Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information

Photocontrolled directional transport using water-in-oil droplets

Yang Xiao,[a,b] Nicolas Martino,[b] Klaudia Wagner,[a,b] Geoffrey M. Spinks,[a,b] David L. Officer[a,b]* and Pawel Wagner[a,b]*

[a] ARC Centre of Excellence for Electromaterials Science

[b] Intelligent Polymer Research Institute, AIIM Faculty, Innovation Campus, University of Wollongong, North Wollongong, NSW 2522, Australia.

E-mail: davido@uow.edu.au; pawel@uow.edu.au

Table of Contents

1 Experimental details

1.1 General methods

All solvents and reagents used for synthesis, chromatography and UV-visible absorption spectroscopy were purchased from Sigma-Aldrich, Tokyo Chemical Industry Co., Ltd. or Chem-Supply Pty Ltd unless otherwise specified. Solvents used for NMR analysis were purchased from Cambridge Isotope Laboratories. All the chemicals were used as received.

UV-visible 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 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.

Density of the droplet was measured by using a pycnometer at 24°C.

The interfacial tension (IFT) was measured using the pendant drop method and performed on a video-based optical contact angle measuring instrument (USA KINO SL200KS). The interfacial tension values were calculated automatically by the CAST3.0 tensiometer software using the Young-Laplace equation. The needle had a diameter of 1.83 mm.

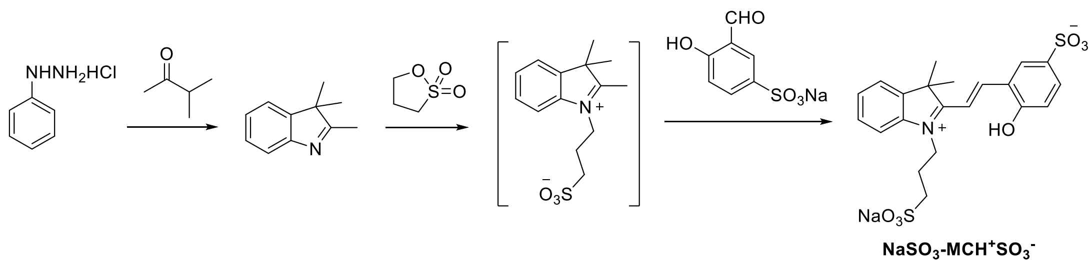
A 365 nm mounted LED (190 mW, M365L2, Thorlabs) equipped with a collimation adapter (SM1P25-A, Thorlabs) and a 405 nm laser pointer (63 mW) were used for light illumination.

All movies were obtained with an iPhone 6 smartphone or the high speed video camera (IDS UI-3370CP, IDS GmbH, Germany) on the goniometer.

Curves of IFT were smoothed with adjacent averaging method by using OriginPro 2015 data analysis and graphing software.

Equations related to force calculation were obtained by polynomial fit using OriginPro 2015.

1.2 Synthesis of $NaSO_3$-$MCH^+SO_3^-$



Scheme S1. Synthetic route to **$NaSO_3$-$MCH^+SO_3^-$**.

The sodium sulphonate-substituted merocyaninesulphonic acid (**$NaSO_3$-$MCH^+SO_3^-$**) was synthesised as depicted in Scheme S1. Phenylhydrazine hydrochloride was obtained by hydrochlorination of phenylhydrazine. 5-sulfosalicylaldehyde sodium salt was synthesized as reported.[1]

2,3,3-Trimethyl-3*H*-indole.[2, 3] Phenylhydrazine hydrochloride (14.43 g, 100 mmol) and 3-methyl-2-butanone (9.32 g, 108 mmol) were dissolved in ethanol (180 mL) at room temperature, and heated to reflux under nitrogen for 30 h. After evaporation under reduced pressure, the residue was purified on a silica gel column with hexane/ethyl acetate (7:1 to 1:1) as the eluent and dried in vacuo to afford 2,3,3-trimethyl-3*H*-indole as an orange oil (14.20 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) 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).

