the same force analysis process as discussed previously for the MC₈H⁺SO₃⁻/H₂O droplet (R = 0.52 mm), the y-t, v-t and F\(_i\)-t equations of these droplets with volumes of 0.13 µL (R = 0.32 mm), 0.28 µL (R = 0.41 mm), 0.90 µL (R = 0.60 mm) and 1.50 µL (R = 0.71 mm) were obtained and are shown in Table 6.3. The droplets with radius of 0.60 mm and 0.71 mm have similar y-t, v-t and F\(_i\)-t equations with the model droplet (R = 0.52 mm) (Table 6.1 and 6.3). However, for smaller droplets (R = 0.32 or 0.41 mm), the y-t, v-t and F\(_i\)-t equations
were in a higher order than the corresponding equations for the model droplet \( (R = 0.52 \text{ mm}) (\text{Table 6.1 and 6.3}) \), indicating that the change in droplet size would change the type of motion under light illumination.

**Table 6.3** The \( y \)-\( t \), \( v \)-\( t \) and \( F_i \)-\( t \) equations obtained by the force analysis for \( \text{MCaH}^+\text{SO}_3^-/\text{H}_2\text{O} \) droplets with different sizes moving up upon 405 nm light irradiation in cyclohexanol.

<table>
<thead>
<tr>
<th>( R/\text{mm} )</th>
<th>( y (\text{mm}) - t (\text{s}) ) equation</th>
<th>( v (\text{mm s}^{-1}) - t (\text{s}) ) equation</th>
<th>( F_i (\mu \text{N}) - t (\text{s}) ) equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.32</td>
<td>( y = 0.29 + 2.69 t - 0.47 t^2 + 0.028 t^3 )</td>
<td>( v = 2.85 - 1.01 t + 0.091 t^2 )</td>
<td>( F_i = 0.70 - 0.20 t + 0.018 t^2 )</td>
</tr>
<tr>
<td>0.41</td>
<td>( y = 0.079 + 2.16 t - 0.62 t^2 + 0.053 t^3 )</td>
<td>( v = 2.20 - 1.29 t + 0.18 t^2 )</td>
<td>( F_i = 0.82 - 0.34 t + 0.047 t^2 )</td>
</tr>
<tr>
<td>0.60</td>
<td>( y = -0.19 + 1.71 t - 0.59 t^2 )</td>
<td>( v = 1.70 - 1.16 t )</td>
<td>( F_i = 1.48 - 0.45 t )</td>
</tr>
<tr>
<td>0.71</td>
<td>( y = -0.096 + 2.03 t - 1.50 t^2 )</td>
<td>( v = 2.14 - 3.15 t )</td>
<td>( F_i = 2.33 - 1.43 t )</td>
</tr>
</tbody>
</table>

Base on the \( y \)-\( t \), \( v \)-\( t \) and \( F_i \)-\( t \) equations for these droplets moving up towards light (Table 6.1 and 6.3), the maximum time (\( t_{\text{max}} \)) and distance (\( y_{\text{max}} \)) of the movement could be calculated, which were found in negative correlation with the radius of the droplet (Table 6.4). When the droplet stopped moving up to the light (\( t = t_{\text{max}} \)), the minimum irradiation force for the movement could be calculated according to the \( F_i \)-\( t \) equation and the resulting values (\( F_{i\text{min}}' \)) were in correlation with \( R \) (Table 6.4). It should be noted that these experimentally determined values (\( F_{i\text{min}}' \) in Table 6.4) compared well with the calculated values (\( F_{i\text{min}} \) in Table 6.2), indicating the validity of these \( F_i \)-\( t \) equations.

**Table 6.4** The maximum time (\( t_{\text{max}} \)), maximum distance (\( y_{\text{max}} \)), minimum irradiation force (\( F_{i\text{min}} \)), maximum irradiation force (\( F_{i\text{max}} \)) and maximum velocity (\( v_{\text{max}} \)) related to the movement of \( \text{MCaH}^+\text{SO}_3^-/\text{H}_2\text{O} \) droplets with different sizes up towards 405 nm light in cyclohexanol calculated by the equations in Table 6.1 and 6.3.

<table>
<thead>
<tr>
<th>( R/\text{mm} )</th>
<th>( t_{\text{max}}/\text{s} ) (( v = 0 ))</th>
<th>( y_{\text{max}}/\text{mm} ) (( v = 0 ))</th>
<th>( F_{i\text{min}}'/\mu \text{N} ) (( t = t_{\text{max}} ))</th>
<th>( F_i/\mu \text{N} ) (( t = 0.3 \text{ s} ))</th>
<th>( v_{\text{max}}/\text{mm s}^{-1} ) (( t = 0.3 \text{ s} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.32</td>
<td>6.27</td>
<td>4.57</td>
<td>0.15</td>
<td>0.64</td>
<td>2.56</td>
</tr>
<tr>
<td>0.41</td>
<td>2.80</td>
<td>2.43</td>
<td>0.24</td>
<td>0.72</td>
<td>1.83</td>
</tr>
<tr>
<td>0.52</td>
<td>2.19</td>
<td>2.15</td>
<td>0.53</td>
<td>1.06</td>
<td>1.53</td>
</tr>
<tr>
<td>0.60</td>
<td>1.47</td>
<td>1.05</td>
<td>0.82</td>
<td>1.35</td>
<td>1.35</td>
</tr>
<tr>
<td>0.71</td>
<td>0.68</td>
<td>0.59</td>
<td>1.36</td>
<td>1.90</td>
<td>1.20</td>
</tr>
</tbody>
</table>
As was discussed before, since $t = 0.3$ was set as the boundary condition to avoid the effect of initial shape change of the droplets, the maximum irradiation force ($F_{\text{max}}$) as well as the maximum velocity ($v_{\text{max}}$) could be calculated. The $F_{\text{max}}$ was in positive correlation with $R$, while $v_{\text{max}}$ was in negative correlation, which was indicated by the $F_{\text{max}}$-R and $v_{\text{max}}$-R cubic curves in Figure 6.9. The results showed that the droplet size had a significant effect on the irradiation force as well as the motion of droplets up towards 405 nm light in cyclohexanol. The driving force provided by the photochemical induced IFT change was in the order of nN to µN, similar to the estimation of Faris and his coworkers.  

