

Supporting Information

Pickering emulsions responsive to CO₂/N₂ and light dual stimuli at ambient temperature

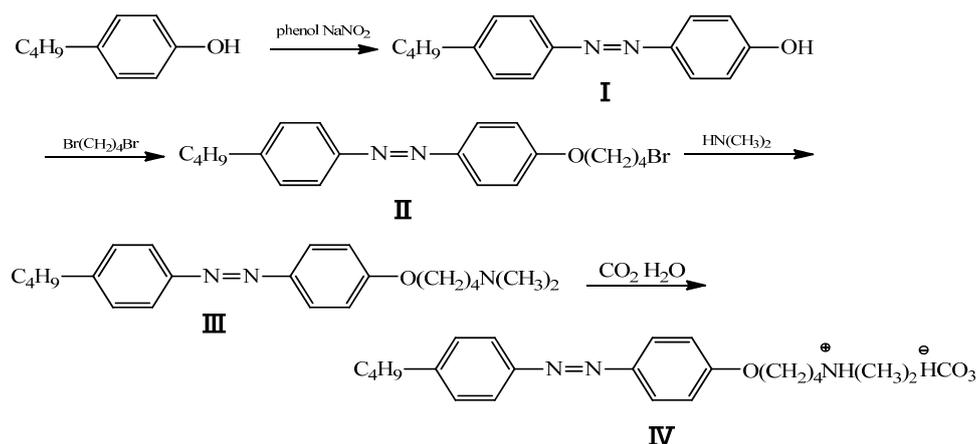
Jianzhong Jiang,^{a*} Yuxuan Ma,^a Zhenggang Cui^{a*} and Bernard P. Binks^{b*}

^a *The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education,
School of Chemical and Material Engineering, Jiangnan University, PR China*

^b *Department of Chemistry, University of Hull, Hull HU6 7RX, UK*

1. Synthesis of AZO-B4 surfactant

The synthetic route for the surfactant 4-butyl-4'-(4-N, N-dimethylbutoxyamine) azobenzene (AZO-B4) is shown in Scheme S1, which involves four reaction steps and three intermediates (I, II, and III).



Scheme S1. Synthesis route of the surfactant AZO-B4.

1.1 Synthesis of intermediate III

The intermediate II, 4-butyl-4'-(3-bromopropoxy) phenyl) azobenzene, was synthesized as described in the literature.¹ An excess of K₂CO₃ (0.045 mol) and dimethylamine solution (0.15 mol) were placed in acetone (20 mL). To this solution, 10 mL solution of II in acetone (3 M) was added and left to react at room temperature for 72 h. The reaction mixture was filtered and the solvent was removed by rotary evaporation. The residue was put into 150 mL deionized water and extracted three times with dichloromethane. The dichloromethane layer was collected and evaporated. The residue was further purified by column chromatography of silica gel and the brown product was then obtained at a yield of 68%. ¹H NMR (400 MHz, DMSO) δ 7.86 (d, *J* = 8.9 Hz, 2H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 9.0 Hz, 2H), 4.08 (s, 2H), 2.66 (s, 2H), 2.25 (s, 2H), 2.11 (d, *J* = 12.4 Hz, 6H), 1.76 (s, 2H), 1.57 (s, 4H), 1.32 (s, 2H), 0.91 (s, 3H). MS *m/z* = 354.2 (M+H⁺).

1.2 Synthesis of target product IV

The target product, AZO-B4, was synthesized by bubbling CO₂ into an aqueous solution of the intermediate III, as described in the literature.²

References

1. E. Chevallier, C. Monteux, F. Lequeux and C. Tribet, *Langmuir*, 2012, **28**, 2308.
2. Y. Liu, P.G. Jessop, M. Cunningham, C.A. Eckert and C.L. Liotta, *Science*, 2006, **313**, 958.

