Supporting Information

Photo-controllable Azobenzene Microdroplets on an Open Surface and their Application as Transporters

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Movies

SI Movie 1. Translational motion of C8AB.
SI Movie 2. Translational motion of C8AB with different size of droplets and crystals.
SI Movie 3. Zigzag motion of C8AB droplets at 5x speed.
SI Movie 4. Translational motion of C8AB under the polarizing optical microscope.
SI Movie 5. Translational motion of C8AB from the side.
SI Movie 6. Droplet deformation into asymmetric shape.
SI Movie 7. Change of droplet shape upon alternate irradiation with UV and VIS lights.
SI Movie 8. Transportation of fluorescent quantum dots by C8AB droplets.

1. Materials

4,4'-Bis(hexyloxy)-3-methylazobenzene (**C6AB**), 4,4'-bis(heptyloxy)-3-methylazobenzene (**C7AB**), 4,4'-bis(octyloxy)-3-methylazobenzene (**C8AB**), 4,4'-bis(nonyloxy)-3-methylazobenzene (**C9AB**), and 4,4'-bis(decyloxy)-3-methylazobenzene (**C10AB**) were synthesized according to the previous reports.[1,2] Potassium hydroxide and ethanol were purchased from Kishida Chemical Co., Ltd. and used as received. CdSe/ZnS core-shell type quantum dots (product number: 900249; emission wavelength: 655-675 nm, quantum yield: ≥ 50%) was purchased from Sigma-Aldrich. Cover glasses (Matsunami Glass Ind., Ltd, square microscope cover glass No.1, 18 mm × 18 mm, thickness: 0.12–0.17 mm) were used as the glass substrates. Mica was purchased from Okenshoji Co., Ltd. and cleaved using sticky tape.

2. General methods

2.1 Instrumentation

For the photoirradiation, LED's were used for 365 nm (CCS Inc., HLV-24UV365-4WNRBTNJ) and 465 nm (CCS Inc., HLV2-22BL-3W). The light intensity was monitored using a Newport 1917-R optical power meter with an 818-ST-UV photodetector. The motion was observed using a Nikon Eclipse Ti microscope, and an Olympus BX51 microscope equipped with polarizers. The observation from side was carried out by a home-made microscopic settings (objective lens: Mitsutoyo 10x, f = 200 mm, backlight: Aitecsystem Co, Ltd., LED spot light (white LED) TSPA22x8-57W). The sample temperature was controlled by a heating stage (Tokai Hit, Thermoplate).

2.2 Sample preparation

Hydrophilic glass was prepared by dipping a cover glass in a saturated KOH/EtOH solution for 1 h and the glass was washed with EtOH. To place small piece of CnAB on a glass, photomolten liquid was deposited on the tip of a brush and rubbing it lightly on the glass surface.

2.3 Photoirradiation

For the experiments on the motion of the droplets on a substrate, photoirradiation was carried out with UV (365 nm) and VIS (465 nm) using the experimental setup shown in Figure S1 under ambient atmosphere otherwise noted. A UV light source is positioned pointing towards the sample at an angle of 40° to the plane of the sample, while a VIS light source is placed in an opposite location and directed towards the sample at an angle of 40° to the plane of the sample. The entire sample area is irradiated by these light sources. To induce the motion, initially UV light was irradiated at 125 mW cm^{-2} to melt the crystals, then VIS light irradiation was started at 230 mW cm^{-2} while the UV light was kept irradiated at the same intensity. For the zigzag motion, two UV lights and two VIS lights were used as the setup is shown in Figure S2. To observe the droplet motion from the side, the experimental setup shown in Figure S5 was used.