![Figure 6.9](image)

**Figure 6.9** The (a) $F_{\text{max}}$-R and (b) $v_{\text{max}}$-R curves of $\text{MC}_8\text{H}^+\text{SO}_3^-/\text{H}_2\text{O}$ droplets with different sizes moving up towards 405 nm light in cyclohexanol at $t = 0.3$ s.

### 6.7 Summary

In this chapter, by using a photoactive material sodium sulphonate-substituted merocyaninesulphonic acid in water droplets, a simple droplet moving system, in which water droplets moved on a hydrophobic surface such as polystyrene and acrylic in fatty alcohol by light was developed. The water droplet contained the water-soluble merocyaninesulphonic acid, which is sensitive to 365 nm or 405 nm light illumination. The photoisomerisation of this merocyaninesulphonic acid is accompanied by an interfacial tension change at water/hexanol interface, which can initiate the Marangoni flow, thus moving the droplet in hexanol towards the light source. The driving force provided by IFT change was calculated and the value was in the order of nN and µN depending on the droplet size, concentration of the
droplet, as well as the intensity of the light source. The motion direction is the same as the internal convection and can be controlled. Interestingly, the results show that small chemical changes at the molecular level led to significant differences in macroscopic behaviour. Additionally, based on this system, new functional microfluidics could be designed and constructed, to investigate chemical or biological transport processes as well as reactions in living systems.

6.8 References


(8) Lagzi, I.; Soh, S.; Wesson, P. J.; Browne, K. P.; Grzybowski, B. A. Maze


(22) Larger droplets tended to lose their spherical shape such that their diameter does not accurately indicate their volume.


(30) Oswal, S. L.; Ghael, N. Y.; Prajapati, K. D. Speeds of Sound, Isentropic
Chapter 7  Application of photocontrolled droplet motion systems

7.1  Introduction

Controlled motion of droplets through another immiscible liquid provides a way to selectively transport materials to a specific location and carry out site-specific chemical reactions.1-3 As synthetic vesicles, droplets have been widely used as vessels to support chemical reactions, as well as models of protocells to investigate biological processes.3,4 Directional motility of these artificial cell-like structures makes it possible for them to communicate with each other and with the environment, thus performing complex intelligent tasks, such as precise cargo transport, drug delivery, chemical or biological sensing, and effecting chemical reactions.3-8

In recent years, several droplet motion systems have been developed. Their movement mechanism is based on Marangoni flow resulting from surfactant-generated interfacial tension (IFT) gradients induced by external stimuli including chemical, temperature, electric field and light.2,3,9,10 The IFT gradient can be either generated from the environment surrounding the droplet or by the droplet itself, although it has been demonstrated that a better control of the movement can be achieved if the change occurs within the droplet.11,12

In the previous chapters, by using the photoactive spiropyran/merocyanine in the droplet, photochemical manipulations of both water droplets in an organic medium (water-in-oil) and organic droplets in water (oil-in-water) were achieved. This opened the way to explore applications in cargo transport and droplet controlled chemical reactions. The droplets could be used as vesicles to transport particles and chemicals to a desired place to undertake tasks, for example, to merge with another droplet to complete chemical reactions. To further explore the applications of these systems, movement of these photoactive liquids in a confined space such as capillaries was investigated. These applications could demonstrate the potential of
the photochemical controlled droplet motion systems in the fields of biology and fluidic for diagnostics, cargo transport and drug delivery.

7.2 Transport of particles

It has been reported that droplets can provide an isolated physical and chemical environment for encapsulated particles as well as a way to transport them. In order to transport particles with the photoinduced droplet motion systems, SPCH$_2$CH$_2$OH/DCE droplet was used to encapsulate expanded graphite (the material exhibits lower density than ordinary graphite). Droplets containing graphite particles were able to be moved away from 365 nm light and then towards 405 nm light in the SDBS (7 mM) aqueous solution containing CaCl$_2$ (0.4 mM).

A 2 µL SPCH$_2$CH$_2$OH droplet containing millimetre-sized graphite particles, was not spherical anymore. However, the droplet was able to be moved away from 365 nm light (Figure 7.1a,c) and then towards 405 nm light (Figure 7.1b,d) in the aqueous solution of SDBS (7 mM) containing CaCl$_2$ (0.4 mM) (Movie 7.1). In this case, the droplet, guided by light, acted as a carrier to move the particle to a desired place in the aqueous solution. When the droplet contacted another graphite particle in the solution (Movie 7.1), the particle was picked up and the photocontrolled movement of the droplet was not affected even though the droplet shape changed again (Movie 7.2). These results open up a promising way to transport or pick-up functional particles with photoactive droplets in a controlled fashion.