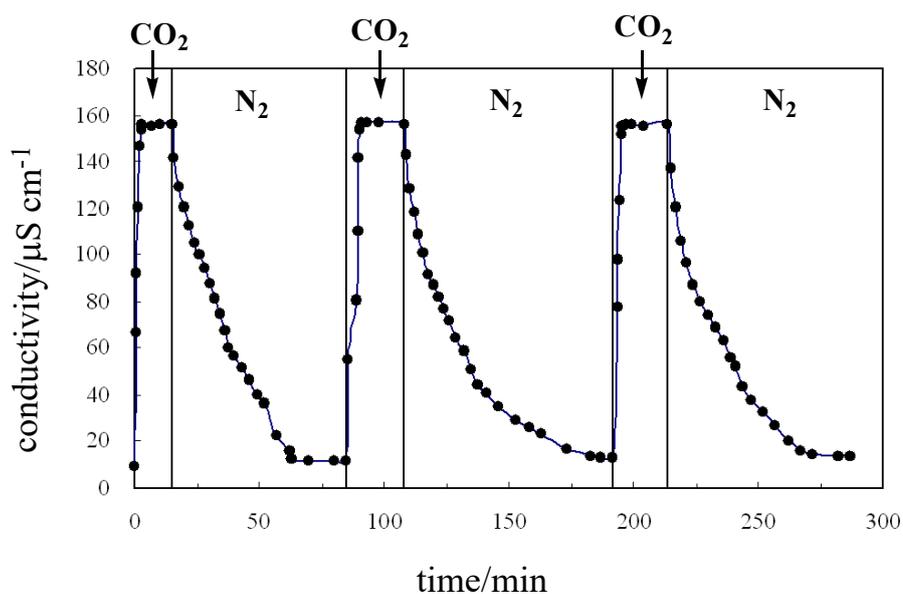


Figure S1. Conductivity of an aqueous acetone solution (50 vol.%) of 5 mM AZO-B4 as a function of the time of bubbling with CO_2 (30 mL/min) followed by bubbling with N_2 (100 mL/min) alternately at 20 °C (three cycles).

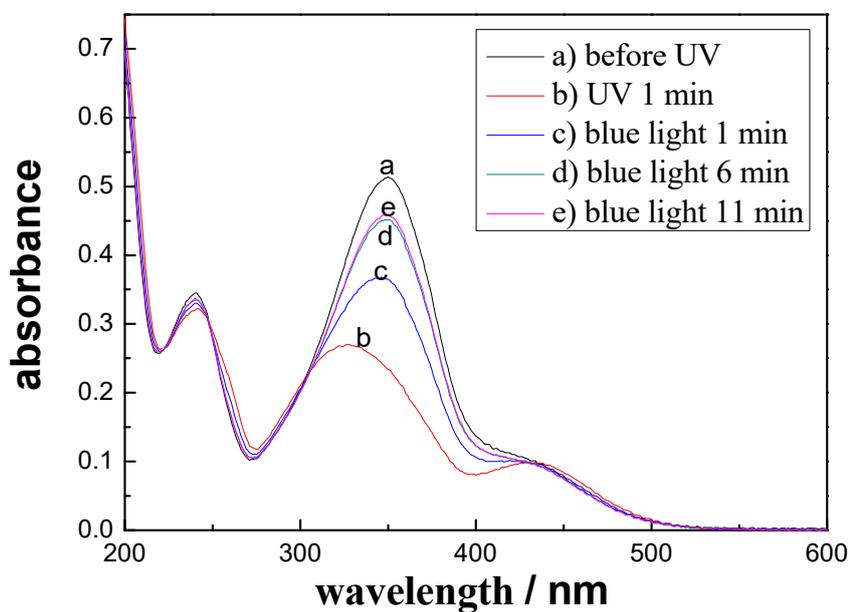


Figure S2. UV-Vis. spectra of 0.03 mM AZO-B4 aqueous solution before and after UV irradiation and after irradiation with blue light with water as reference.