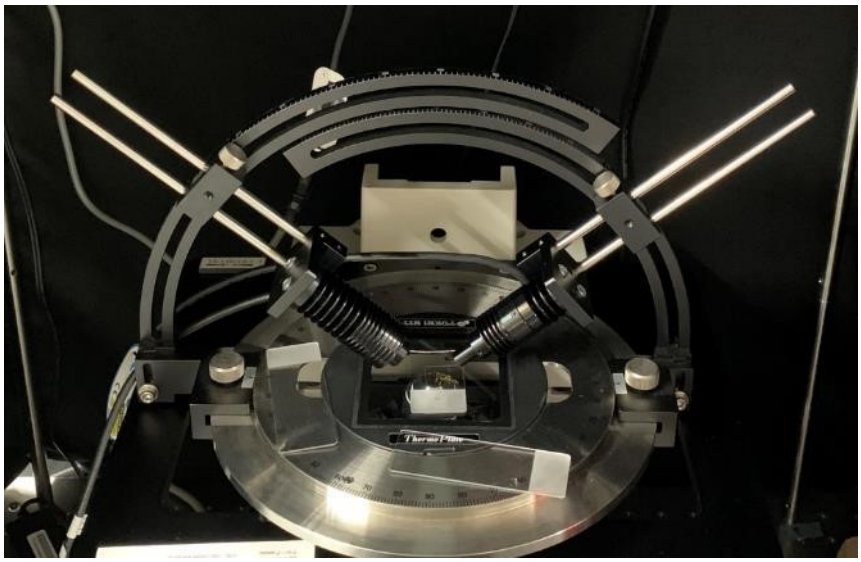
2.4 Data analyses of motion

In each experiment for the translational motion, the motion was recorded as a movie and the lateral distances of the droplets in the whole field of view were measured. The velocity of the motion was measured based on the center of the droplets. The initial diameter of the droplets or crystals was used for plotting the velocity vs. size. To analyze the speed and the droplet size dependence, the objects observed in SI Movie 2 was numbered as shown in Figure S3. The trajectory of all objects was analyzed, then plotted as shown in Figure S4. The diameter of the initial frame was used for plotting the dependence of diameter on the velocity (Figure 2(d)).

2.5 Transport experiment

A chloroform solution (100 μL) containing 3.95 mg of C8AB and a toluene solution (12.5 μL) containing 6.25×10^{-6} g of CdSe/ZnS core-shell type quantum dots were mixed. The solution was deposited on a hydrophilic cover glass and let it to dryness. The light irradiation was carried out by using the optical setup described above. The motion was recorded and analyzed.

(a)



(b)

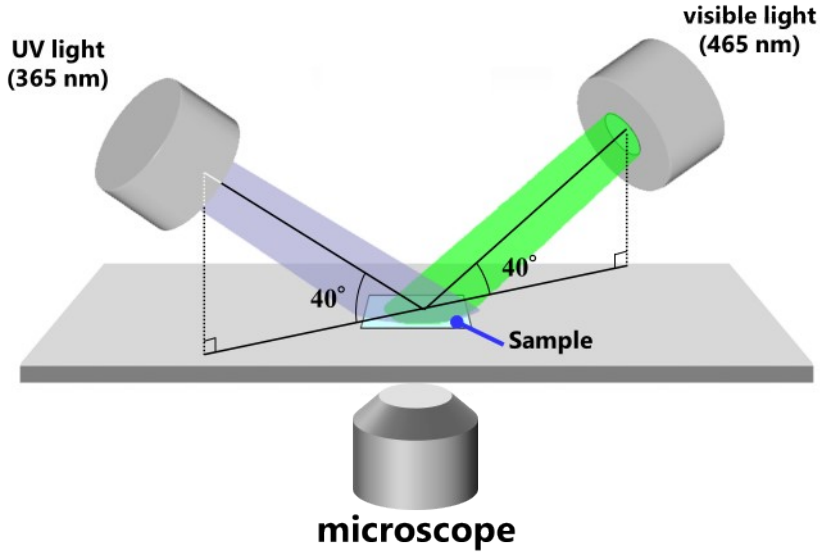


Figure S1. Experimental setup for the light irradiation. (a) Photograph and (b) schematic diagram for the setup for inverted optical microscopy observations.