**Figure 7.1** Illustration of the movement of a SPCH$_2$CH$_2$OH droplet (a) away from 365 nm light and then (b) towards 405 nm light in the aqueous solution of SDBS (7 mM) and CaCl$_2$ (0.4 mM), and the corresponding movement of an expanded graphite particle-encapsulated SPCH$_2$CH$_2$OH droplet (2 µL) (c) away from 365 nm and then (d) towards 405 light illumination. The illumination direction is indicated by red arrows. All the photos were taken from Movies 7.1 and 7.2.
### 7.3 Transport of chemicals to initiate chemical reactions

The two types of droplet motion systems, developed during this study, made it possible to construct droplets either with organic solvents or with water. As a result, a variety of chemical reactions could potentially occur within the droplets.\(^{16-20}\)

Since the movement of the droplets with chemicals can be manipulated by light, the droplet can be used as a carrier for chemicals and guided to a specific location to complete chemical reactions.

#### 7.3.1 Transport of chemicals with an oil-in-water droplet system

As was demonstrated in Chapter 4, the droplet composed of $\text{MCH}^+\text{DBS}^-$ in nitrobenzene was able to move towards 365 nm or 405 nm light in DI water. This organic droplet could be used as a carrier to transport functional materials to a desired spot under water to complete certain tasks, which holds great promise for practical applications in microfluidics and drug delivery. The $\text{MCH}^+\text{DBS}^-$ droplet was used to pick up another droplet containing a functional chemical species and transport it to a third droplet to complete the chemical reaction. 5,10,15,20-Tetraphenylporphyrin ($\text{TPP}$), which appears purple, can be easily protonated in the presence of acid to give the green deprotonated porphyrin $[\text{H}_2\text{TPP}]^{2+}$ (Figure 7.2) and was chosen as the functional chemical. As is shown in the sequence of photographs (Figure 7.2) and Movie 7.3, a $\text{MCH}^+\text{DBS}^-$ droplet (Droplet 1) with a dark yellow colour was moved by a 405 nm light laser pointer towards a purple TPP droplet (Droplet 2) at a speed of $4.5\pm0.4 \text{ mm s}^{-1}$. To promote the merger between droplets, a small amount of surfactant Triton X-100 was used in the TPP droplet. The $\text{MCH}^+\text{DBS}^-$ droplet was able to pick up the TPP droplet to form a larger droplet (Droplet 4). DBSA is a strong acid and can protonate TPP to generate $[\text{H}_2\text{TPP}]^{2+}$, so the resulting droplet appeared green. The green droplet was still photoactive and able to be guided to an oleylamine droplet (Droplet 3) with a velocity of $4.2\pm0.1 \text{ mm s}^{-1}$. Oleylamine is an organic base that can deprotonate $[\text{H}_2\text{TPP}]^{2+}$ to reproduce TPP. As a result, the final droplet (Droplet 5) was purple. Since a wide range of solvents can be used to construct this photoactive
droplet, various functional materials, which are compatible with the $\text{MCH}^+\text{DBS}^-$ and DBSA, could be used in this transport system.

![Diagram of TPP and [H$_2$TPP]$^2+$](image)

**Figure 7.2** (a) Conversion between TPP and [H$_2$TPP]$^2+$ in the presence of acid and base. (b) Before light illumination, the photoactive yellow MCH$^+\text{DBS}^-$ droplet (Droplet 1), purple TPP droplet with 1% Triton X-100 (Droplet 2) and colourless oleylamine droplet (droplet 3) were loaded into a Petri dish filled with DI water. (c) Droplet 1 was guided by 405 nm light towards Droplet 2 with the illumination direction indicated by the white arrow. (d) Merger of Droplet 1 and 2 gave a green droplet (Droplet 4) due to the formation of [H$_2$TPP]$^2+$. (e) The resulting Droplet 4 was directed to Droplet 3 by 405 nm laser with the illumination direction indicated by the white arrow. (f) Deprotonation of [H$_2$TPP]$^2+$ by oleylamine gave a purple colour of Droplet 5. All the photos were taken from Movie 7.3.

### 7.3.2 Transport of chemicals with a water-in-oil droplet system

In Chapter 4, it was demonstrated that a water droplet containing $\text{MC}_8\text{H}^+\text{SO}_3^-$ was able to move towards 365 nm or 405 nm light under fatty alcohol. To demonstrate that this droplet can be used to carry cargo to transport chemicals to a desired spot to initiate a chemical reaction, the violent decomposition of hydrogen peroxide (H$_2$O$_2$) catalysed by potassium iodide (KI) was used as an example.$^{21}$ Thus, a 2 µL photoactive $\text{MC}_8\text{H}^+\text{SO}_3^-/\text{H}_2\text{O}$ droplet containing KI (2.5 M) (Droplet 1) was
placed under hexanol along with a 2 µL droplet of 32% H₂O₂ (Droplet 2) (Figure 7.3 and Movie 7.4). Droplet 1 was guided to merge with droplet 2 to give the violent decomposition of H₂O₂ with oxygen bubbles generated. This simple example demonstrated that the photoactive droplets were able to be guided to a specific spot by light to complete a specific task.

Figure 7.3 Light-directed droplet collision and the resulting chemical reaction. (a) Photoactive orange droplet 1 (0.2 M MC₆H₄SO₃⁻ and 2.5 M KI in H₂O) and colourless droplet 2 (32% H₂O₂). (b) Laser (405 nm) light-directed movement of droplets 1 towards 2 with the white arrow showing the direction of the laser beam. (c) Droplet 3 formed as a result of the merger of droplets 1 and 2 with the generation of oxygen bubbles due to the decomposition of H₂O₂. All the photos were taken from Movie 7.4.