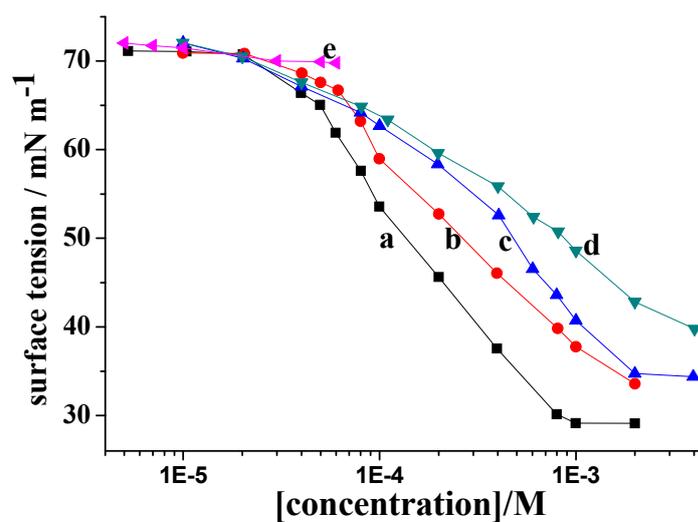


Figure S3. Surface tension of aqueous solutions of AZO-B4 without and with 0.1 wt.% silica nanoparticles as a function of initial surfactant concentration at 25 °C. (a) before UV irradiation without silica, (b) before UV irradiation with silica, (c) after UV irradiation without silica, (d) after UV irradiation with silica, (e) neutral form without silica.

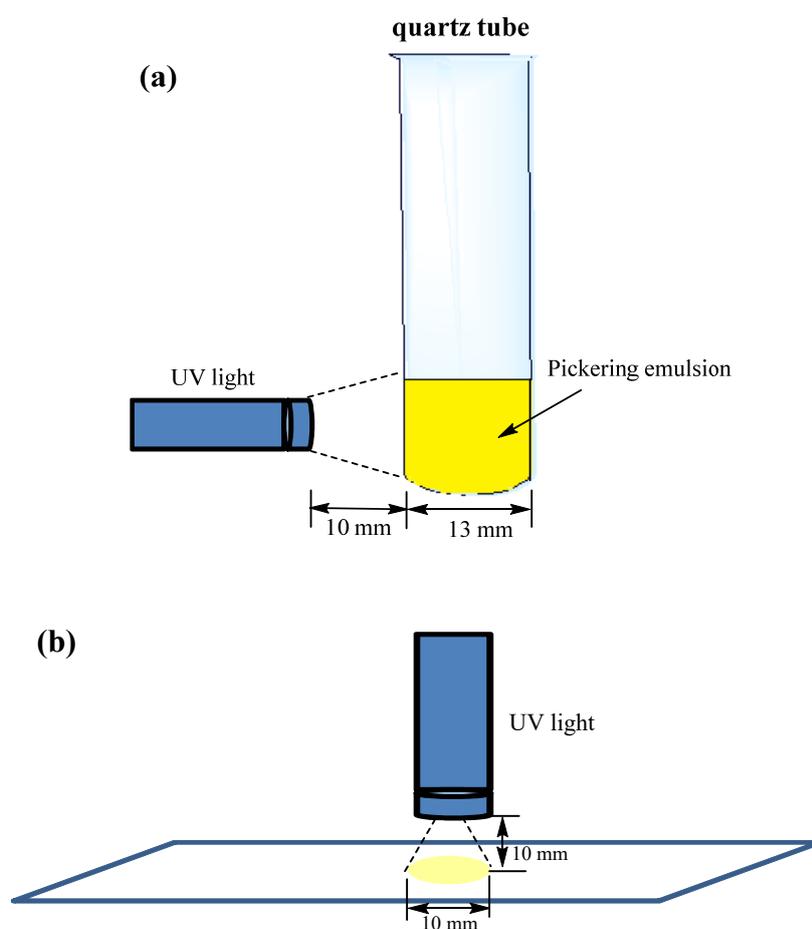


Figure S4. Illustration of light irradiation. (a) Pickering emulsion (2 mL) in a quartz vessel (diameter = 1.3 cm) was irradiated with UV light in a dark room; (b) droplets of the Pickering emulsion were placed on a glass slide for irradiation with UV light from above.

