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Phototactic Behavior of Self-Propelled Micrometer-Sized Oil droplets in a Surfactant Solution

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We demonstrate the phototactic behavior of self-propelled micrometer-sized oil droplets in the presence of azobenzene-containing surfactants. These droplets respond sensitively to UV light irradiation due to a variation in the interfacial tension at the droplet surface induced by the molecular conversion of the azobenzene-containing surfactants.

Mobile objects including liquids and solids have attracted increased attention in recent years because of their potential application as probes or sensors for exploring hazardous areas and as carriers for transporting or removing compounds.[1-6] Among these objects, liquid droplets perform simple tasks and their motion is programmable using various external stimuli.[7–11] Thus, the liquid droplets can mimic the taxis behavior of living organisms. Their motion mode can be controlled by the system components and/or chemical reactions.[12–14]

Despite considerable progresses, precise control over droplet locomotion by external physical or chemical stimuli still remains a major challenge in the application of mobile droplets. One highly promising approach towards achieving this goal is the use of photoresponsive materials that can change the surface properties of solids and both water and oil droplets.[15–19] For example, Baigl and co-workers reported a manipulation system comprising a millimeter-sized oil droplet on a water surface controllable by photoisomerization of a cationic surfactant containing an azobenzene moiety.[20] Suzuki et al. demonstrated a phototactic system comprising micrometer-sized underwater oil droplets that responded to the photolysis of oil compounds.[21] In both of these systems, the phototaxis was considered to be induced from an equilibrium state because the oil droplets only moved when the emulsion system was irradiated. However, there are no reports on the taxis of self-propelling oil droplets in a far-from-equilibrium state.

Herein, we report the development of a self-propelling system using oil droplets that exist in a far-from-equilibrium state and whose motion mode can be controlled using irradiation. The self-propelled motion of oil droplets in surfactant solutions is driven by the Marangoni effect based on heterogeneity in the interfacial tension at the droplet surface.[22] We used a photoresponsive gemini cationic surfactant containing an azobenzene moiety in the linker moiety (CnAzo) (Fig. 1). Recently reported studies have used azobenzene-containing surfactants to control the interfacial properties of aqueous solutions[23, 24] and the morphology of self-assemblies.[25, 26] In addition, an instantaneous change in the interfacial tension of an oil-water interface induced by the photoisomerization of azobenzene-containing gemini surfactants was found to cause reversible demulsification and emulsification.[27] Therefore, when CnAzo is added to an emulsion system containing the surfactant *N*-hexadecyl-*N*,*N*,*N*-trimethylammonium bromide (C16TAB), we expect controlled motion to occur upon irradiation (phototaxis) due to the triggering of heterogeneity in the droplet-surface interfacial tension.

First, we investigated the effect of surfactant composition on the oil droplet dynamics in an emulsion (200 μL) at room temperature (23-25 °C). Details of the synthesis of CnAzo are described in the Supplementary Information (ESI). *n*-Heptyloxybenzaldehyde (HBA) was dispersed into a mixed surfactant solution composed of 30 mM C16TAB and 10 mM

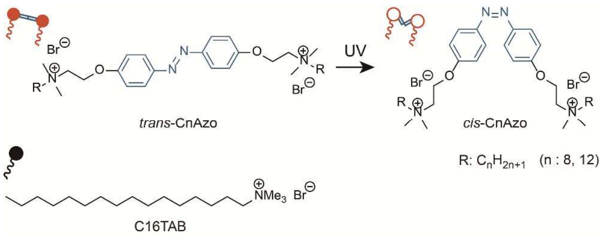

Fig. 1 Molecular structure of the photoresponsive surfactant CnAzo and a non-reactive surfactant (C16TAB).

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Electronic Supplementary Information (ESI) available: [Experimental procedures, synthesis, optical microscopic observation and analytical data of oil droplet dynamics, ^{1}H NMR spectra of compounds, UV-Vis spectrum of HBA (Figure S1-S6 and Table S1-S4), and four video clips (Movie S1-S4)]. See DOI: 10.1039/x0xx00000x