7.4 Transport of liquids in capillaries

In order to develop applications of the photoactive droplet motion systems in microfluidics, movement of the droplets in a confined space such as capillaries was investigated. The droplet comprised a DCE solution of spiropyran (0.1 M) and the aqueous phase was SDBS solution (7 mM) containing hydrochloric acid (0.1 M). As has been discussed in Chapter 4 (Section 4.3.2.5), this droplet moves away from 365 nm light and then towards 405 nm light with a relatively high velocity and a long distance. A 5 µL SPCH₂CH₂OH/DCE droplet was placed in a Petri dish filled with SDBS solution (7 mM) containing hydrochloric acid (0.1 M) together with a glass capillary (both ends open, inner diameter 1.1 mm) (t = 0 s, Figure 7.4). The droplet moved away from 365 nm light with a speed of 4 mm s⁻¹ (t = 12.94 s, Figure
7.4, Movie 7.5) and was guided into the capillary to become a liquid plug (t = 31.52 to 32.86 s, Figure 7.4, Movie 7.5). Interestingly, this liquid plug moved towards 365 nm light source within the capillary with a velocity of 0.7 mm s\(^{-1}\) (t = 44.54 to 53.67 s, Figure 7.4, Movie 7.5). Illumination of the rear back of the plug with 405 nm light could accelerate the motion to 2 mm s\(^{-1}\) (t = 53.70 to 67.91 s, Figure 7.4, Movie 7.5). The plug stopped moving as soon as it reached the opposite end.

![Figure 7.4](image)

Figure 7.4 Light-directed movement of a 5 µL \(\text{SPCH}_2\text{CH}_2\text{OH}/\text{DCE}\) droplet (0.1 M) in a Petri dish and then in a capillary under the SDBS solution (7 mM) containing hydrochloric acid (0.1 M). The illumination directions for 365 and 405 nm light were indicated by purple and violet arrows, respectively. All the photos were taken from Movie 7.5.

To get an insight into the movement of the aqueous phase in the capillary while the photoactive plug moved under light illumination, a glass capillary (both ends open, inner diameter 1.1 mm) was initially partly filled with a DCE solution of \(\text{SPCH}_2\text{CH}_2\text{OH}\) (14 µL), then a small amount of aqueous solution of SDBS (7 mM) and hydrochloric acid (0.1 M), and finally with a larger volume of aqueous solution of SDBS (7 mM) and hydrochloric acid (0.1 M) containing a blue dye indigo carmine (1 mM) by dipping opposite ends of the capillary into the appropriate solution. The capillary was carefully placed in a Petri dish filled with an aqueous solution of SDBS (7 mM) and hydrochloric acid (0.1 M) (t = 0, Figure 7.5, Movie 7.6).

The \(\text{SPCH}_2\text{CH}_2\text{OH}/\text{DCE}\) plug was illuminated by 365 nm light from the blue-dyed side and the organic liquid moved toward the light source with a speed of 0.9 mm s\(^{-1}\), pushing the blue solution out of the capillary (t = 4.65 to 13.29 s, Figure 7.5 Movie 7.6). Illumination of the organic plug with 405 nm light at the same time from the colourless side promoted the motion by increasing the velocity to about 2 mm s\(^{-1}\) (t = 13.7 to 35.0 s, Figure 7.5, Movie 7.6). The organic plug stopped moving
as soon as it reached the end of the capillary and all the solution of indigo carmine was pushed out into the bulk solution. Lack of blue colouration at the other end of the organic plug indicated that there was no exchange of the two aqueous phases on the two sides of the organic plug.

![Figure 7.5](image)

**Figure 7.5** Light-directed movement of a 14 µL \(\text{SPCH}_2\text{CH}_2\text{OH}/\text{DCE} \) plug (14.9 mm) in a glass capillary (both ends open, inner diameter 1.1 mm) under a SDBS solution (7 mM) containing hydrochloric acid (0.1 M). One side of the capillary was filled the same surfactant solution (6.7 mm, 6 µL) and the other side with the same surfactant solution containing indigo carmine (40.3 mm, 6 µL). The illumination directions for 365 and 405 nm light are indicated by purple and violet arrows, respectively. All the photos were taken from Movie 7.6.

When the glass capillary was replaced with a polytetrafluoroethylene (PTFE) tube (2 mm in diameter), similar movement was observed. A DCE solution of \(\text{SPCH}_2\text{CH}_2\text{OH} \) plug (3.1 mm, 10 µL) moved towards 365 nm light with a velocity of 0.4 mm s\(^{-1}\) within the PTFE tube, which was placed under the SDBS solution (7 mM) containing hydrochloric acid (0.1 M) (Figure 7.6, Movie 7.7).
Figure 7.6 Light-directed movement of a 10 µL SPCH\textsubscript{2}CH\textsubscript{2}OH/DCE plug (3.1 mm) in a PTFE tube (both ends open, inner diameter 2 mm) under the SDBS solution (7 mM) containing hydrochloric acid (0.1 M). The illumination directions for 365 nm light was indicated by the purple arrows. All the photos were taken from Movie 7.7.