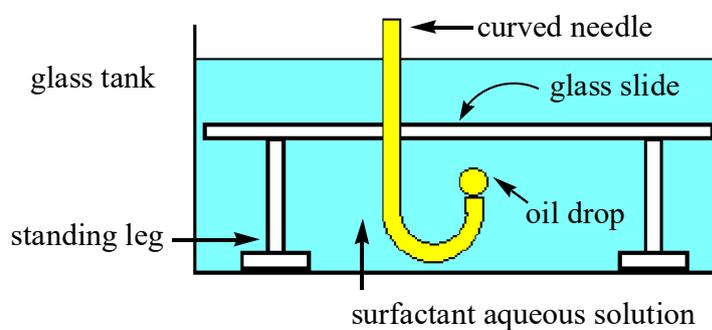


Figure S5. Schematic diagram of setup for contact angle measurement.

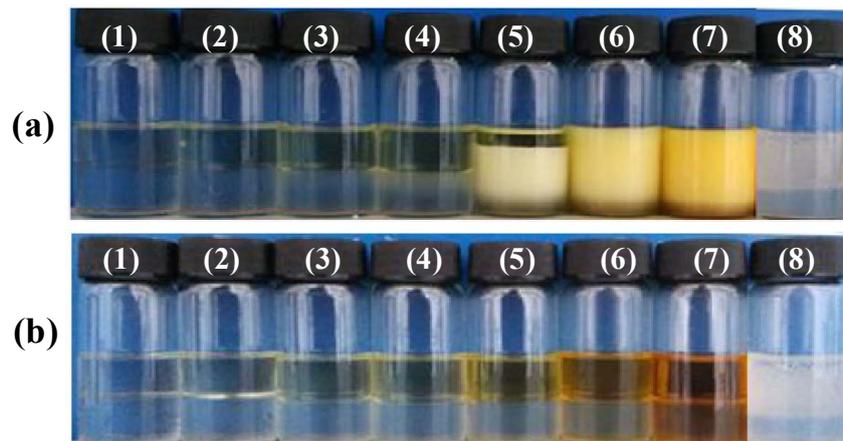


Figure S6. Photographs of *n*-octane-in-water emulsions ($7 \text{ cm}^3/7 \text{ cm}^3$) stabilised by *trans*-AZO-B4 surfactant alone, taken (a) 1 h and (b) 1 week after preparation. Concentration of *trans*-AZO-B4 in the aqueous phase from (1) to (7) is 0.01, 0.04, 0.08, 0.1, 0.3, 1.0 and 3.0 mM, respectively. Vessel (8) contains an *n*-octane-in-water emulsion ($7 \text{ cm}^3/7 \text{ cm}^3$) stabilized by 0.5 wt.% silica nanoparticles alone.

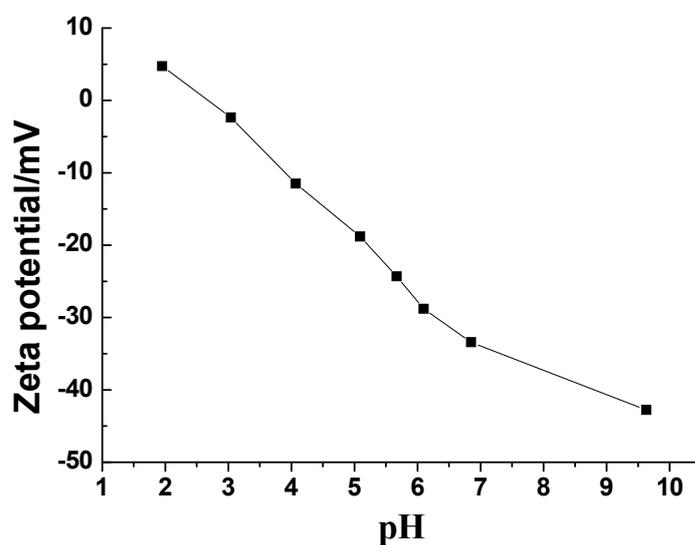


Figure S7. Zeta potential of 0.1 wt.% silica nanoparticles as a function of pH value in water.