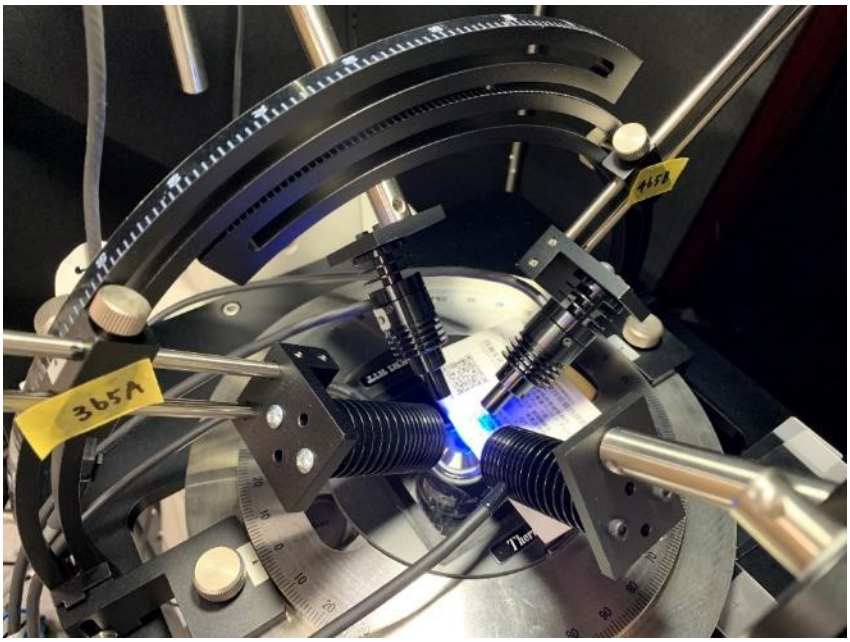


Figure S2. Photograph of the experimental setup for the light irradiation for the zigzag motion.

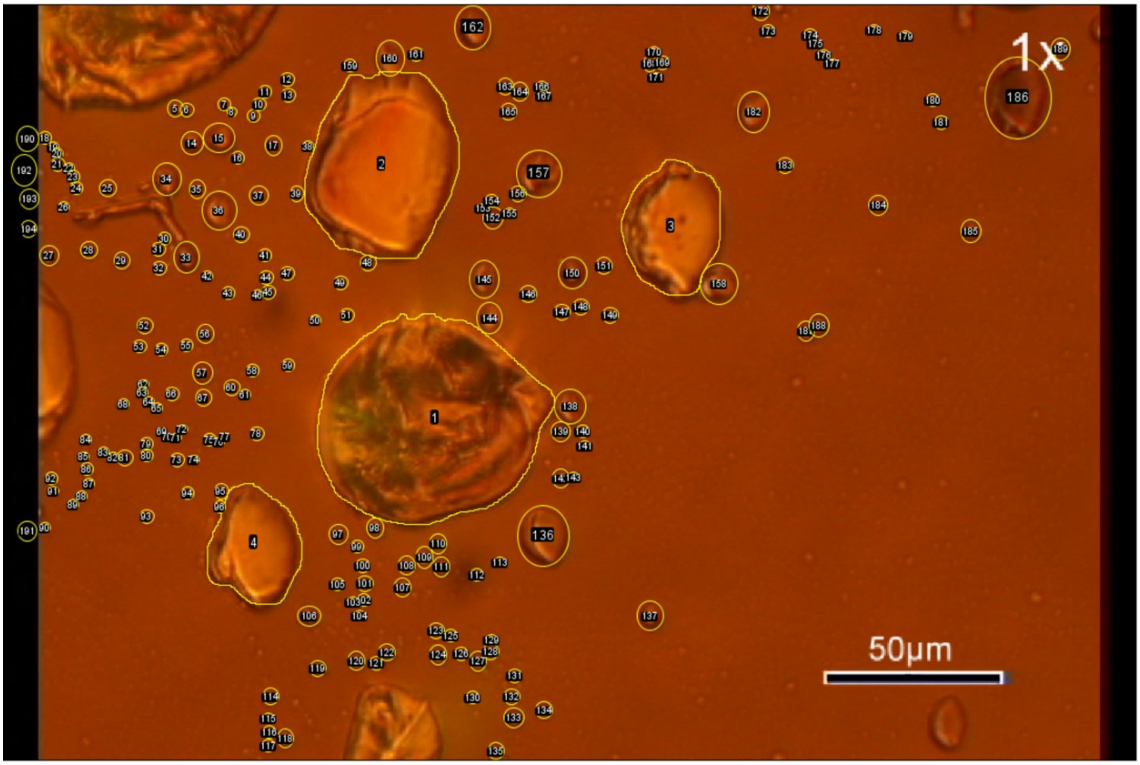


Figure S3. Numbering of the droplets and crystals for analyzing the trajectory of SI Movie 2.

