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Supplementary Information

Phototactic Behavior of Self-Propelled Micrometer-Sized Oil droplets

in a Surfactant Solution

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Materials and Methods

Reagents

Commercially-available reagents and solvent were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan) and Kanto Chemical Co. (Tokyo, Japan), and were used without further purification.

Synthesis of gemini cationic surfactant containing an azobenzene moiety (CnAzo)

CnAzo was synthesized according to method of Takahashi et al. (Scheme S1).¹



Scheme S1 Synthesis of CnAzo

Synthesis of 4,4'-dihydroxy azobenzene (1)

To a mixture of *p*-aminophenol (3.00 g, 27.5 mmol) in 30 mL of water, 2.75 M HCl aqueous solution (50 mL) was added dropwise over 30 min at room temperature (23–25 °C), and an aqueous solution (172 mL) of NaNO₂ (2.07 g, 30.0 mmol) was then slowly added over 120 min at 0 °C. The reaction mixture was added dropwise to an aqueous solution consisting of water (27.5 mL), CuSO₄•5H₂O (12.3 g, 49.3 mmol), 28% NH₃

aq. (8.3 mL), and hydroxyammonium chloride (1.95 g, 28.1 mmol) at 0 °C. The reaction mixture was filtered, and the crude product was then washed with 1 M HCl, and dried. Purification was carried out by reprecipitation using acetone (10 mL) as a good solvent and water (40 mL) as a poor solvent to obtain 4,4'-dihydroxy azobenzene (1) as a yellow solid at a yield of 54% (1.58 g, 7.38 mmol).

¹H-NMR (500 MHz, DMSO- d_6) δ 10.12 (s, 2H), 7.72 (d, J = 8.5 Hz, 4H), 6.91 (d, J = 8.0Hz, 4H). Electrospray ionization mass spectroscopy (ESI-MS) in acetonitrile (m/z): 215.08 [M + H]⁺; calcd, 215.07 [M + H]⁺.

Synthesis of 4,4'-bis{1-[2-(N,N-dibromo)]ethoxy}azobenzene (2)

The reaction mixture of **1** (1.34 g, 6.3 mmol), K_2CO_3 (6.06 g, 43.8 mmol), 1,2-dibromoethane (11.8 g, 62.6 mmol), and acetone (63 mL) was refluxed for 50 h. After the reaction, the solvent was evaporated. Purification was carried out by reprecipitation using acetone (30 mL) as a good solvent and water (40 mL) as a poor solvent in two times to obtain 4,4'-bis{1-[2-(*N*,*N*-dibromo)]ethoxy} azobenzene (**2**) as a yellow solid at a yield of 30% (1.59 g, 3.71 mmol).

¹H-NMR (500 MHz, DMSO- d_6) δ 7.85 (d, J = 9.0 Hz, 4H), 7.15 (d, J = 9.5 Hz, 4H), 4.43 (t, J = 5.5 Hz 4H), 3.85 (t, J = 5.5 Hz, 4H). ESI-MS in acetonitrile (m/z) : 428.96 [M + H]⁺ ; calcd, 428.96 [M + H]⁺.

Synthesis of 4,4'-bis{1-[2-(N,N-dimethylamino)]ethoxy}azobenzene (3)

The reaction mixture of 2 (1.59 g, 3.71 mmol), 40% aqueous solution of dimethylamine (13.0 mL, 102.6 mmol), and acetone (60 mL) was stirred at room temperature for 5 d. After the volatile components were removed by evaporation in *vacuo*, the residue was extracted using chloroform and dried by using MgSO₄. The chloroform layer was evaporated to obtain the crude product. Purification was carried out by reprecipitation using acetone (30 mL) as good solvent and water (40 mL) as poor solvent to obtain 4,4'-bis{1-[2-(*N*,*N*-dimethylamino)]ethoxy}azobenzene (**3**) as a yellow solid at a yield of 69% (0.900 g, 2.52 mmol).

¹H-NMR (500 MHz, DMSO- d_6) δ 7.82 (d, J = 8.5 Hz, 4H), 7.11 (d, J = 8.5 Hz, 4H), 4.14 (t, J = 6.0 Hz, 4H), 2.65 (t, J = 6.0 Hz, 4H), 2.22 (s, 12H). ESI-MS in acetonitrile (m/z): 357.23 [M + H]⁺; calcd, 357.22 [M + H]⁺.

Synthesis of C8Azo and C12Azo

The reaction mixture of **3** (0.200 g, 0.560 mmol), 1-bromooctane (0.326 g, 1.68 mmol) or 1-bromododecane (0.421 g, 1.69 mmol) in acetonitrile (7 mL) was refluxed under Ar atomosphere for 55 h. After the reaction, the reaction mixture was filtered and the solvent was evaporated. Purification was carried out by recrystallization using acetonitrile (20 mL) to obtain C8Azo and C12Azo as a yellow solid at a yield of 74% (0.305 g, 0.410 mmol) and 81% (0.385 g, 0.450 mmol), respectively.