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C8Azo. This emulsion was packed into a 280 μm-thick compartment consisting of two glass slides and a spacer. The oil droplets therein were then observed using phase-contrast microscopy. In the mixed solution, the HBA droplets exhibited self-propelled motion for 4 min, and then ceased. When the emulsion was entirely irradiated with 950 mW/cm^2 ultraviolet (UV) light, the self-propelling droplets immediately exhibited negative phototaxis in the opposite direction to the light source (Fig. 2a and Movie S1, ESI). The droplet trajectory in Fig. 2a clearly indicates that the direction of droplet movement immediately changed in response to the UV light irradiation. When the motion speed of oil droplets was relatively fast, oil droplets moved randomly after UV irradiation. In addition, stationary droplets that had ceased self-propelled motion also exhibited the negative phototaxis under UV irradiation and they sustained the directional motion away from the light source for 6 s, followed by random motion for 60 s (Fig. 2b and Movie S2, ESI). The convective flow observed within the mobile droplets was as illustrated in Fig. 2a (see also Movies S1 and S2, ESI), and indicated that their locomotion was caused by the Marangoni effect.[28] Similar negative phototaxis was also observed in a mixed solution composed of 30 mM C16TAB and 10 mM C12Azo. On the other hand, HBA oil droplets did not exhibit any locomotion in solutions containing only 1-10 mM C8Azo even with UV irradiation. In a 30 mM C16TAB solution, HBA droplets exhibited self-propelled motion for 7 min, whereas they did not respond to the UV irradiation. These results clearly suggest that the azo surfactants are necessary for the negative phototaxis of HBA droplets.

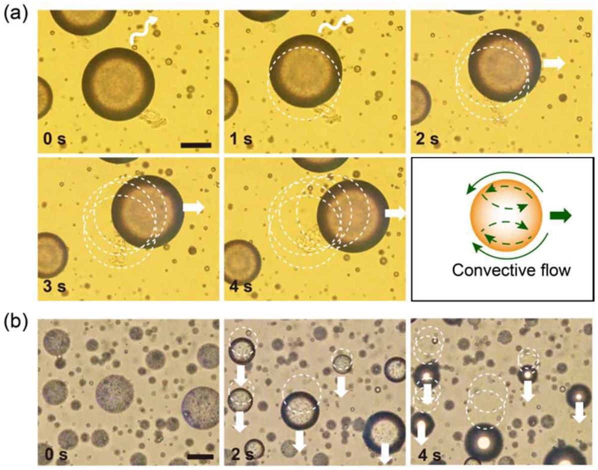

Fig. 2 Typical sequential micrographs of HBA droplet locomotion in response to UV irradiation in a solution of C16TAB (30 mM) and C8Azo (10 mM) at room temperature (23-25 °C). The wavy-lined and block white arrows represent random and directional motion, respectively. The dotted white circles in the micrographs represent the trajectories of mobile oil droplets. Scale bar: 100 μm. (a) Negative phototaxis of self-propelling droplets induced by UV irradiation from the left-hand side 2 s after starting observation. (b) Negative phototaxis of stationary droplets that had ceased self-propelled motion induced by UV irradiation from the upper side.

^{1}H NMR analysis of a D_2O solution containing 30 mM C16TAB and 10 mM C8Azo was carried out at room temperature (23-25 °C) to probe the isomerization kinetics of the azo surfactants induced by the 950 mW/cm^2 UV irradiation. The isomerization ratio of the *trans*- to *cis*-isomer of C8Azo was calculated by the shifting of benzene methine protons (see Fig. S1, ESI). Figure 3a shows the time-course of the C8Azo isomerization ratio, indicating that isomerization readily occurred under UV irradiation and the isomerization ratio exceeded 50% within 1 min. Because the UV irradiation induced a temperature increase (Fig. S2, ESI), a temperature gradient probably formed in the oil droplets. However, the addition of 60 °C hot water to an emulsion, where the oil droplets had ceased any motion, did not cause the droplets to move. We thus concluded that the negative phototaxis of oil droplets was induced not by the formation of a temperature gradient but by the partial photoisomerization of the azo surfactants.

Next, we measured the variation in interfacial tension between HBA and an aqueous surfactant solution of 30 mM C16TAB and 10 mM C8Azo upon UV irradiation using the Wilhelmy vertical plate technique with a sandblasted glass plate. The interfacial tension between HBA and 30 mM C16TAB aqueous solution gradually decreased under UV irradiation, whereas that between HBA and an aqueous solution composed of C16TAB and C8Azo increased slightly but instantaneously after UV irradiation and then gradually decreased over time (Fig. 3b). The mechanism of the interfacial tension variation can be explained as follows. The area of the oil-water interface occupied per molecule of the straight *trans*-isomer is larger than that of the bent *cis*-isomer.[22] Therefore, the contact area between the water and oil phases increases