1'-(3-Sulfopropyl)-3',3'-dimethyl-6-sulfo-1',3'-dihydrospiro[chromene-2,2'-indole] sodium salt ($NaSO_3$-$MCH^+SO_3^-$). 2,3,3-Trimethyl-3*H*-indole (8.08 g, 51 mmol) and propane sultone (6.84 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-sulfosalicylaldehyde sodium salt (6.00 g, 27 mmol), the mixture was allowed to reflux for 28 h and then cooled to room temperature. The orange solid was collected by filtration, washed with ethanol, and dried in vacuo (7.78 g, 31% yield). ^{1}H NMR (400 MHz, DMSO-d_6) 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 (t, J = 7.4, 2H), 2.65 (t, J = 6.4, 2H), 2.19 (m, 2H), 1.79 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 182.3, 159.4, 150.4, 143.6, 141.0, 140.7, 132.9, 129.09, 129.05, 122.9, 120.1, 115.7, 115.2, 112.6, 52.0, 47.6, 45.8, 26.1, 24.4; UV–vis (DMSO) λ_{max} nm (log ε) 369 (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 $C_{21}H_{21}NNaO_7S_2$ [M-H]$^-$ 486.0662, found 486.0663.

1.3 ^{1}H NMR experiments

For characterization, ^{1}H NMR experiments were performed in DMSO-d_6 (Figure S1a). For light illumination experiment, **$NaSO_3$-$MCH^+SO_3^-$** was dissolved in D_2O (0.025 M) and the ^{1}H NMR spectra of this solution were obtained just after preparation, followed by 405 nm light illumination for 10 min (Figure S1b).

1.4 UV/Vis experiments

$NaSO_3$-$MCH^+SO_3^-$ was dissolved in DI water (3×10^{-5} M) and the UV/vis spectrum of this solution was obtained just after preparation, followed by 365 or 405 nm light illumination for 5 s and then in dark for 2 h, respectively (Figure S2).

2 Droplet experiments

2.1 Droplet movement

$NaSO_3$-$MCH^+SO_3^-$ 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 autopipette onto the bottom of a polystyrene Petri dish (5 cm) filled with fatty alcohol (~ 10 mL). On irradiation with 405 nm light, the droplet moved towards the light, in whichever direction the light was pointed (see Movie S1 and S2). All the fatty alcohols were saturated with water prior use.

2.2 Droplet swarm

The droplet suspension was prepared by shaking up the standard **$NaSO_3$-$MCH^+SO_3^-$**/H_2O (0.2 M) solution with cyclohexanol in a glass vial and then loaded into a glass cuvette with a pathlength of 10 x 10 mm. The suspension was illuminated by a 405 nm lamp from the front and the movie was taken from the side (Movie S3). It should be noted that the movie shows just one part of the suspension. The diameter of the largest droplet in the movie is measured to be 0.27 mm.

2.3 3D movement of a water droplet in cyclohexanol

$NaSO_3$-$MCH^+SO_3^-$ was dissolved in DI water to give a concentration of 0.2 M. A water droplet (1.0 mm diameter, 0.58 µL volume) was generated by loading the above solution using a syringe onto a polystyrene substrate in a glass cuvette (20 × 50 × 20 mm) filled with cyclohexanol (~ 16 mL). On irradiation with 405 nm light from the top, the droplet moved up towards the light (see Movie S4). An IDS camera was used to take videos with a speed of 91 fps.

2.4 Droplet chemistry

The moving droplet was 2 µL of **$NaSO_3$-$MCH^+SO_3^-$** aqueous solution (0.2 M) containing potassium iodide (2.5 M) and was placed into a polystyrene Petri dish filled with 1-hexanol. Using 405 nm light, the moving droplet was directed to and merged with a 2nd droplet containing 2 µL of 32% aqueous hydrogen peroxide solution to effect the chemical reaction as can be seen in Movie S8.

2.5 Observation of Marangoni currents

$NaSO_3$-$MCH^+SO_3^-$ was dissolved in DI water to give a concentration of 0.2 M. A water droplet (5 μL) was generated by loading the above solution using an autopipette onto the bottom of an acrylic cuvette (20 × 60 × 20 mm) filled with hexanol (~ 20 mL). A 405 nm laser was used to illuminate the droplet from the front (x direction-Movie S5), the top (y direction-Movie S6) or the side (z direction-Movie S7) as indicated in Figure 3b. At the same time, an IDS camera was used to take videos from the front (x direction) with a speed of 103 fps.

2.6 IFT measurements

The pendant drop method was used to measure the IFT of $NaSO_3$-$MCH^+SO_3^-/H_2O$ droplet in 1-hexanol and $NaSO_3$-$MCH^+SO_3^-/H_2O$ droplet in cyclohexanol with or without corresponding light illumination. IFTs of water/1-hexanol, and water/cyclohexanol were measured to be 7.0 and 2.6 mN m^{-1}, respectively.