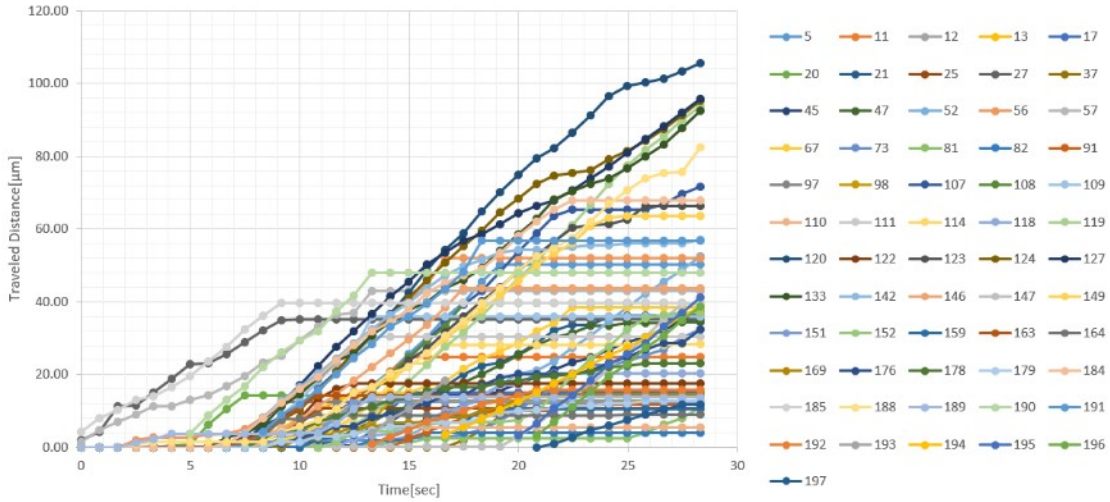


Figure S4. Traveled distance of the droplets observed in SI Movie 2. The numbers are the identification number of droplets and crystals shown in Fig. S3.

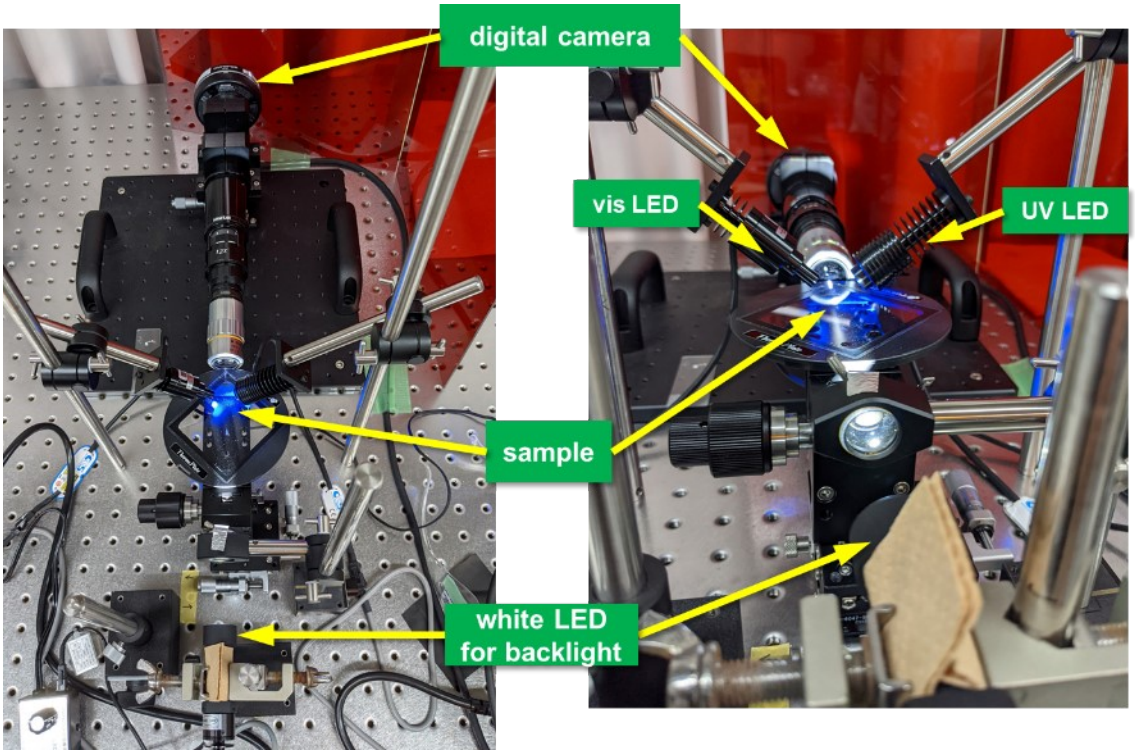
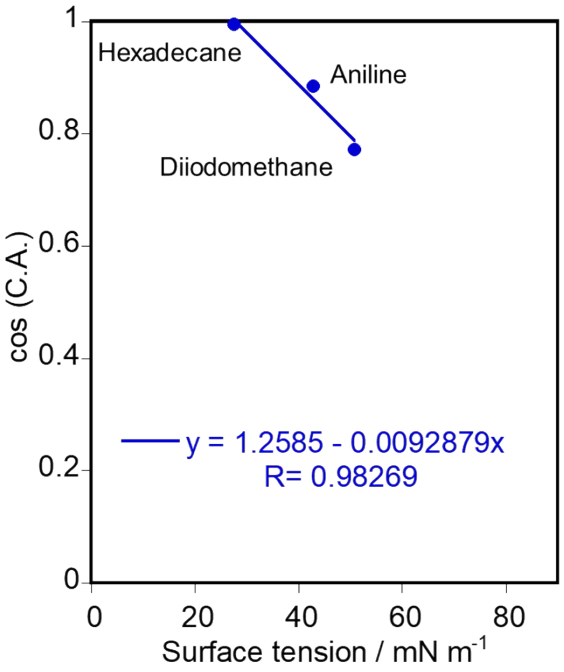