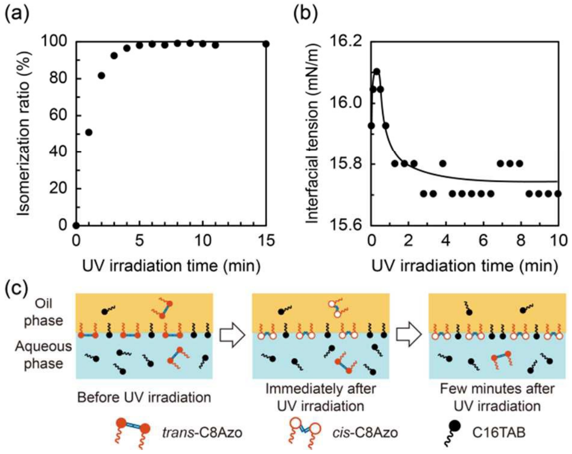

Fig. 3 (a) Time-course of the C8Azo (10 mM) isomerization ratio in a D_2O solution containing C16TAB (30 mM) upon UV irradiation at room temperature (23-25 °C). (b) Variation in the interfacial tension between HBA and a mixed aqueous solution composed of 30 mM C16TAB and 10 mM C8Azo at at room temperature (23-25 °C). The solid line is present to aid visualization. (c) Schematic representation of the UV irradiation induced dynamics of surfactant molecules at the oil-water interface.

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upon photoisomerization from *trans*- to *cis*-C8Azo, inducing the observed slight instantaneous increase in the interfacial tension. Because the interfacial tension activity of the *cis*-isomer is higher than that of the *trans*-isomer,[27] it gradually decreased to reach the equilibrium value (Fig. 3c).

Furthermore, the relationship between the HBA droplet dynamics and both the UV intensity and surfactant concentration were evaluated. The UV irradiation intensity was varied between 60-950 mW/cm^2 in solution of 30 mM C16TAB and 10 mM C8Azo. The negative phototaxis of stationary droplets occurred instantaneously when the irradiation was ≥ 60 mW/cm^2 (Table S1, ESI), while at 60 and 95 mW/cm^2 stationary droplets exhibited negative phototaxis 10 s and 5 s, respectively, after the initiation of UV irradiation. This shows that photoisomerization of C8Azo takes longer with a weaker UV light intensity (Table S1, ESI). On the other hand, self-propelling droplets instantaneously responded to all tested UV irradiation intensities (Table S1, ESI). The C8Azo concentration was varied from 1-20 mM in a 30 mM C16TAB solution, and 950 mW/cm^2 UV irradiation was found to induce negative phototaxis of both self-propelling and stationary droplets at all C8Azo concentrations (Table S2, ESI). The irradiation time was also tested and even 1 s of 950 mW/cm^2 UV irradiation induced a change in the direction of the self-propelled droplets and locomotion of stationary droplets (Table S3, ESI). These results indicate that the oil droplet system containing C16TAB and C8Azo is sensitive to UV irradiation and the negative phototaxis is induced regardless of the UV irradiation conditions and surfactant concentration. Furthermore, we analyzed the response time upon UV irradiation for self-propelling droplets to change direction and stationary droplets to start the motion. No significant difference in the response time was observed between self-propelling and stationary droplets (Fig. S3a, ESI). In both cases, the droplet speed immediately after UV irradiation was almost identical and did not depend on the droplet size (Fig. S3b, ESI). This implies the instantaneous (within 0.5 s) formation of new flow fields that induce the negative phototaxis of oil droplets regardless of the presence or absence of initial flow fields. In addition, several seconds after UV irradiation a larger droplet tended to be faster, indicating that this locomotion mechanism are proposed from viewpoints of the flow fields as described by Thutupalli et al.[28]

On the basis of these results, we have proposed a mechanism for the sensitive negative phototaxis of self-propelling HBA droplets upon UV irradiation (Fig. 4). The self-propelled motion of oil droplets is due to the Marangoni effect based on an imbalance in the interfacial tension at the droplet surface.[17] The droplets can take up more surfactants whilst continuing to move (Fig. 4a). When the self-propelling oil droplets are irradiated with UV light, photoisomerization of the azo surfactants from the *trans*- to *cis*-isomer readily occurs mainly on the side of the droplet surface facing the irradiation because HBA does not transmit UV light due to its strong absorption in the 300–400 nm UV region (Fig. S4, ESI). Thus, the interfacial tension at this local area on the droplet surface increases slightly but instantaneously (Fig. 4b). This is sufficient for the formation of new flow fields that induce the negative phototaxis of droplets (Fig. 4c). However, this controlled locomotion becomes random within several seconds as other flow fields are formed by the adsorption of surfactant molecules on the droplet surface from all directions (Fig. 4d). The locomotion is sustained until the interfacial tension around the oil droplet equilibrates, at which point the droplet slows down and becomes stationary. When stationary droplets are irradiated with UV light, they start the negative phototaxis because of an instantaneous increase in the interfacial tension on the side of the droplet surface facing the UV irradiation.