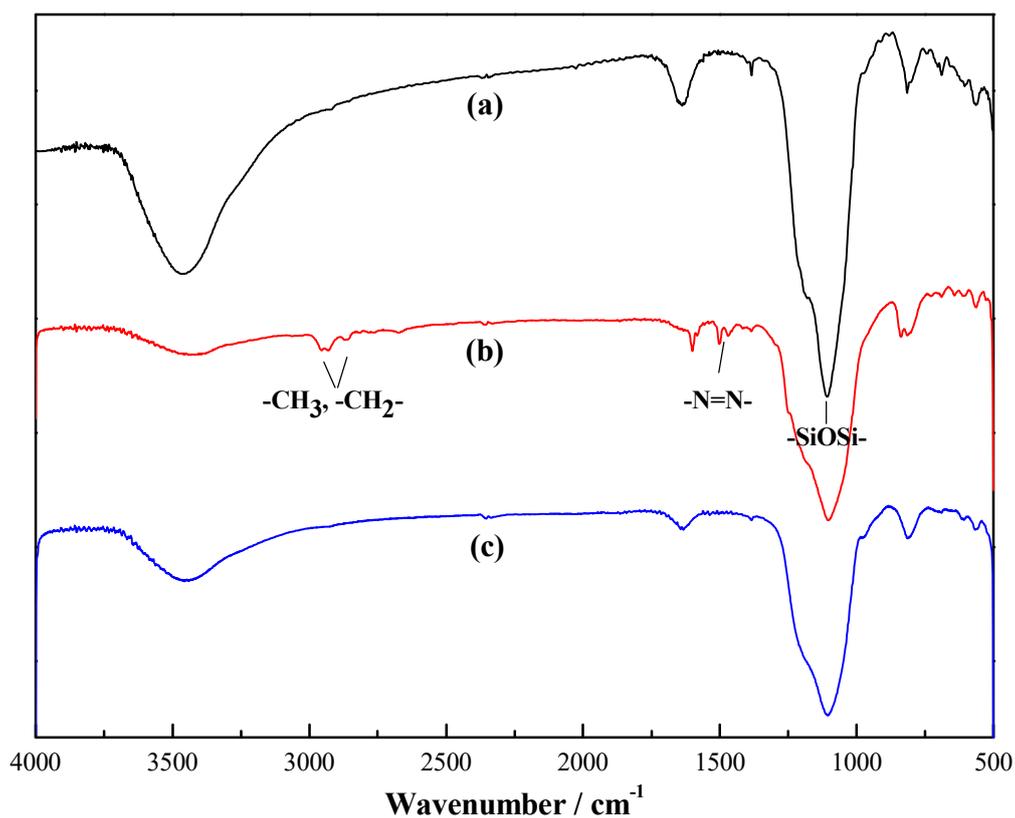


Figure S8. FTIR characterization of the silica nanoparticles. (a) Bare silica before contact with surfactant; (b) silica nanoparticles separated from an aqueous dispersion of 0.5 wt.% particles in 3×10^{-4} mol/L surfactant; (c) silica nanoparticles separated from an aqueous dispersion of 0.5 wt.% particles in (3×10^{-4} mol/L) surfactant after bubbling with N_2 .

The spectra need a y-axis label and numbers

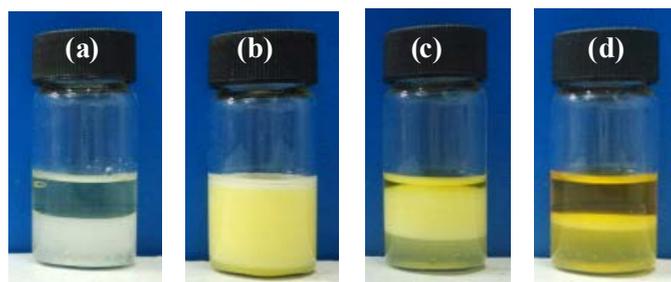


Figure S9. Photographs of *n*-octane-in-water emulsions ($7 \text{ cm}^3/7 \text{ cm}^3$) stabilized by *trans*-AZO-B4 alone: (a) 0.06 mM immediately after preparation and (b)-(d) 0.6 mM taken (b) immediately after preparation, (c) 1.5 h after preparation and (d) after 1.5 h of UV irradiation of sample (b).

