Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information

Smart worm-like micelles responsive to CO_2/N_2 and light dual stimuli

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1. Experimental

1.1. Materials

4-butyl-4’-(6-N,N-dimethylhexyloxyamine) azobenzene bicarbonate (herein referred to as AZO-B6) was synthesized in our lab. as described below. Cetyltrimethyl ammonium bromide (CTAB, ≥ 99.5%) and sodium salicylate (NaSal, ≥ 99.0%) were purchased from Sinopharm Chemical Reagent LTD and used without further purification. Pure water with a resistance of 18.2 MΩ cm and a pH of 6.1 at 25 °C was produced from a Simplicity Pure Water System (Merck Millipore).

1.2 Synthesis of AZO-B6

The synthetic route of 4-butyl-4′-(6-N,N-dimethylhexyloxyamine) azobenzene surfactant (AZO-B6) is shown in Scheme S1.

1.2.1 Synthesis of 4-butyl-4′-(6-N,N-dimethylhexyloxyamine) azobenzene (AZO-B6)

4-butyl-(4’-(6-bromohexyloxy) phenyl) azobenzene was synthesized as described in the literature.[1] An excess of K_2CO_3 (1.51 g, 0.01089 mol) and dimethylamine (33%, 4.96 g, 0.0363 mol) aqueous solution were placed in acetone (20 mL). To this solution, 4-butyl-(4’-(6-bromohexyloxy) phenyl) azobenzene (3.0 g, 0.00726 mol) which dissolved in 10 mL acetone solution was added and the mixture was allowed to react at room temperature for 72 h. The reaction mixture was then 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. Yield 68%. ^{1}H NMR (400 MHz, CDCl3) δ 7.92 – 7.85 (m, 2H), 7.79 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 7.02 – 6.95 (m, 2H), 4.03 (t, J = 6.5 Hz, 2H), 2.72 – 2.62 (m, 2H), 2.27 (dd, J = 13.5, 5.8 Hz, 2H), 2.22 (d, J = 5.1 Hz, 6H), 1.87 – 1.78 (m, 2H), 1.69 – 1.59 (m, 2H), 1.55 – 1.46 (m, 4H), 1.44 – 1.34 (m, 4H), 0.97 – 0.90 (m, 3H). MS m/z= 382.2(M+H$^+$).

1.2.2 Synthesis of 4-butyl-4′-(6-N,N-dimethylhexyloxyamine) azobenzene bicarbonate (AZO-B6-CO_2)

AZO-B6-**CO_2** was synthesized by bubbling CO_2 into AZO-B6 aqueous solution as described in the literature.[2] The AZO-B6-CO_2 molecules can be converted between *trans*-isomer and *cis*-isomer following UV/blue light irradiation. The ^{1}H NMR of the product following light irradiation is shown in Figure S2.

1.3 Preparation of aqueous solutions

A certain quantity of AZO-B6-CO_2 as bicarbonate surfactant was dissolved in 10 mL pure water in a glass bottle followed by bubbling with CO_2 to obtain a transparent solution.[2] Then a certain amount of CTAB (solid) was dissolved in the AZO-B6-CO_2 solution by ultrasonic dispersion using an ultrasound bath (FS-250), followed by adding an appropriate amount of NaSal (also solid). The mixture (referred to as "CTAB-NaSal-AZO-B6-CO_2") was gently agitated for at least 24 h to reach equilibrium before measurements were carried out.

1.4 UV/blue light irradiation

The UV light was produced from a UV point light (9 W) whose wavelength is 365 ± 5 nm. The blue light was from a LED light (9 W) whose wavelength is 436 ± 5 nm. The solutions were placed in a glass bottle and irradiated by UV or blue light from 1 cm above.

1.5 UV-Vis spectroscopy

The UV/Vis absorption spectra of the AZO-B6-CO_2 solution were recorded using a TU-1901 (Beijing) UV-Vis spectrophotometer at room temperature, with the wavelength range from 200 nm to 500 nm. Water was utilized as blank.