C8Azo

¹H-NMR (500 MHz, DMSO-*d*₆) δ 7.93 (d, *J* = 8.5 Hz, 4H), 7.22 (d, *J* = 9.0 Hz, 4H), 4.61 (t, *J* = 4.0 Hz, 4H), 3.86 (t, *J* = 4.5 Hz, 4H), 3.51–3.40 (m, 4H), 3.20 (s, 12H), 1.83–1.70 (m, 4H), 1.42–1.24 (m, 21H), 0.89 (t, *J* = 7.0 Hz, 6H). ESI-MS in acetonitrile (*m*/*z*) : 291.24 [M – 2Br]²⁺; calcd, 291.24 [M – 2Br]²⁺.

C12Azo

¹H-NMR (500 MHz, DMSO-*d*₆) δ 7.89 (d, *J* = 9.0 Hz, 4H), 7.18 (d, *J* = 9.0 Hz, 4H), 4.57 (t, *J* = 4.5 Hz, 4H), 3.82 (t, *J* = 4.5 Hz, 4H), 3.45–3.35 (m, 4H), 3.16 (s, 12H), 1.79–1.64 (m, 4H), 1.40–1.16 (m, 38H), 0.84 (t, *J* = 7.0 Hz, 6H). ESI-MS in acetonitrile (*m*/*z*) : 347.30 [M – 2Br]²⁺; calcd, 347.31 [M – 2Br]²⁺.

Optical microscopic observation of oil droplet dynamics

The observation specimen was prepared as follows. An emulsion of *n*-heptyloxybenzaldehyde (HBA) was formed by agitating 200 μ L of the surfactant solution with 10 μ L of HBA. Immediately after mixing HBA with the surfactant and encasing the emulsion sample in a thin glass-chamber (15×15×0.28 mm; Frame Seal Chamber, MJ Research Inc., Waltham) real-time observations of the micrometer-sized oil droplet dynamics were conducted at room temperature (23–25 °C) using a phase-contrast microscope (BX51, Olympus, Japan) equipped with a CCD camera (DP22, Olympus, Japan).

Measurements of surface and interfacial tensions

The surface tension of aqueous C8Azo solutions and the interfacial tension between oil (HBA) and surfactant aqueous phases were measured using a Wilhelmy vertical plate technique with a sandblasted glass plate and a digital Kyowa Precise Surface Tensiometer CBVP-A3 (Kyowa Kagaku Co. Ltd., Tokyo, Japan) at room temperature (23–25 °C). The interfacial tension between the oil (HBA) and surfactant aqueous phases was also measured in a petri dish with UV ($\lambda = 370\pm20$ nm) irradiation of the interface (diameter × height = 4.5 × 2 cm) from 1 cm above the oil surface.

Time-course measurement of azo surfactant isomerization ratio

To confirm the isomerization of azo surfactants, the isomerization ratio of C8Azo from the *trans*- to the *cis*isomer under 950 mW/cm² UV irradiation was analyzed by ¹H NMR measurement of a D₂O solution containing 30 mM hexadecyltrimethylammonium bromide (C16TAB) and 10 mM C8Azo. The ratio was then calculated by integration of the ratio of the benzene methine proton signals from the *trans*-isomer of C8Azo at δ 7.94 and 7.14 ppm and those from the *cis*-isomer of C8Azo at δ 6.93 ppm (Fig. S1).

Figures



Fig. S1 ¹H NMR spectra (D₂O solution) of 10 mM C8Azo before and after photoisomerization in a 30 mM C16TAB solution at room temperature (23–25 °C). A sample of the reaction mixture was examined before and after 2 min of UV irradiation. The isomerization ratio was calculated by integration of the ratio between the benzene methine proton signals from the *trans*-isomer of C8Azo, at δ 7.94 and 7.14 ppm, and those from the *cis*-isomer of C8Azo, at δ 6.93 ppm, using the signal of the methyl groups in the alkyl chains of C16TAB and C8Azo at δ 0.97 ppm as an internal standard.



Fig. S2 A control experiment to determine the solution temperature increase caused by 950 mW/cm² UV irradiation. (a) Experimental set-up of the temperature measurement using cotton in water. The temperature of cotton in water and a paper surface upon UV irradiation were monitored by a thermography camera. (b) The change in temperature of the paper surface (blue) and cotton in water (red) over time upon UV irradiation. The UV irradiation caused the temperature of the paper surface and the cotton in water to increase, indicating that a temperature gradient was formed in the emulsions studied here upon UV irradiation.



Fig. S3 (a) Relationship between the droplet diameter and the response time of self-propelled droplets (red) and stationary droplets (blue) to 950 mW/cm² UV irradiation. The response time upon UV irradiation was defined as the time taken for stationary droplets to start the motion and for self-propelling droplets to change direction. (b) The velocity of oil droplets with diameters of 43 μ m (red), 78 μ m (green), 117 μ m (blue), and 140 μ m (orange) before and after 950 mW/cm² UV irradiation.