Figure S5. Experimental setup for the observation from the side.



Sample	S.T. (mN m^{-1})	C.A. (°)	cos C.A.
Diiodomethane	50.8	39.53	0.771
Aniline	42.9	27.93	0.884
Hexadecane	27.6	6.17	0.994

	C.A.(°) @26℃	cos C.A.	S.T. (mN m^{-1})
after vis	35.295	0.816	47.64
after UV	50.276	0.639	66.70

Figure S6. Zisman plot to estimate the surface tension of droplet of C8AB upon exposure to visible light and UV light.

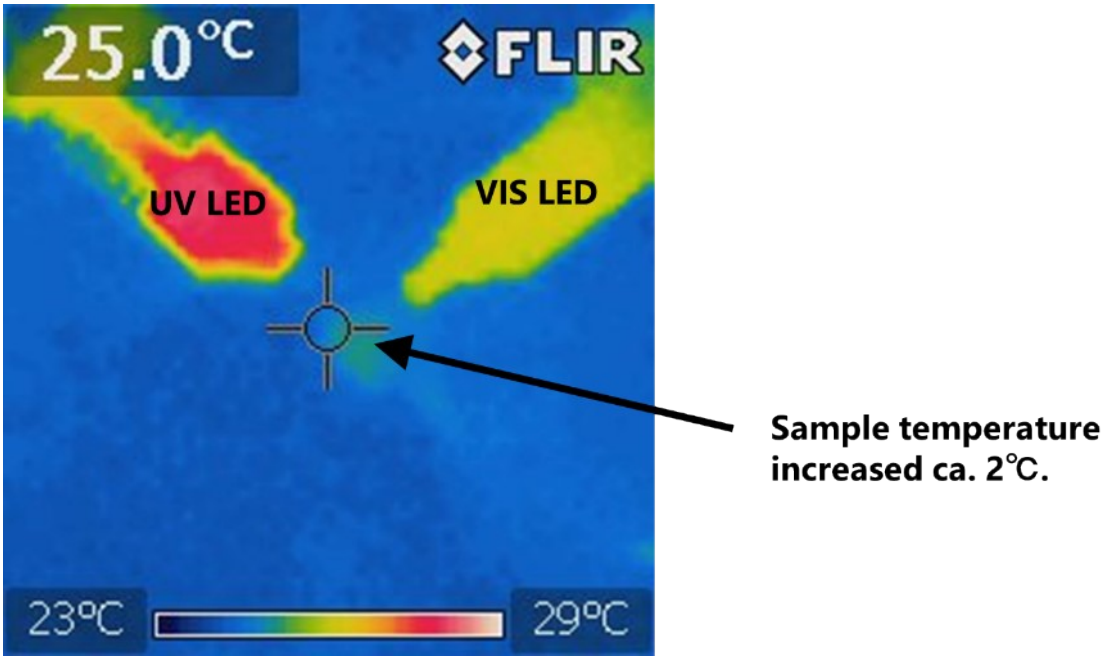


Figure S7. Photograph by IR camera observed during the exposure of UV and visible lights. The sample temperature increased about 2°C. No clear temperature gradient was detected.