In order to simplify the motion system, the capillary containing the photoactive plug and the surfactant solution was placed in air instead of the bulk surfactant solution. Typically, a SPCH\textsubscript{2}CH\textsubscript{2}OH/DCE plug (0.1 M, 11.9 mm, 11 µL) was added into a glass capillary (both ends open to air, inner diameter 1.1 mm). One side of the organic plug was filled with a layer of SDBS aqueous solution (7 mM) containing 0.1 M hydrochloric acid (11.7 mm, 11 µL) and the other side with a layer of the same surfactant solution containing 1 mM blue indigo carmine (9.4 mm, 9 µL) (t = 0 s, Figure 7.7, Movie 7.8). Irradiation of one side of the yellow photoactive plug with 365 nm light resulted in the movement of the three layers towards the light source with a speed of 1 mm s\textsuperscript{-1} (t = 1.85 to 10.08 s, Figure 7.7, Movie 7.8). The movement could be accelerated by using a 405 nm light laser to irradiate the other side simultaneously with the 365 nm light (t = 19.2 s, Figure 7.7, Movie 7.8) leading to faster movement (black arrow, 2 mm s\textsuperscript{-1}) away from the 405 nm light (violet arrow) and towards the 365 nm light (purple arrow) as observed previously (t = 19.2 to 33.9 s, Figure 7.7, Movie 7.8). Interchange of the two lights led to movement of the plug in the opposite direction (t = 39.9 to 67.6 s, Figure 7.7, Movie 7.8). No colouration of the aqueous layer without indigo carmine was observed after the movement, further indicating that the two aqueous parts were totally separated by the organic plug. If the amount of the photoactive liquids was decreased to half (5.9 mm, 5.5 µL) and the amount of the aqueous solutions were kept similar, the speed of the movement using only 365 nm light was decreased to
0.3 mm s\(^{-1}\) and to 0.7 mm s\(^{-1}\) using both 365 nm and 405 nm lights, but the motion direction did not change (Movie 7.9).

**Figure 7.7** Light-directed movement of an 11 µL \textit{SPCH\textsubscript{11}CH\textsubscript{2}OH/DCE} plug (11.9 mm) in a glass capillary (both ends open to air, inner diameter 1.1 mm) with one side of the organic plug filled with a plug of SDBS aqueous solution (7 mM) containing 0.1 M hydrochloric acid (11.7 mm, 11 µL) and the other side with a plug of the same surfactant solution containing 1 mM blue indigo carmine (9.4 mm, 9 µL). The illumination directions for 365 and 405 nm light are indicated by purple and violet arrows, respectively. All the plugs moved in the opposite direction of 365 nm light (purple arrows) while in the same direction as 405 nm light (violet arrows). Movement direction is indicated by the black arrows. All the photos were taken from Movie 7.8.

While this capillary work opened up new opportunities for using this droplet system such as the development of photo-driven pumps for microfluidics, it raised many questions about the mechanism of movement. The organic plug motion differed from the motion of a droplet in a Petri dish, which was surrounded solely by the aqueous solution and the droplet moved due to liquid-liquid interaction. The capillary plug motion resulted from not only the liquid-liquid interaction but also the liquid-solid interaction since the plug was surrounded by the aqueous solution as well as the wall of the capillary. Photoinduced IFT and contact angle change most likely played roles in the movement in the capillary, which made the plug motion opposite to that in a Petri dish under light illumination.\textsuperscript{22-25} Further investigation of the mechanism would be needed to understand this process but this could not be done in the time frame of this thesis.
7.5 Summary

Based on the photocontrolled droplet motion systems, a variety of applications including the transport of particles, chemicals and liquids were developed. The photoactive droplets could be used as carriers to transport particles or chemicals to a desired spot to complete specific tasks, which opened up a new way to construct intelligent droplets to complete complex tasks in the future. The light-controlled movement of photoactive liquids in capillaries or tubes opens the way to develop a new generation of photodriven pumps.

7.6 References


Chapter 8 Conclusion and Future Work

8.1 Conclusion

In this dissertation, a variety of light-controlled droplet motion systems have been developed, based on photochemistry of a series of spiropyran derivatives. Depending on the solubility of the photoactive materials, two types of droplet motion systems were developed, organic droplets in water and water droplets in organic medium. 2D and 3D movement were achieved for both systems. In general, even the droplets behave differently under light illumination in those systems, all the motions can be explained by the same mechanism based on the Marangoni effect.\(^1\)\(^-\)\(^7\) This effect was clearly observed during conducted experiments and were recorded on movies. When light irradiation decreases interfacial tension (IFT) in the illuminated part at the droplet/water interface, the droplet moves towards light. In contrast, when light irradiation increases IFT, the droplet moves away from light. These droplet motion systems open up new ways for light-controlled cargo transport and light-driven pump in microfluidics and have potential to emulate the biological transport and motion process in nature. It also created a pathway for beginning a selected chemical process at specific location at the desired time.