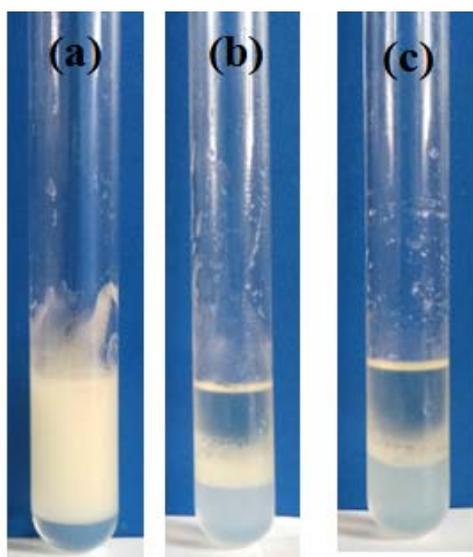
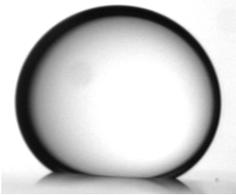
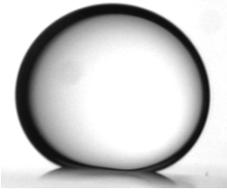
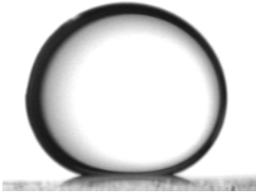
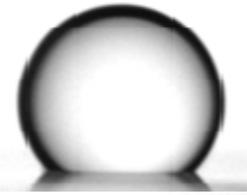
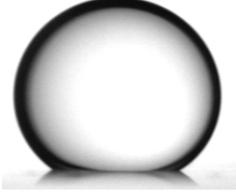
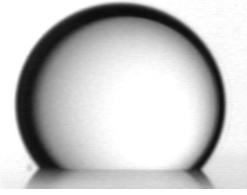
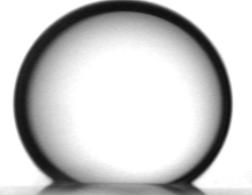
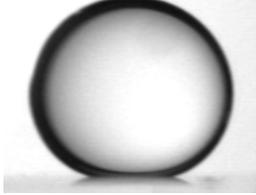
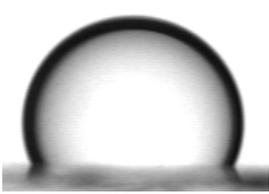
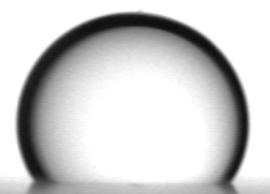
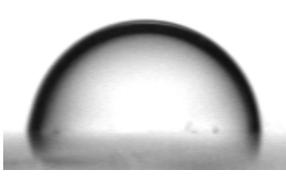
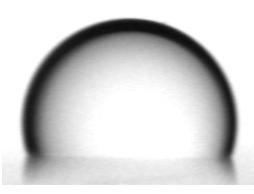
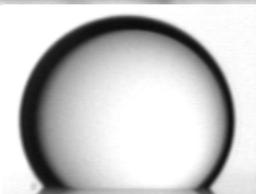
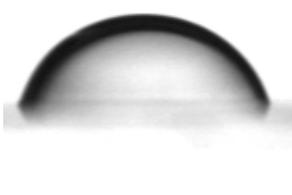
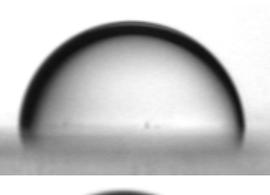
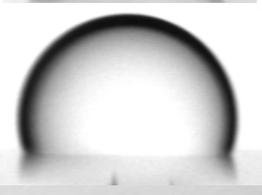


Figure S10. Photographs of *n*-octane-in-water emulsions ($7 \text{ cm}^3/7 \text{ cm}^3$) in quartz vessels. (a) Before any stimuli, (b) bubbling N_2 at $35 \text{ }^\circ\text{C}$ for 40 min, (c) bubbling N_2 in conjunction with UV irradiation at $35 \text{ }^\circ\text{C}$ for 30 min.

Table S1. Inverted photographs of octane drops captured by glass strip immersed in aqueous solutions of AZO-B4 at 25 °C.

[AZO-B4]/ mM	Before UV irradiation	After UV irradiation	AZO-B4 in neutral amine state (inactive form)
0.003			
0.006			
0.01			
0.03			
0.06			
0.10			
0.30	