1.6 Rheological measurements

Steady and dynamic rheological measurements were performed on a rotational rheometer (Discovery DHR-2, TA Instruments), which was equipped with a cone-plate accessory of radius 40 mm and taper angle of 2 degrees. Samples were equilibrated at 25 °C for no less than 10 min prior to the experiments. Dynamic frequency spectra were conducted in the linear viscoelastic region, as determined from prior dynamic stress−sweep measurements. All measurements were carried out in stress-controlled mode, and the temperature was controlled by a Peltier device. A solvent trap was used to minimize water evaporation during the measurements.

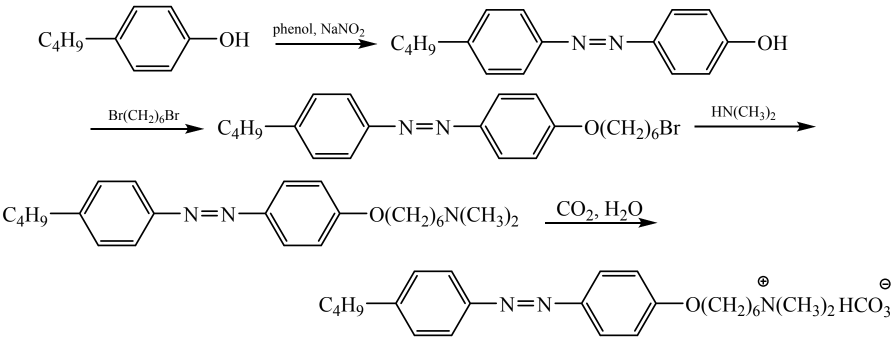
1.7 Cryo-TEM

The cryo-TEM samples were prepared in a controlled environment vitrification system (CEVS). A solution of the sample (4 μL) was coated onto a TEM copper grid and the grid was blotted with two pieces of filter paper for about 4 s, leading to the formation of a thin film. Then, the grid was quickly plunged into a reservoir of liquid ethane (−165 °C, cooled by liquid nitrogen) and kept in liquid nitrogen until the observation. After transferring the grid to a cryogenic sample holder (Gatan 626) and putting the holder into a JEOL JEM 1400 Plus TEM (120 kV) instrument at −174 °C, the nanostructures were imaged.

1.8 Surface tension measurements

All the surface tensions were measured in a dark room using the du Noüy ring method at 25 ^{o}C by means of a home-made apparatus. A platinum ring (radius 0.955 cm) was hung on a hook at the bottom of an electronic balance of 0.1 mg sensitivity. The measuring cup was placed in a glass jacket on a perpendicularly moveable platform. The jacket contained water from a water bath at 25 ^{o}C. The ring was immersed in the solution by raising the platform and was then pulled out by lowering the platform slowly. The maximum force required to just break the liquid meniscus was recorded. The surface tension was calculated by multiplying the measured maximum force F (in mN/m) by the appropriate correction factor. Using this apparatus, the surface tension of pure water at 25 ^{o}C was measured to be 71.9 ± 0.2 mN/m in good agreement with literature values.

2. Supplementary Figures



Scheme S1. Synthesis route of AZO-B6-CO_2.