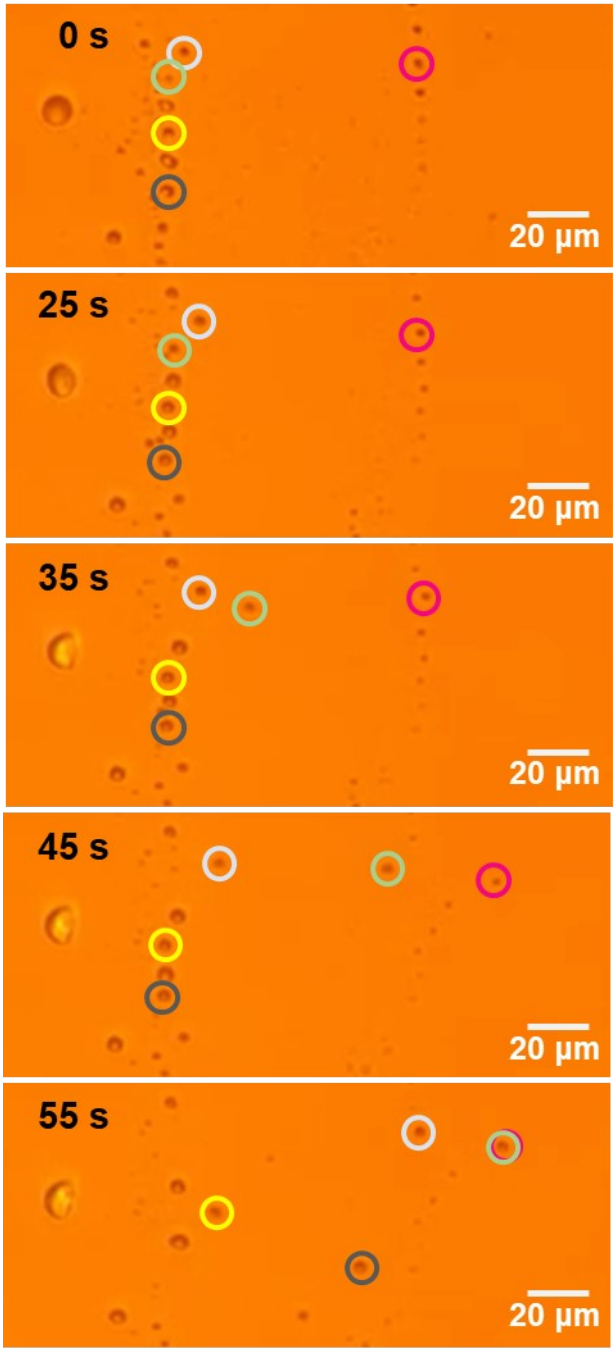


Figure S8. Snapshots of the crawling droplets of C8AB on freshly cleaved mica surface. Selected droplets are indicated by colored circles to clarify the motion.

