SUPPLEMENTARY INFORMATION

Depinning of Multiphase Fluid Using Light and Photo-Responsive Surfactants

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Synthesis of SP-DA-PEG

SP-DA-PEG was prepared as described in the Methods section of the main text from SP-NBD (634 mg, 1.01 mmol, 1.53 eq) and mal-PEG (528 mg, 0.660 mmol, 1.00 eq) to afford the desired SP-DA-PEG (475 mg, 0.342 mmol, 52%) as green/pink viscous liquid. 1H NMR (600 MHz, CDCl3) 8.02–8.00 (m, 2H), 7.20 (t, 1H), 7.08 (d, 1H), 6.93 (dd, 1H), 6.89 (t, 1H), 6.75 (d, 1H), 6.67(d, 1H), 5.89 (d, 1H), 4.68 (dd, 1H), 4.30 (dd, 1H) 4.27–4.19 (m, 4H), 3.64 (m, 47H), 3.55–3.53 (m, 2H), 3.38 (s, 3H), 2.63–2.54 (m, 4H), 2.48–2.45 (m, 2H), 2.19–2.14 (m, 1H), 1.82–1.77 (m, 1H), 1.71 (d, 1H), 1.50–1.47 (m, 2H) 1.37–1.18 (m, 9H), 1.17 (s, 3H), 0.87 (t, 3H). Mn(NMR) = 1390 g/mol. The pump-probe kinetics measurements of SP-DA-PEG are presented in Figure S1b-c and demonstrate the rapid response and excellent reversibility of SP-DA-PEG.¹

Figure S1. Characterization of SP-DA-PEG. (a)¹H NMR (600 MHz, CDCl₃) SP-DA-PEG. Pump probe kinetics measurements of SP-DA-PEG in (b) water and (c) toluene irradiated with 365 nm light.
Temperature rise of droplets due to direct laser heating

To eliminate the possible effect of thermal Marangoni effect induced by the direct laser on the toluene droplet, we carried out finite element simulations to study the temperature change of the toluene droplet when it is heated by the UV laser. The droplet outline is directly extracted from our experiments on a 11 μL droplet. A uniform volumetric heating is applied on the top region of the droplet at t = 0 s to mimic the laser heating, since surfactants exist both in the bulk and the interface. The heating power is set to be 0.06 W. The temperature change of the toluene droplet before the droplet departure at t = 0.38 s is shown in Figure S2. Despite the high laser power density (2.8 W/cm²), the temperature rise of the toluene droplet is limited to 0.25 °C in 0.38 s.

Figure S2. The temperature contours of the toluene droplets under direct laser heating before departing.
We further measured the temperature rise of the toluene droplet using a K-type thermocouple probe. The experimental setup is shown in Figure S3a. In this time, we generate a small toluene droplet that could not depart even with the photo-Marangoni effect. A K-type thermocouple probe is placed in the top region of the toluene droplet and the temperature is recorded once per second. In Figure S3b, it is shown that the droplet temperature is fluctuating around 23.2 ℃. This is because the droplet temperature quickly reaches its equilibrium distribution within 1 second according to our simulation results.

Figure S3. Measuring the temperature rise of the droplet top. (a) Experimental setup to measure temperature of the top of the toluene droplet. (b) The measured temperature change after the UV laser is turned on.

Temperature rise of bubbles due to UV LED irradiation

The departure of air bubbles immersed in the 0.1 mM toluene solution is also subject to the possible effect of thermal Marangoni flow. Therefore, we used a K-type thermocouple probe to measure the temperature variations of the toluene solution after the UV LED is turned on, as shown in Figure S4. After one minute of direct UV LED heating, the solution temperature is increased only by 0.5 ℃. Therefore, the effect of temperature variations on bubble dynamics can be neglected.
Effect of apparent contact angle

As discussed in the manuscript, in the extreme case of microgravity applications, or of immiscible fluids with matched densities where buoyancy is negligible, the criterion for the photo-Marangoni force to overcome the totality of the pinning surface force is

\[ \Delta \gamma \sin^2 \varphi \geq \frac{\Delta \gamma}{\gamma} \sin^2 \varphi, \]

where \( \varphi \) is the contact angle, \( \Delta \gamma \) is the difference in surface tension across the droplet, and \( \gamma \) is the surface tension at the droplet base. It can be seen that the lower the contact angle \( \varphi \), the easier for this criterion to be satisfied since the right-hand-side of this equation is smaller.