3 Force calculations

The driving force originates from the photoinduced IFT change that occurs following initial light irradiation. The 3D movement of the **$NaSO_3$-$MCH^+SO_3^-$** 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. An IFT decrease for a **$NaSO_3$-$MCH^+SO_3^-$**$/H_2O$ (0.2 M) droplet in cyclohexanol of around 0.3 mN m^{-1} was observed over 4 s during 405 nm light irradiation (Figure S3b).

A **$NaSO_3$-$MCH^+SO_3^-$** organic droplet was added to cyclohexanol in a cuvette. To measure the irradiation force, a 405 nm light laser with a power of 2.7 mW and a beam size of around 2.5 × 1.5 mm, was used to move this droplet up towards light under water. For the **$NaSO_3$-$MCH^+SO_3^-$**$/H_2O$ droplet moving up towards 405 nm light source in cyclohexanol, according to Newton's second law:

$$\sum F = \frac{dp}{dt} \qquad (1)$$

with F the force applied to the droplet and *p* the momentum of the droplet of mass *m* and moving with velocity *v*.

$$p = mv \qquad (2)$$

$$\sum F = F_i + F_b - G - F_v \qquad (3)$$

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 S4a).

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

$$F_i = G + F_v - F_b + m\frac{dv}{dt} \qquad (4)$$

The equation for gravity is

$G = m_d\, g = \rho_d\, V_d\, g$ (5)

where m_d is the mass of the droplet, ρ_d is the density of the droplet (1.0547 g mL^{-1}), V_d is the volume of the droplet 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 ρ_l is the density of cyclohexanol (0.9624 g mL^{-1}).

The Stokes drag force (F_v) as described[4] for a small soft sphere moving through a viscous fluid is given by

$F_v = 5\pi R \eta v$ (7)

where η is the viscosity of cyclohexanol surrounding the droplet, which is 41.07 mPa s.[5]

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

$F_i = (\rho_d - \rho_l)\, V_d\, g + 5\pi R \eta v + m\frac{dv}{dt}$ (8)

Using the above equations, the gravity and buoyant forces of a **$NaSO_3$-$MCH^+SO_3^-$**/H_2O droplet with a volume of 0.58 µL (1.0 mm in diameter) moving up towards 405 nm light under cyclohexanol were calculated to be 6.0 and 5.5 µN, respectively. By analyzing Movie S3 with Tracker 5.0 software, the vertical distance travelled by the droplets was determined (Figure S4b). This data was fitted with a polynomial function and differentiated to determine the velocity-time profile (Figure S4c). A further polynomial curve fit and differentiation gave the acceleration (*dv/dt*) so that equation (8) could be solved to obtain the irradiation force as a function of time (Figure S4d).

Solving for Equation 8 gives a maximum driving force of 1.1 µN, diminishing to around 0.5 µN over a few seconds.