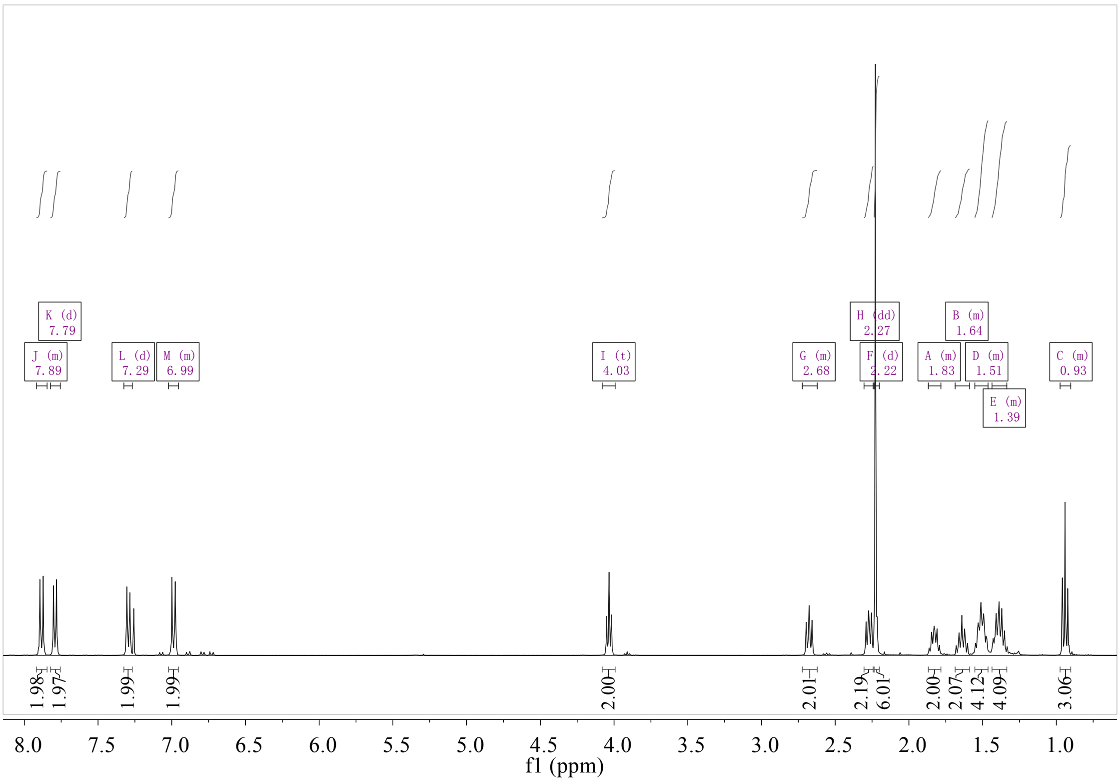


Figure S1. ^1H NMR spectrum of AZO-B6-CO_2.

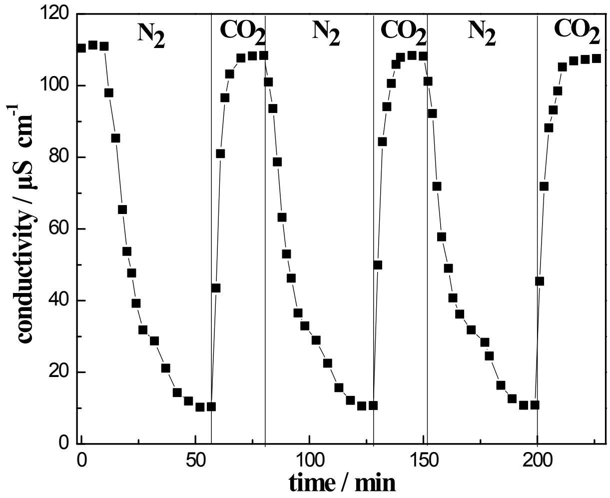


Figure S2. Conductivity of aqueous acetone solutions of AZO-B6-CO$_2$ (5 mM, $V_{water}/V_{acetone}$ = 1) as a function of time during two cycles of treatment with CO$_2$ (30 mL/min) followed by N$_2$ (100 mL/min) at 25 ^{o}C.

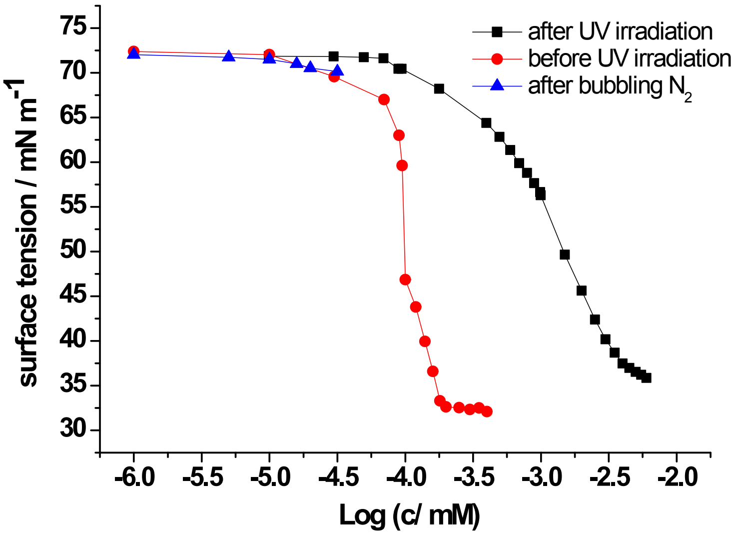


Figure S3. Surface tension of aqueous solutions of AZO-B6-CO$_2$ at 25 ^{o}C.