To experimentally verify the effect of the apparent contact angle \( \varphi \), we compared the departure behaviors of a toluene drop and an \( m \)-xylene drop in water. Figure S5a presents time-lapse images of a toluene droplet (0.1 mM SP-DA-PEG) solution departing in \( t_{\text{d,t}} = 2.04 \text{ s} \). The droplet has a volume of 10.98 mL and a UV laser with intensity of 29.08 mW/mm\(^2\) is applied on the top of the droplet. The apparent contact angle is measured to be \( \varphi_t = 43.2^\circ \). In Figure S5b, we produced a 0.1 mM \( m \)-xylene droplet in DI water. The droplet has a volume of 11.33 mL and an apparent contact angle of \( \varphi_t = 50.9^\circ \). Figure S5b shows that the \( m \)-xylene droplet departs from the substrate in \( t_{\text{d,x}} = 3.26 \text{ s} \), a 60% percent increase compared to \( t_{\text{d,t}} \). Since \( m \)-xylene and toluene share similar physical and interfacial properties (density, viscosity, surface tension, etc.) due to their similar molecular structure, if we assume that the interfacial tensions of \( m \)-xylene-water and toluene-water are similar, the increase of the apparent contact angle leads to a stronger vertical component of the pinning force \( F_{\text{pin,vertical}} \sim \gamma d_b \sin^2 \varphi \) and hence delays the droplet departure.
Figure S5. Time-lapse images of droplet departure with different contact angles. (a) The toluene droplet exhibiting an apparent contact angle of $43.2^\circ$ departs in 2.04 s. (b) The $m$-xylene droplet exhibiting an apparent contact angle of $50.9^\circ$ departs in 3.26 s.

Reference:
(1) Seshadri, S.; Bailey, S. J.; Zhao, L.; Fisher, J.; Sroda, M.; Chiu, M.; Stricker, F.; Valentine, M. T.; Read de Alaniz, J.; Helgeson, M. E. Influence of Polarity Change and Photophysical Effects on Photosurfactant-Driven Wetting. *Langmuir* **2021**, *37* (33), 9939–9951. https://doi.org/10.1021/acs.langmuir.1c00769.
Description of Additional Supplementary Files

File Name: Supplementary Movie 1
Description: **Swift departure of the toluene droplet activated by a UV laser.** A toluene solution droplet (0.1 mM SP-DA-PEG) is irradiated by an Argon Ion UV laser (351.1+363.8 nm, beam diameter of 1.3 mm, incidental light power density of 44 mW/cm²) and the video is recorded by a Canon EOS 80D camera. The movie is played in real time.

File Name: Supplementary Movie 2
Description: **Flow visualization inside a 0.1 mM toluene solution droplet.** A toluene solution droplet is irradiated by an Argon Ion UV laser (351.1+363.8 nm, beam diameter of 1.3 mm, incidental light power density of 44 mW/cm²) and the video is recorded by a Phantom VEO 640L camera. The movie is played at 4X speed. Particles are flowing downward near the interface and moving upward near the center. Particle circulation is immediately expedited by the Marangoni convection once the UV laser is turned on. Eventually the droplet departed.

File Name: Supplementary Movie 3
Description: **Flow visualization inside a 0.1 mM toluene solution droplet.** A toluene solution droplet is irradiated by an Argon Ion UV laser (351.1+363.8 nm, beam diameter of 1.3 mm, incidental light power density of 44 mW/cm²) and the video is recorded by a Phantom VEO 640L camera. The movie is played at 4X speed. Particles are flowing downward near the interface and moving upward near the center when the UV laser is turned on the photo-Marangoni flow takes effect.

File Name: Supplementary Movie 4
Description: **Droplet departure under UV irradiation at different heights.** A toluene solution droplet (11.5 µL, 0.1 mM SP-DA-PEG) is irradiated by a fiber-coupled UV LED (M365FP1, Thorlabs, Inc.). On the left panel, the UV LED is aligned at the top of the droplet. On the right panel, the UV LED is aligned at the bottom of the droplet. Both videos are played at 5X speed.