4 Supplementary figures

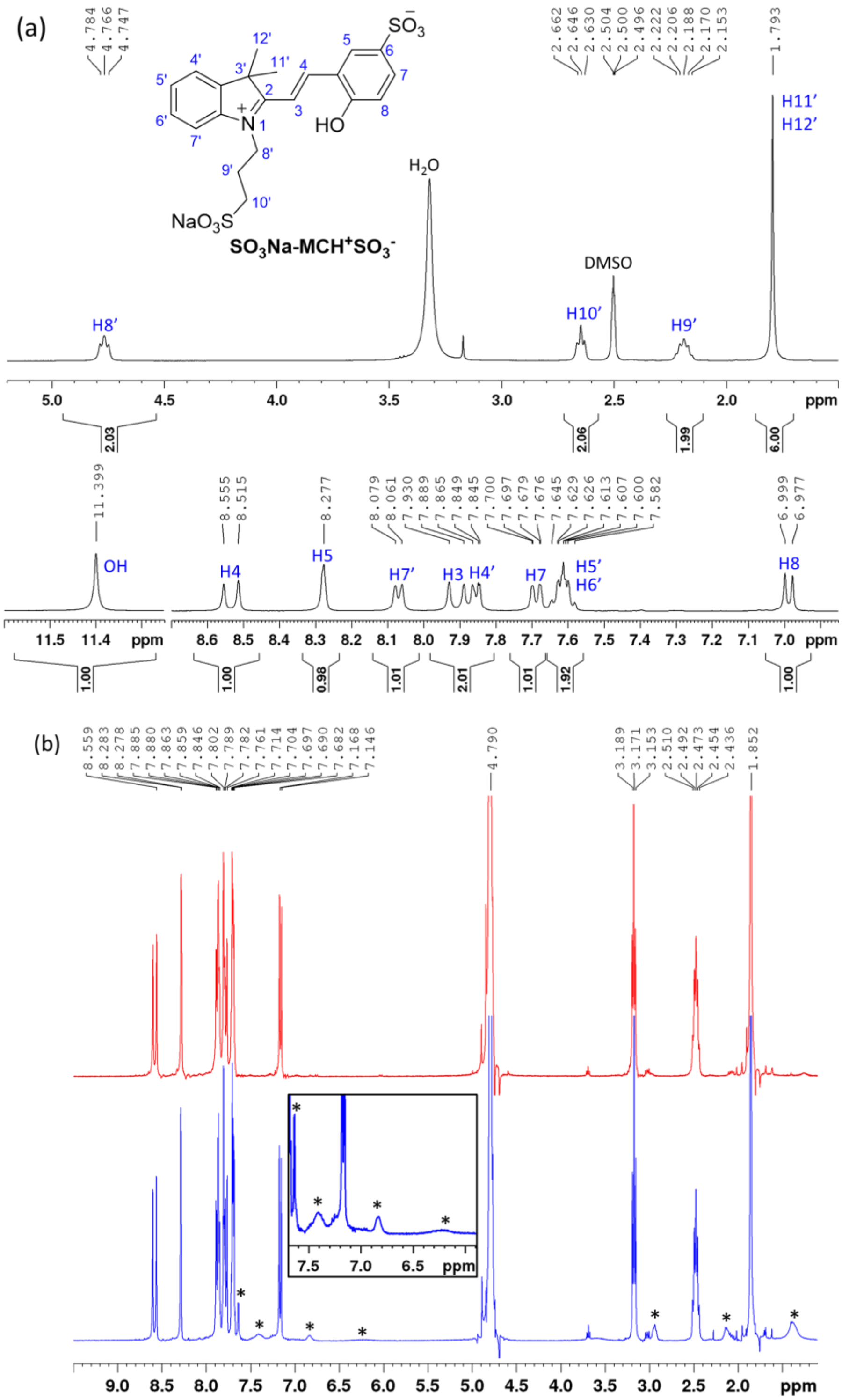


Figure S1. (a) ^{1}H NMR spectrum of **NaSO$_3$-MCH$^+$SO$_3^-$** in DMSO-d_6. (b) ^{1}H NMR spectra of **NaSO$_3$-MCH$^+$SO$_3^-$** in D_2O after preparation (red line), followed by 405 nm light illumination for 10 min (blue line). The signals for NaSO$_3$-SPSO$_3$H generated by 405 nm light irradiation are indicated by the asterisks and are of low intensity due to the rapid conversion of NaSO$_3$-SPSO$_3$H back to **NaSO$_3$-MCH$^+$SO$_3^-$** in the dark during data collection.

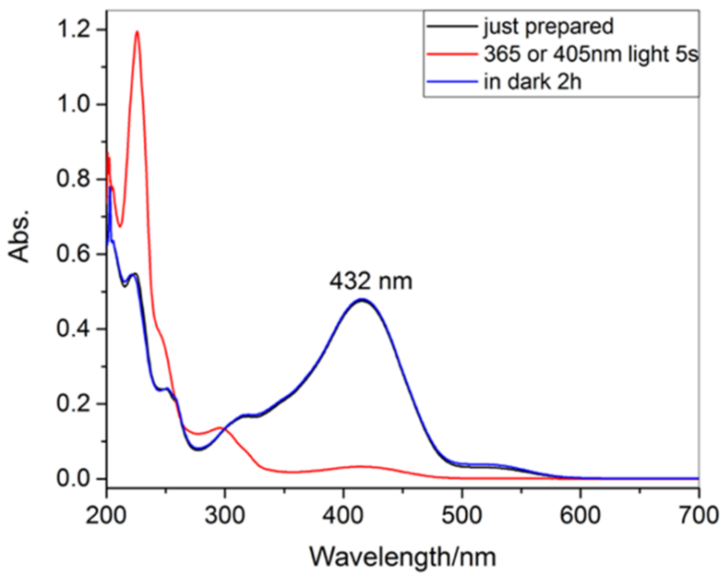


Figure S2. UV/visible spectra of the freshly prepared **$NaSO_3$-$MCH^+SO_3^-$** aqueous solution (3×10^{-5} M) showing the initial characteristic absorption of MCH^+ at 432 nm (black line), followed by irradiation with 365 nm or 405 nm light for 5 seconds (red line), and then in dark for 2 h.