Fig. S4 UV-Vis spectrum of HBA showing a strong absorption in the 300–400 nm UV region, indicating that HBA does not transmit the UV light used in this study ($\lambda = 370\pm20$ nm). Therefore, the photoisomerization of azo surfactants from the *trans*- to *cis*-isomer is believed to occur mainly at the side of the droplet surface facing the UV irradiation.



Fig. S5 Typical sequential micrographs of the trajectory of benzaldehyde droplet locomotion in response to UV irradiation. The multiple 950 mW/cm² UV irradiation of the emulsion was carried out from left-hand (red), right-hand (blue), and then upper side (yellow). White and colored arrows indicate the same droplet and the direction of self-propelled motion, respectively. Stationary droplets exhibited negative phototaxis upon UV irradiation from the left-hand side (red arrows), and the mobile droplets then changed their direction upon subsequent UV irradiation from the right-hand (blue arrows) and upper (yellow arrows) sides. Scale bar: 200 μ m.



Fig. S6 (a) Typical sequential micrographs of positive phototaxis of HBA droplets after 130 s of 950 mW/cm² UV irradiation from the upper side in a solution of 30 mM C16TAB and 10 mM C8Azo at room temperature (23–25 °C). (b) Reaction scheme of HBA oxidation to produce HBCA. (c) Time-course of HBCA production in a 30 mM C16TAB solution induced by 950 mW/cm² UV irradiation at room temperature (23–25 °C). The HBCA production was calculated by integration of the ratio of the benzene methine proton signals from HBA at δ 7.83 ppm and those from HBCA at δ 8.05 ppm in the respective ¹H NMR spectra (CDCl₃ solution). (d) Variation in the interfacial tension between HBA and an aqueous solution of 30 mM C16TAB upon 950 mW/cm² UV irradiation at room temperature (23–25 °C).

Tables

Entry	Intensity of UV light (mW/cm ²)	Response time	
		Self-propelling ^[a]	Stationary ^[b]
1	950	Immediately after	Immediately after
2	700	Immediately after	Immediately after
3	480	Immediately after	Immediately after
4	260	Immediately after	Immediately after
5	95	Immediately after	5 s
6	60	Immediately after	10 s

Table S1 Effect of UV irradiation intensity on the dynamics of self-propelling andstationary droplets in solution of 30 mM C16TAB and 10 mM C8Azo

^[a] Time taken for self-propelling droplets to change direction after UV irradiation

^[b] Time taken for stationary droplets to start motion after UV irradiation

Entry C8Azo (m	C^{2} A π_{2} (mM)	Response time	
	C8A20 (IIIM)	Self-propelling ^[a]	Stationary ^[b]
1	20	Immediately after	Immediately after
2	10	Immediately after	Immediately after
3	5	Immediately after	Immediately after
4	1	Immediately after	Immediately after

Table S2 Effect of C8Azo concentration on the dynamics of self-propelling and stationarydroplets upon 950 mW/cm² UV irradiation in 30 mM C16TAB solution

^[a] Time taken for self-propelling droplets to change direction after UV irradiation

^[b] Time taken for stationary droplets to start motion after UV irradiation

Entry	UV irradiation	Response time	
	time (s)	Self-propelling ^[a]	Stationary ^[b]
1	1	Immediately after	Immediately after
2	3	Immediately after	Immediately after
3	5	Immediately after	Immediately after
4	10	Immediately after	Immediately after

Table S3 Effect of 950 mW/cm² UV irradiation time on the dynamics of self-propellingand stationary droplets droplets in solution of 30 mM C16TAB and 10 mM C8Azo

^[a] Time taken for self-propelling droplets to change direction after UV irradiation ^[b] Time taken for stationary droplets to start motion after UV irradiation

Entry	Oil compound	Before UV irradiation	After UV irradiation
1	<i>n</i> -Decane	Stationary	n.o.
2	Decanol	Stationary	n.o.
3	Heptyloxybenzene	Stationary	n.o.
4	Undecanal	Stationary	Negative phototaxis
5	Benzaldehyde	Stationary	Negative phototaxis

Table S4 Dynamics of droplets composed of different oily compounds before and after950 mW/cm² UV irradiation in a solution of 30 mM C16Tab and 10 mM C8Azo

n. o. = not observed.

Video clip description

Four video clips are attached to show the phototaxis of micrometer-sized oil droplets in a solution of 30 mM C16TAB and 10 mM C8Azo in response to 950 mW/cm² UV irradiation at room temperature (23–25 °C). All movies except for Movie S3 are shown at real-time speed. Movie S3 was recorded at 24 frame/s and converted to 3 times the speed of real time.

Movie S1: Typical negative phototaxis of self-propelling HBA oil droplets.

Movie S2: Initiation of motion and negative phototaxis of stationary HBA oil droplets.

Movie S3: Negative phototaxis of benzaldehyde oil droplets in response to multiple UV irradiations from three different directions.

Movie S4: Positive phototaxis of stationary oil droplets comprising HBA 130 s after the initiation of the UV irradiation.

Reference

1 Y. Takahashi, K. Fukuyasu, T. Horiuchi, Y. Kondo and P. Stroeve, Langmuir, 2014, 30, 41.