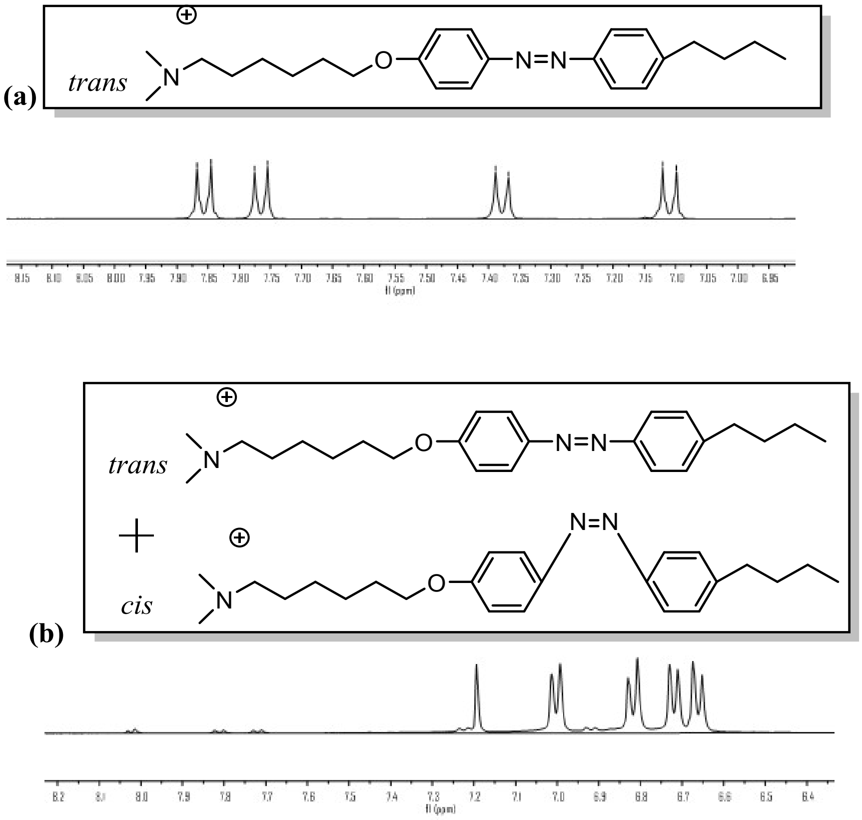


Figure S4. ^{1}H NMR spectra of aromatic protons in AZO-B6-CO_2: (a) *trans*-isomer and (b) *cis/trans* mixtures after UV light irradiation. The ratio of *cis/trans* is calculated based on ^{1}H NMR spectra of aromatic proton's integral calculation.[3]

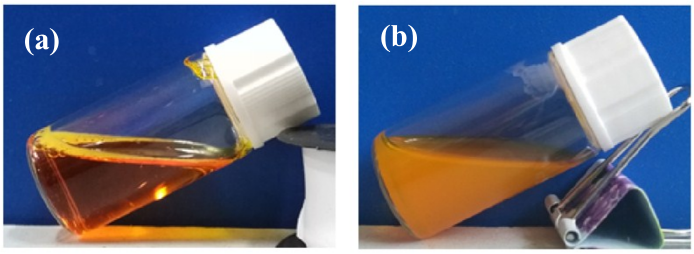


Figure S5. Digital photographs of (a) AZO-B6-CO_2 aqueous solution at 50 mM and (b) AZO-B6-CO_2-NaSal binary solution at 50 mM/50 mM at 25 °C.