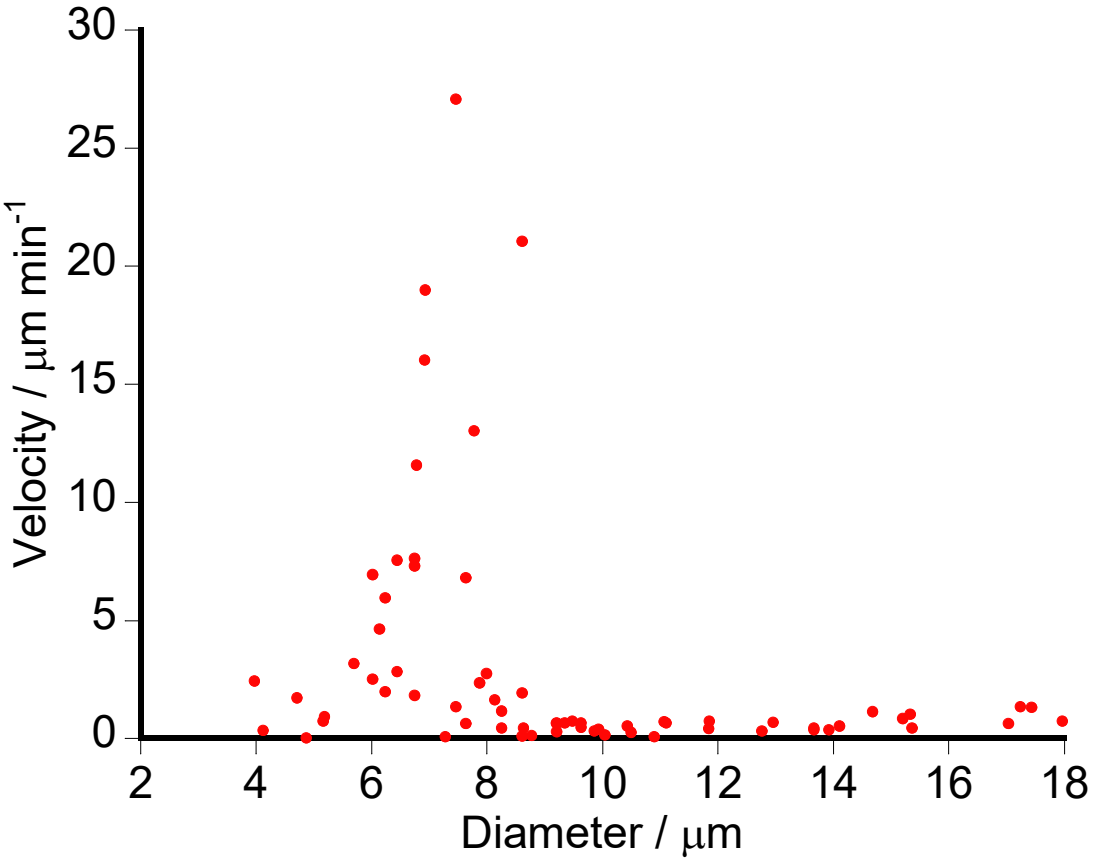


Figure S9. Dependence of diameter on the average velocity during the crawling motion of droplets containing fluorescent quantum dots.

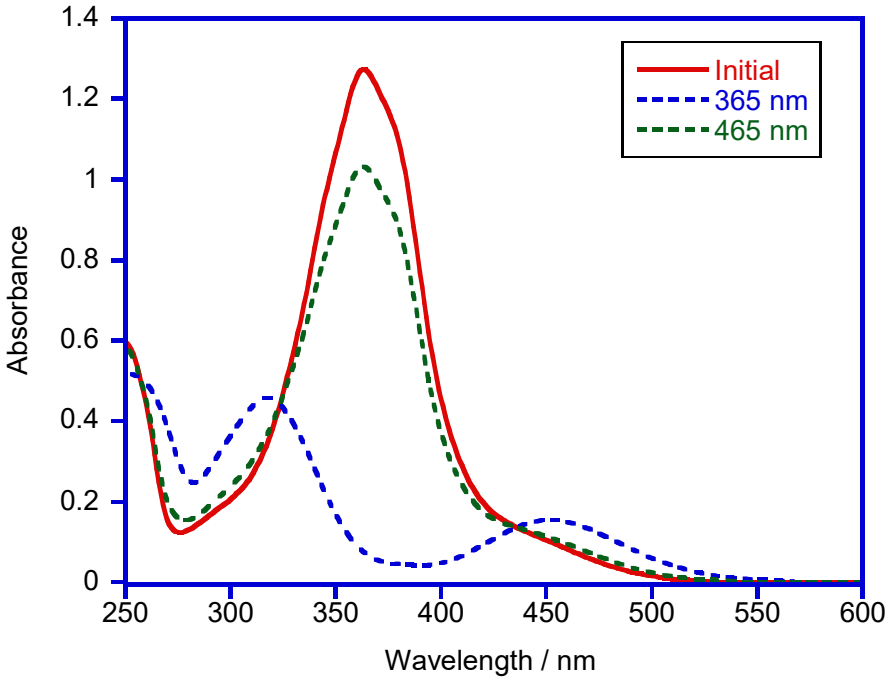


Figure S10. Absorption spectra of C8AB in chloroform before photoirradiation (Initial), after establishing the photostationary state (PSS) by irradiation of 365 nm (365 nm), and after establishing the PSS by irradiation of 465 nm (465 nm).

References

(1) Y. Norikane, E. Uchida, S. Tanaka, K. Fujiwara, E. Koyama, R. Azumi, H. Akiyama, H. Kihara, M. Yoshida, *Org. Lett.* **2014**, *16*, 5012-5015.
(2) Y. Norikane, E. Uchida, S. Tanaka, K. Fujiwara, H. Nagai, H. Akiyama, *J. Photopolym. Sci. Technol.* **2016**, *29*, 149–157.