In Chapter 3 (Chapter 1 is an introduction and Chapter 2 is an experimental), a series of merocyanine sulphonic acids were synthesised and characterised. These merocyaninesulphonic acids were found to act as photoacids and changed pH of the solution, under light illumination. This property was explored in following chapters for light-induced droplet motion systems. The high solubility of the resulting sodium sulphonate substituted merocyaninesulphonic acid (\(\text{MCaH}^+\text{SO}_3^-\)) in water made it a material of choice for the construction of water-in-oil droplet motion systems. It has been found that these compounds could be also deprotonated in organic solvents such as DMSO by triethylamine giving, in some cases, unstable merocyanine intermediates that rapidly convert to the SP. For the reaction of merocyaninesulphonic acids bearing a nitro group on the phenol moiety with
gaseous base, an intensely coloured purple merocyanine was observed that was stable in its open form for hours. In contrast, the merocyaninesulphonic acids lacking nitro group produced short lived blue MC intermediate solutions that rapidly decolourised in seconds. Based on these results, a basic gas sensor was developed by embedding a merocyaninesulphonic acid and 4-dodecylbenzenesulphonic acid into PDMS. This material changes its colour in the presence of dry ammonia gas. Such detection is desired in food industry where ammonia frequently accompanies decaying processes.8-10

In Chapter 4, a photoactive droplet was prepared by dissolving an ethanol substituted spiropyran (SPCH₂CH₃OH) in an organic solvent. The resulting SPCH₂CH₃OH droplet moved away from 365 nm light and then towards 405 nm light in the presence of surfactant. The motion was promoted by acid either in the droplet or in the aqueous phase. It has been found that CaCl₂ in the aqueous phase also helped the movement, although the reason was not clear. A SPCH₂CH₃OH organic droplet moved away from 365 nm light in the aqueous solution containing a surfactant sodium dodecylbenzenesulphonate (SDBS). The moving speed was less than 0.1 mm/s and the distance was less than 10 mm. Addition of acids like hydrochloric acid, methanesulphonic acid, oxalic acid and phthalic acid in the surfactant solution could largely accelerate the motion away from 365 nm light and extend the moving distance. The fastest movement was obtained by moving a SPCH₂CH₃OH organic droplet away from 365 nm light in SDBS (7 mM) and oxalic acid (0.1 M) aqueous solution and the velocity was up to 14.9 mm/s. Interestingly, after the droplet stopped under 365 nm light, it was able to move towards 405 nm light and then move away from 365 nm light again. To sustain the movement, the droplet had to be illuminated by 365 nm light and 405 nm light alternatively. The overall distance of movements, including all the movements away from 365 nm light and all those towards 405 nm light, was up to 2388 mm. Another approach to promote the motion of a SPCH₂CH₃OH organic droplet in surfactant solution was to add acid into the organic droplet. The acids used were all carboxylic acids such as acetic acid, octanoic acid, lipoic acid and benzoic acid (not strong acids which can protonate a merocyanine). A SPCH₂CH₃OH organic droplet containing octanoic acid, the total moving distance including both the
movement away from 365 nm light and towards 405 nm light in SDBS (7 mM) aqueous solution was up to 2817 mm and the fastest speed was 10.7 mm/s.

To make the droplet more versatile and independent of the environment, all the materials including \textbf{SPCH$_2$CH$_2$OH}, surfactant and acid (octanoic acid) were dissolved in the chloroform droplet and DI water was used as the external medium. This droplet moved away from 365 nm light with a speed of up to 8 mm/s. However, the moving distance was relatively short – just 52 mm due to the fast loss of SDBS from the droplet into the water phase. Without the presence of surfactant either in the droplet or in the aqueous phase, the \textbf{SPCH$_2$CH$_2$OH} drop was still able to move under 365 nm light illumination, but the direction was towards the light source. The velocity was up to 3.3 mm/s and the distance was 24 mm.

The mechanism for all the motions was investigated. It has been concluded that in the presence of surfactant, the photoisomerisation of spiropyran to merocyanine under 365 nm light affected the distribution of surfactant on the droplet surface, which dominated the IFT change. As a result, 365 nm light increased IFT in the illuminated area thus generating a Marangoni flow directed towards the illuminated area on the droplet surface and an internal convective flow away from the light source through the centre of the droplet. The droplet moved in the same direction as the internal convection, away from 365 nm light. Then after 365 nm light, merocyanine formed in the droplet. In this case, illumination of 405 nm light created an area of low IFT on the droplet surface thus forming a Marangoni flow directing the non-illuminated area on the droplet surface and an internal convective flow towards the illuminated side through the centre of the droplet. The droplet moved in the same direction as the internal convection, towards 405 nm light. To confirm the mechanism, further study needs to be undertaken to investigate how the photoisomerisation between spiropyran and merocyanine affects the distribution of surfactant on the droplet surface, thus changing the IFT. The presence of acid either in the aqueous phase or in the droplet accelerated the photoisomerisation between spiropyran and merocyanine therefore promoting the movement. For a \textbf{SPCH$_2$CH$_2$OH} droplet in DI water, 365 nm light decreased IFT in the illuminated area by converting spiropyran to merocyanine thus forming a Marangoni flow directing the non-illuminated area on the droplet surface and a
convective flow towards the illuminated side through the centre of the droplet. The droplet moved in the same direction as the internal convection, towards 405 nm light.