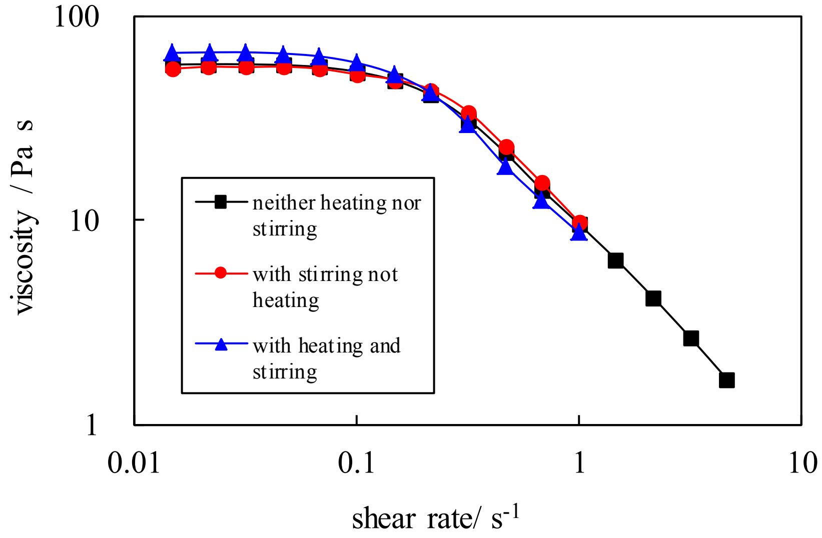


Figure S6. Viscosity of binary CTAB-NaSal (50 mM each) aqueous solutions as a function of shear rate for different conditions measured at 25 °C.

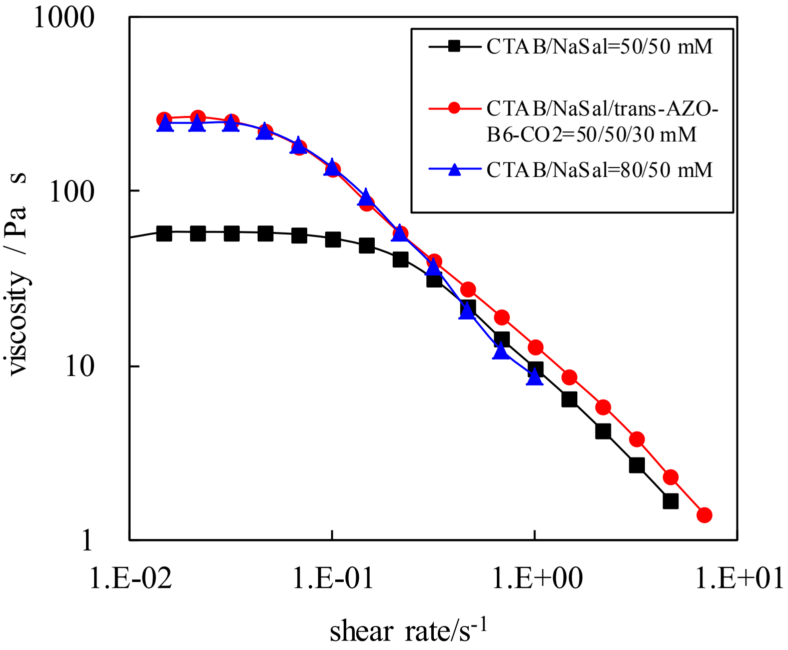


Figure S7. Viscosity of binary CTAB-NaSal (50 mM each) aqueous solutions as a function of shear rate upon addition of 30 mM *trans*-AZO-B6-CO_2 or CTAB respectively measured at 25 °C.

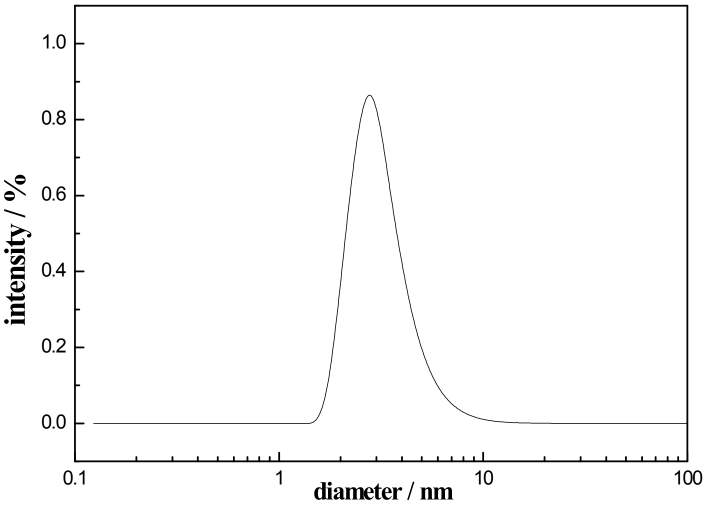


Figure S8. Dynamic light scattering of the CTAB-NaSal-AZO-B6-CO_2 ternary solution (50/50/30 mM) after bubbling N_2 at 25 °C.