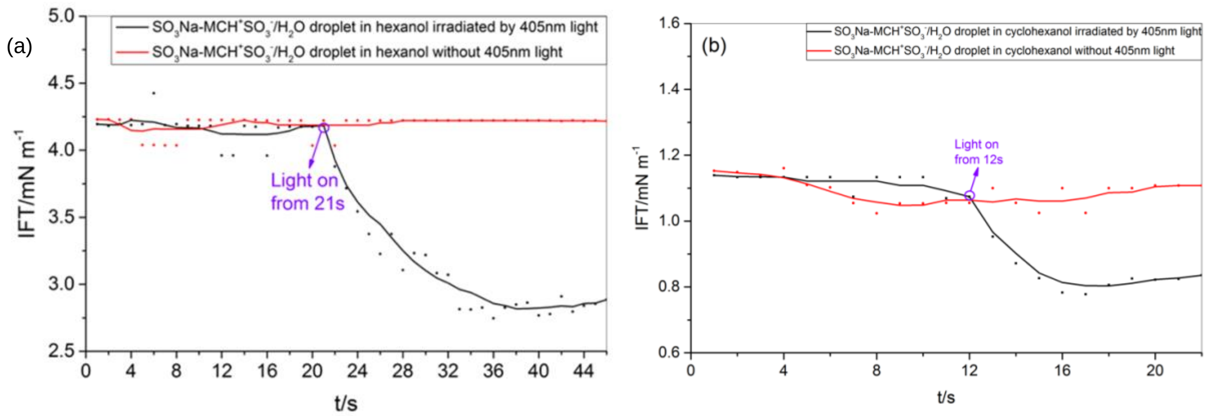


Figure S3. IFT measured by the pendant drop method for **$NaSO_3$-$MCH^+SO_3^-$**/H_2O droplet (0.2 M) in (a) 1-hexanol and (b) cyclohexanol without 405 nm light illumination (red line) and with 405 nm light illumination from (a) 21 s and (b) 12 s (black line). The curves were smoothed by adjacent averaging of 10 points for (a) and 4 points for (b).

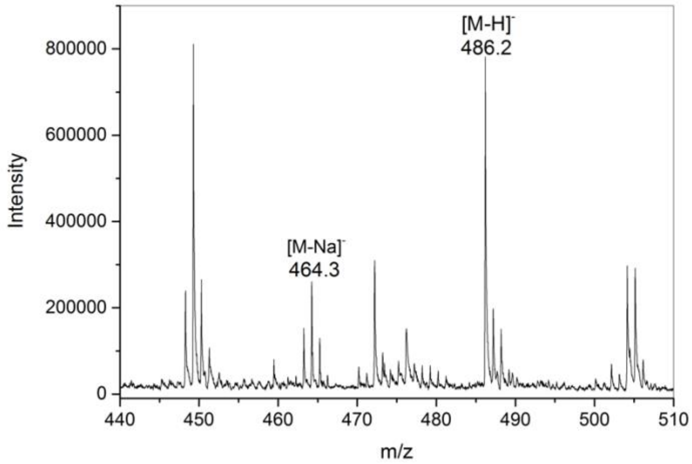


Figure S4. MALDI-TOF MS spectrum for the plume generated by moving **$NaSO_3$-$MCH^+SO_3^-$** (M = 487) water droplets in hexanol.