Chapter 5 describes the optimisation of the movement of the organic droplet containing all the materials including \( \text{SPCH}_2\text{CH}_2\text{OH} \), surfactant and carboxylic acid in DI water (described in Chapter 3). \( \text{SPCH}_2\text{CH}_2\text{OH} \) was treated with a strongly acidic surfactant 4-dodecylbenzenesulphonic acid in organic solvents. Consequently, a protonated merocyanine/surfactant salt (\( \text{MCH}^+\text{DBS}^- \)) was obtained. By using this salt as a photoactive component, the droplet moved towards 365 nm light or 405 nm light in DI water with a speed of up to 15.8 mm/s. The overall moving distance was 315 mm under 365 nm light. It should be noted that the distance was obtained by continuously moving the droplet under 365 nm light until it ran out of “fuel”. It was different from the overall moving distance (2817 mm) in the previous chapter obtained by moving \( \text{SPCH}_2\text{CH}_2\text{OH} \) organic droplet containing octanoic acid in SDBS aqueous solution alternatively with 365 nm light and 405 nm light. The movement of \( \text{MCH}^+\text{DBS}^- \) organic droplet was relatively independent from the aqueous environment and the aqueous phase could be DI water or sea water, and the pH range was −0.3 to 11. The mechanism of this motion was similar to that described in Chapter 3. 365 nm or 405 nm light was able to convert \( \text{MCH}^+\text{DBS}^- \) to \( \text{SPH}^+\text{DBS}^- \), and spiropyran and free DBSA were therefore generated by the deprotonation of \( \text{SPH}^+\text{DBS}^- \) at the organic/water interface. As a result, a low IFT area was created by the presence of DBSA in the illuminated area thus forming a Marangoni flow, directed towards the non-illuminated area on the droplet surface and an internal convective flow towards the illuminated part through the centre of the droplet. The droplet moved in the same direction as the internal convection, towards the light source. The droplet was able to move in 3D with light by adjusting its density to make it similar to that of water. Based on the 3D movement, the force provided by IFT change was measured and calculated, which is at the scale of nanonewtons. The relatively high speed, long moving distance and simple aqueous environment made this droplet motion system applicable in the area of cargo transport.
In Chapter 6, in order to develop a “reverse system” to move water droplets in organic media, \( \text{MC}_8\text{H}^+\text{SO}_3^- \), the water soluble merocyaninesulphonic acid synthesised in Chapter 3, was used. The aqueous merocyanine droplet moved towards 405 nm light in fatty alcohols including 1-hexanol, 1-octanol, 1-decanol and cyclohexanol with a velocity up to 7 mm/s. However, the moving distance was short just 52 mm. The motion mechanism could would be similar to described in previous chapters: 405 nm light decreased interfacial tension (IFT) in the illuminated area by converting \( \text{MC}_8\text{H}^+\text{SO}_3^- \) to its spiropyran form and forming a Marangoni flow directed towards the non-illuminated area on the droplet surface, and the droplet moved in the opposite direction which was towards light. 3D movement was achieved by using cyclohexanol whose density was close to that of the water droplet, as the organic medium. The driving force provided by light-induced IFT change was calculated for the 3D movement of droplets and the values were of the order of nN to \( \mu \)N depending on the type of droplet and conditions. Based on this system, new functional microfluidics could be designed and constructed, to investigate chemical or biological transport process as well as reactions in living systems.

In Chapter 7, applications of the photocontrolled droplet motion systems were developed. The droplets were able to encapsulate particles and transport them to a desired location. Transport of chemicals with the photoactive droplets was also realised in both oil-in-water and water-in-oil droplet motion systems. The organic droplet containing \( \text{MCH}^+\text{DBS}^- \) was used as a carrier to merge with another droplet containing tetraphenylporphyrin (TPP) as a chemical cargo, which reacted with the DBSA in the first droplet to generate protonated TPP (\([\text{H}_2\text{TPP}]^{2+}\)). This larger droplet was then moved to merge with a third droplet containing an amine to effect another chemical reaction, which was the deprotonation of \([\text{H}_2\text{TPP}]^{2+}\). By simply using a 405 nm laser to guide the motion, two chemical reactions were completed in the process. The water droplet containing \( \text{MC}_8\text{H}^+\text{DBS}^- \) was used to carry KI and moved to \( \text{H}_2\text{O}_2 \) droplet with light to initiate the decomposition of \( \text{H}_2\text{O}_2 \) with the generation of oxygen bubbles. The photoactive liquids could be moved in a confined space like capillaries, which had promising applications in microfluidics as light-driven pumps.
8.2 Future Work

In this thesis, a variety of photocontrolled droplet motion systems were developed and their mechanisms investigated. Some “proof of concept” applications were also demonstrated. However, still some challenges and questions remained, so further investigations into the mechanisms of these systems should be undertaken and more practical applications developed.

8.2.1 Insight into mechanism of the droplets movement

It has been reported that the IFT of SPCH$_2$CH$_2$OH organic droplets in water can be decreased by 365 nm light due to the photoisomerisation of SP to MC.$^{11-13}$ Accordingly, SPCH$_2$CH$_2$OH organic droplets moved towards 365 nm light in this work. Addition of surfactant in the aqueous phase was able to reverse the IFT change of the SPCH$_2$CH$_2$OH organic droplet in water, that is, to increase the IFT under 365 nm light, thus making the droplet move away from the light source. It is postulated, in this thesis, that interactions between the SP or MC form of SPCH$_2$CH$_2$OH and the surfactant take place at the organic/water interface and affect the distribution of surfactant at the interface, thus increasing IFT under 365 nm light. However, it is still unclear what the interactions could be and how the interactions increase IFT upon 365 nm light irradiation. Further investigation of the interactions between SPCH$_2$CH$_2$OH and the surfactant need to be carried out.

It was also found that the addition of acid either in the aqueous solution or in the droplet could significantly promote the motion of SPCH$_2$CH$_2$OH organic droplets in the aqueous solution of surfactant (SDBS). The protonated merocyanine is probably involved in this process and this needs to be clarified. The presence of the protonated spiropyran species (SPH$^+$) generated by treating SPCH$_2$CH$_2$OH by DBSA needs to be further confirmed. The mechanism of the generation of SPH$^+$ and its pathway to the protonated merocyanine/surfactant salt (MCH$^+$DBS$^-$) also needs to be further investigated. Because of the complex and transient nature of SP/MCs, a separate study needs to be dedicated to fully explain these phenomena.
For most of the droplet motion systems developed in this dissertation, a fluorescent plume could be observed while the droplet was moving. However, the detailed generation mechanism of the plume needs to be further investigated, so that the role of the plume played in the droplet motion could be studied.