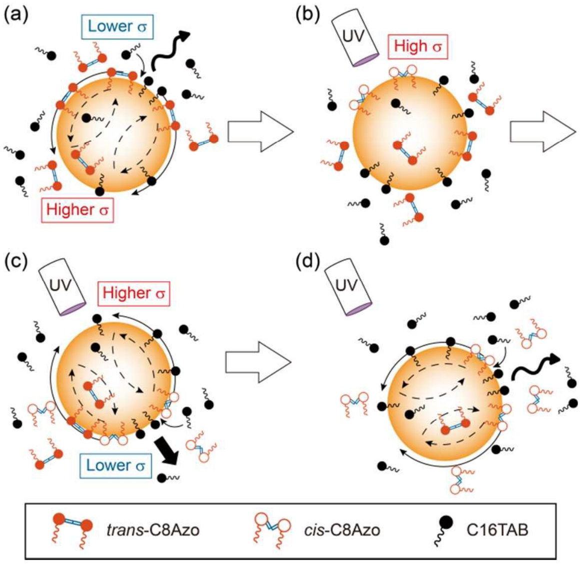

Fig. 4 Proposed mechanism for the negative phototaxis of self-propelling HBA droplets induced by UV irradiation. The wavy-lined and block white arrows represent random and directional motion, respectively. σ is the local interfacial tension at the oil droplet surface.

Furthermore, under 950 mW/cm^2 UV irradiation, we investigated the dynamics of *n*-decane, decanol, heptyloxybenzene, undecanal and benzaldehyde oil droplets, instead of HBA, in the mixed surfactant solution of 30 mM C16TAB and 10 mM C8Azo (Table S4, ESI). *n*-Decane, decanol and heptyloxybenzene droplets did not exhibit self-propelled motion or respond to the UV irradiation. Even though the oil droplets composed of undecanal and benzaldehyde, which contain a formyl group, were not self-propelled they exhibited negative phototaxis in response to the UV irradiation. We then conducted multiple UV irradiations from three different directions on the emulsion system comprising benzaldehyde oil droplets, C8Azo, and C16TAB (Fig. S5 and Movie S3, ESI). The following discussion of the direction of UV irradiation and subsequent droplet movement is relative to the images in Fig. S5. Negative phototaxis of the stationary droplets was first induced by irradiation from the left-hand side, and a second irradiation from the right-hand side then changed their direction. A final third irradiation from the upper side caused the droplets to move downwards. This sequential control over droplet motion has potential applications in the targeted delivery of molecules or small objects.[7–11]

Under continuous 950 mW/cm^2 UV irradiation in a 30 mM C16TAB solution in both the presence and absence of C8Azo, we found that HBA droplets self-propelled and then ceased, and after

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120 s the stationary droplets then locomoted toward the light source, i.e. positive phototaxis (Fig. S6a and Movie S4, ESI). Because initial negative phototaxis also occurred when C8Azo was present, the locomotion mode of the oil droplets transferred from negative to positive against the UV irradiation. Under similar UV irradiation that induced the photoisomerization of C8Azo, HBA was slowly but steadily oxidized to *n*-heptyloxybenzcarboxylic acid (HBCA) at the minute time-scale (Fig. S6b and S6c, ESI). In addition, the interfacial tension between HBA and aqueous C16TAB solution was almost constant over time without the UV irradiation, while it decreased gradually over time upon UV irradiation (Fig. S6d, ESI). It has been reported that the surface activities in a complex system composed of a cationic surfactant and a fatty acid are higher than those in an individual surfactant system.[29] Even though the precise mechanism of the positive phototaxis is not completely understood, we consider it to be a result of HBCA production at the minute time-scale mainly at the droplet-side facing the UV irradiation because HBA droplets do not transmit UV light. This molecular conversion induces lowering the interfacial tension around the droplets, thus gradually forming the flow fields that cause the positive phototaxis of the droplets.

In conclusion, we have demonstrated the phototactic behavior of micrometer-sized oil droplets in a far-from-equilibrium state using photoresponsive surfactants. The controlled motion of droplets was explained by heterogeneity in the interfacial tension at the droplet surface that was induced by the molecular conversion of system components. The negative phototaxis was very sensitive and exhibited directional change within 0.5 s. Such sensitivity is highly effective for applications in the spatial arrangement of micrometer-sized objects and also as transporters.[17, 18] In addition, the locomotion mode of oil droplets in the azo surfactant system transferred from negative to positive against the UV irradiation over time. Therefore, our emulsion system provides living-organism-mimetic properties, such as the adaptation to an external stimulus, in this case irradiation.[30–32]

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