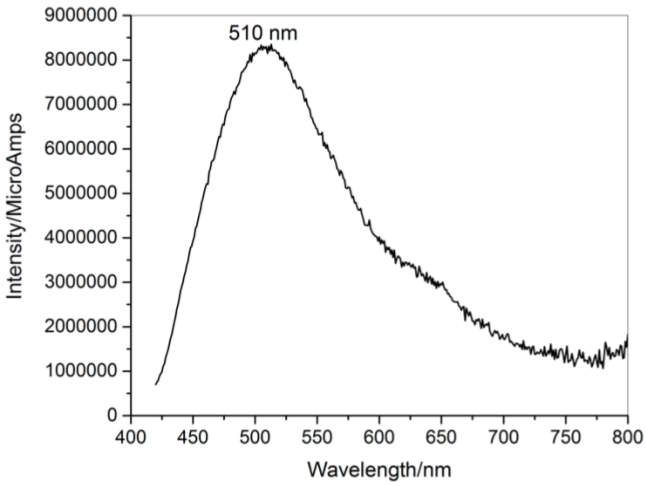


Figure S5. Fluorescence emission spectrum of the plume generated by moving **$NaSO_3$-$MCH^+SO_3^-$** water droplets in hexanol.

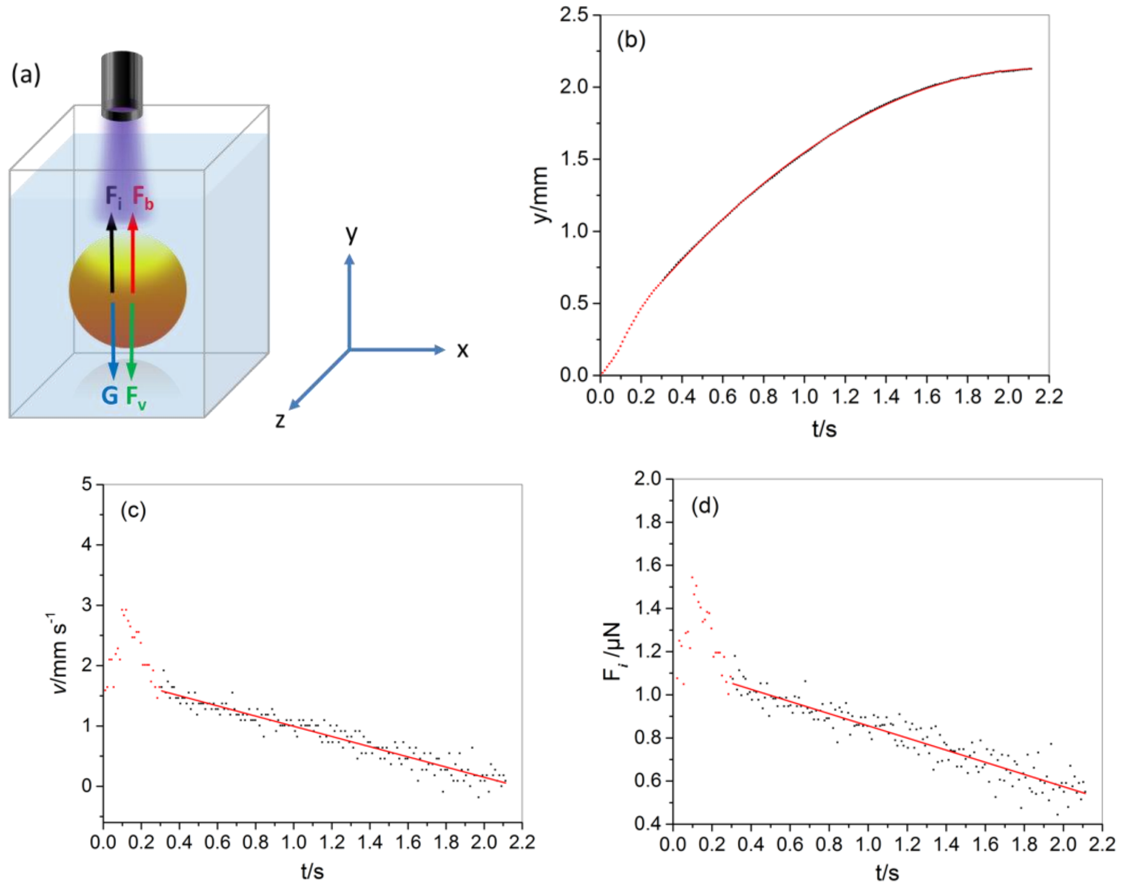


Figure S6. (a) Force analysis for a **$NaSO_3$-$MCH^+SO_3^-$** droplet moving up in cyclohexanol under light illumination. Plots of (b) vertical distance (y) travelled versus time (t) fitted with the polynomial function $y = 0.13 + 1.84\ t - 0.42\ t^2$ giving an adjusted R^2 of 0.9999, (c) velocity (v) versus time (t) obtained from (b) and fitted with linear function $v = 1.84 – 0.84\ t$ giving an adjusted R^2 of 0.9155 and (d) the force resulting from IFT change (F_i) versus time (t) obtained from (c) and fitted with linear function $F_i = 1.14 – 0.28\ t$ giving an adjusted R^2 of 0.8813 for a 0.58 μL **$NaSO_3$-$MCH^+SO_3^-$** 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.