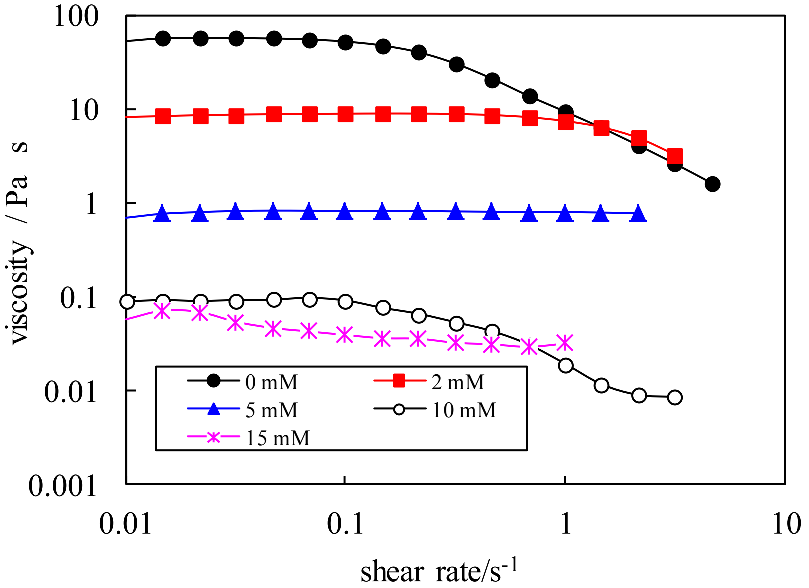


Figure S9. Viscosity of binary CTAB-NaSal (50 mM each) aqueous solutions as a function of shear rate upon addition of AZO-B6-CO_2 (in neutral or surface-inactive form) of different concentration shown at 25 °C.

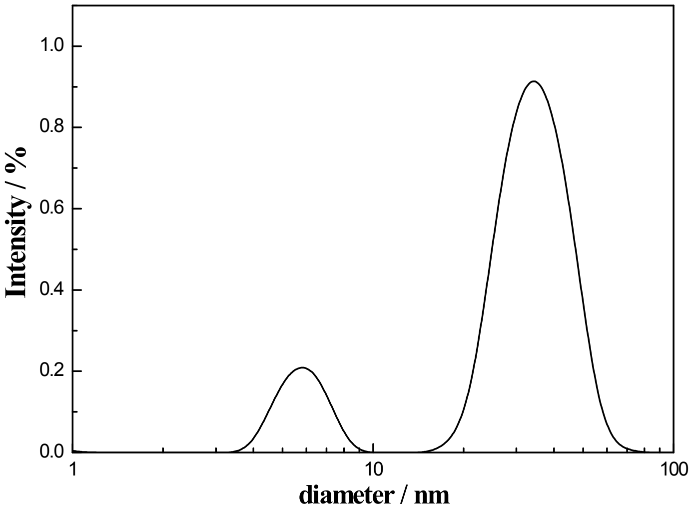


Figure S10. Dynamic light scattering of the CTAB-NaSal-AZO-B6-CO_2 ternary solution (50/50/30 mM) after UV irradiation at 25 °C.

References

1. Chevallier, E., Monteux, C., Lequeux, F. and Tribet C. *Langmuir*, 2012, **28**, 2308.
2. Liu, Y., Jessop P. G., Cunningham M., Eckert C.A. and Liotta, C.L. *Science*, 2006, **313**, 958.
3. Kang, H.-C., Lee, B.M, Yoon, J., Yoon, M. *J. Colloid Interface Sci.*, 2000, **231**, 255.