### 8.2.2 Extension of the droplet motion systems

For the movement of SPCH₂CH₂OH organic droplets in the aqueous solution of surfactant (SDBS), the distribution of surfactant is affected by photoisomerisation of spiropyran to merocyanine thus changing the IFT and moving the droplet. Basing on that fact, the use of other photoactive materials, which can undergo photochemistry and affect the distribution of surfactant at the oil/water interface under light illumination, should also be possible and can be pursued.

Inspired by this, some preliminary studies were undertaken. SPCH₂CH₂OH was replaced with phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO), a photoinitiator for polymerisation, which generated radicals upon light irradiation (Figure 8.1a). The resulting BAPO organic droplet (0.5 M) moved away from 365 nm light in the aqueous solution of surfactant (SDBS, 7 mM) with a speed of 3 mm/s (Figure 8.1b). Marangoni flow was observed when the droplet moved away from 365 nm light (Figure 8.1c). Further investigation on this new system is currently being carried out by my fellow researcher, Ms Sara Zarghami.

![Figure 8.1](image-url) (a) Photoreaction of BAPO under light illumination. (b) Illustration of the movement direction. (c) Visualization of the system.
away from light of a BAPO droplet (0.5 M) under the aqueous solution of SDBS (7 mM) following irradiation with 365 nm. (c) Marangoni flow observed when the droplet moved away from 365 nm light.

2-Nitrobenzaldehyde (NBA) is another photoactive molecule, which can undergo irreversibly conversion to 2-nitrosobenzoic acid (NSBA) upon UV light irradiation (Figure 8.2a),18-24. DCE droplet containing NBA and series of amines (Figure 8.2b) was developed. The resulting photoactive droplet was able to move away from 365 nm light. Further study on this new system needs to be carried out.

![Figure 8.2](image)

**Figure 8.2** (a) Photo reaction of 2-nitrobenzaldehyde. (b) Illustration of the movement away from light of a DCE droplet containing NBA and an amine or amide in the aqueous solution of SDBS (7 mM) following irradiation with 365 nm.

Malachite green carbinol base (MGCB), which can undergo reversible photolysis to generate hydroxide (photobase) anions upon UV light irradiation, is another interesting option (Figure 8.3a).25-27 This compound is soluble in organic solvents such as dichloromethane and chloroform, so it can be used to prepared photoactive organic droplets and the droplets might be moved in aqueous solution with UV light. It has been reported that MCGB can be modified into a water soluble compound by treating it with methyl iodide in toluene (Figure 8.3b).25,28 The resulting water soluble derivative can be used to prepared photoactive water droplets and the droplets might be moved in organic phase with UV light.
The development of light-induced droplet motion systems based on the photoactive materials, including spiropyrans/merocyanines, BAPO and NBA, described in this thesis, shows that photochemical reactions can be successfully used in light-activated transport in general terms. With the wide variety of already available photoactive materials such as radical photoinitiators, photoacids and photobases, these discoveries open up a way for novel light-activated transport systems for chemistry and biology.

8.2.3 Application

It has been demonstrated that droplets can be used as carriers to transport chemical species to a desired spot to complete certain tasks. However, the toxic solvents or materials used in these systems have limited the application in the area of biology, for example transporting living cells or drug delivery to living cells. The photoactive materials \( \text{SPCH}_2\text{CH}_2\text{OH} \) or \( \text{MCH}^+\text{DBS}^- \) are only soluble in organic solvents such as dichloromethane, 1,2-dichloroethane, chloroform and toluene, which are toxic to living systems. In order to use bio-friendly solvents like edible oil, fatty alcohol and fatty acid to construct organic droplets and move them in aqueous phases, new type of photoactive species, which are soluble in these solvents, need to be prepared. For \( \text{MC}_8\text{H}^+\text{SO}_3^- \) water droplets, which can be moved in fatty alcohol with light, all the solvents including water and fatty alcohols used in this system are bio-friendly. However, the strong acidity of \( \text{MC}_8\text{H}^+\text{SO}_3^- \) under 365 nm light is able to kill most living organisms, which limits its application in...
bio-systems. This was proven by attempts to move living cells with that droplet system. Unfortunately the cells did not survive the harsh environment within the droplet. A water soluble spiropyran or other species, which are less corrosive with and without light illumination, need to be design and synthesised. The light sources used in our systems to move droplets are 365 nm and 405 nm lights, which can damage bio-systems. To avoid using these short wavelength light sources, spiropyrans or other species, which can be photoactivated by a long wavelength light (for example, around 600 nm), need to be designed and prepared.

In droplet motion systems developed in this thesis, light energy is converted, through chemical energy, to the energy of motion. The force provided by light-induced IFT change is at nanonewton range. More useful larger forces could be generated by using more concentrated photoactive droplets, light sources with higher intensities, or other more efficient photoactive materials. The photoactive droplets could then be used as propulsion sources to provide the driving force under water.

The motion system of photoactive liquids in capillaries has potential to be used for light-driven pumps in microfluidics to replace traditional electrical or mechanical pumping systems. Before application in microfluidics as a light-driven pump, this system needs to be further optimised and the mechanism for the movement needs to be fully investigated.

8.3 References


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