5 Supplementary movies

Movie S1

Movie of the light (405 nm) activated movement of a 2 µL **$NaSO_3$-$MCH^+SO_3^-$**/H_2O (0.2 M) droplet in 1-hexanol.

Movie S2

Movie of the controlled movement of a 2 µL **$NaSO_3$-$MCH^+SO_3^-$**/H_2O (0.2 M) droplet under 405 nm light illumination in 1-hexanol showing the effect of changing the light direction.

Movie S3

Swarming of **$NaSO_3$-$MCH^+SO_3^-$**/H_2O (0.2 M) droplets (diameter < 0.27 mm) towards a 405 nm light source in cyclohexanol in a fluorescence cuvette (pathlength 10x10 mm).

Movie S4

Movie of the controlled 3D movement of a 0.58 µL **$NaSO_3$-$MCH^+SO_3^-$**/H_2O (0.2 M) droplet up towards 405 nm light source in cyclohexanol. The velocity of the droplet motion in the video is 1.5 times slower than the real velocity.

Movie S5

Movie of the Marangoni convection flow inside a 5 µL **$NaSO_3$-$MCH^+SO_3^-$**/H_2O (0.2 M) droplet in 1-hexanol irradiated by a 405 nm laser from the front (x direction, Figure 3b). The flow in the movie is 5 times slower than its real speed.

Movie S6

Movie of the Marangoni convection flow inside a 5 µL **$NaSO_3$-$MCH^+SO_3^-$**/H_2O (0.2 M) droplet in 1-hexanol irradiated by a 405 nm laser from the top (y direction, Figure 3b). The flow in the movie is 5 times slower than its real speed.

Movie S7

Movie of the Marangoni convection flow inside a 5 µL **$NaSO_3$-$MCH^+SO_3^-$**/H_2O (0.2 M) droplet in 1-hexanol irradiated by a 405 nm laser from the side (z direction, Figure 3b). The flow in the movie is 5 times slower than its real speed.

Movie S8

Movie of the light (405 nm) directed collision of a 2 µL **$NaSO_3$-$MCH^+SO_3^-$**/H_2O (0.2 M) droplet containing KI (2.5 M) with a droplet of 32% aqueous H_2O_2 (2 µL) under 1-hexanol.

6 References

(1) Kirker, G. W. AN EFFICIENT SYNTHESIS OF 5-SULFOSALICYLALDEHYDE SODIUM SALT. *Org. Prep. Proced. Int.* **1980,** *12* (3-4), 246-249, DOI: 10.1080/00304948009458562.

(2) Tomasulo, M.; Kaanumal, S. L.; Sortino, S.; Raymo, F. M. Synthesis and Properties of Benzophenone−Spiropyran and Naphthalene−Spiropyran Conjugates. *J. Org. Chem.* **2007,** *72* (2), 595-605, DOI: 10.1021/jo062004d.

(3) Gossweiler, G. R.; Hewage, G. B.; Soriano, G.; Wang, Q.; Welshofer, G. W.; Zhao, X.; Craig, S. L. Mechanochemical Activation of Covalent Bonds in Polymers with Full and Repeatable Macroscopic Shape Recovery. *ACS Macro Lett.* **2014,** *3* (3), 216-219, DOI: 10.1021/mz500031q.

(4) Maass, C. C.; Krüger, C.; Herminghaus, S.; Bahr, C. Swimming Droplets. *Annu. Rev. Condens. Matter Phys.* **2016,** *7* (1), 171-193, DOI: 10.1146/annurev-conmatphys-031115-011517.

(5) Oswal, S. L.; Ghael, N. Y.; Prajapati, K. D. Speeds of sound, isentropic compressibilities, viscosities and excess molar volumes of cyclohexanol+cyclohexane at 303.15K. *Thermochim. Acta* **2004,** *419* (1), 59-65, DOI: https://doi.org/10.1016/j.tca.2004.01.034.