Soft Matter

Optical motion control of liquid crystalline droplets by host-guest molecular interaction

Journal:	*Soft Matter*
Manuscript ID	SM-ART-06-2019-001265.R3
Article Type:	Paper
Date Submitted by the Author:	07-Aug-2019
Complete List of Authors:	Sakai, Yota; Chuo University, Department of Chemistry Sohn, Woon Yong; Chuo University, Department of Applied Chemistry Katayama, Kenji; Chuo University, Department of Chemistry; Kagaku Gijutsu Shinko Kiko, Precursory Research for Embryonic Science and Technology

Optical motion control of liquid crystalline droplets by host-guest molecular interaction

Yota Sakai,[1] Woon Yong Sohn,[1] and Kenji Katayama[1,2*]

1 Department of Applied Chemistry, Chuo University, Tokyo 112-8551, Japan;

2 PRESTO, Japan Science and Technology Agency (JST), Saitama 332-0012, Japan

*Corresponding authors:

K. Katayama, Phone: +81-3-3817-1913, E-mail: kkata@kc.chuo-u.ac.jp

Abstract

Photo-induced motion is demonstrated for a photo-responsive dye-doped liquid crystal (LC) droplet in a surfactant solution. The LC droplets started rolling on a substrate during UV irradiation and moved either toward or away from the UV light, depending on the functional groups of the guest dyes. The mechanism is explained by the Marangoni flow caused by the photo-isomerization-induced adsorption and desorption of the dye molecules to and from the LC/solution interfaces.

Keywords: liquid crystalline droplet, surfactant solution, active matter, host-guest interaction

Introduction

Active matter refers to objects that move spontaneously by consuming chemical, physical, or biological energy, which has attracted much attention in recent years.[1–5] Janus particles, possessing two different materials on each half of a sphere,[6–8] have been investigated as active matter using catalytic or photocatalytic energy.[9–11] Tube materials are also one of the categories of active matter by inducing gas formation reactions on their catalyzed surfaces.[12,13] Liquid crystalline (LC) materials have been frequently utilized for this application, because they have long-range molecular interaction, they can potentially convey force to a distant position, and macroscopic motion and/or shape changes have been demonstrated.[14–21]

The oscillatory motion of an LC vesicle including microtubules and a kinesin motor was observed and controlled by defect-defect interaction.[16] Similar behavior was observed for a particle in an LC medium by forming topological defects outside of the particle.[17,18] The electrophoresis of spheres was demonstrated using the distortion of the LC orientation.[19,20] A macroscopic flow was also generated on an alignment layer in an LC with bacteria on a patterned alignment layer.[21]

A new type of active LC droplet has been reported in recent years. Self-propelled motion was induced by the convective flow inside an LC droplet in a surfactant solution with a concentration higher than the critical micellar concentration (CMC).[22] The mechanism of motion was explained by the melting of LC molecules, which are taken into the micelles of the surfactants. As a result, a gradient was induced in the surface tension of the LC droplet, which causes Marangoni flow inside and outside of the LC droplet.[23]

The interaction of multiple LC droplets was studied to understand the collective behavior of clustering.[24] Helical motion was reported for a nematic droplet when coupling between the director and the convective flow caused symmetry breaking.[25] Similar motion was induced for an LC droplet with a helical director made of cholesteric LC containing chiral dopants.[26] Various motions were found for a simple system of 4-pentyl-4'-cyanobiphenyl (5CB) droplets dispersed in a surfactant solution, which depended on the velocity. The results were explained by the position of the topological defects.[27]

Photo-responsive molecules can sometimes control the phase and orientation of LC, and the color and pattern were changed by stretching the nanostructure and changing the phase. Cholesteric droplets with photo-responsive dopants can show various color and communication patterns.[28] Control of the color and color pattern has been demonstrated by controlling the pitch of cholesteric LC through the photo-response of added chiral molecules.[29] We also studied the dynamic change of the topological defects through the photo-induced phase transition of LC double emulsions.[30]

Light is regarded as a promising tool for the motion control of active matter because of the directionality and controllability of the beam spot. Recently, 'oil' droplets containing photo-active molecules were demonstrated to move toward and away from a light source in a surfactant solution, which was caused by dissolution triggered by photo-isomerization.[3] We also demonstrated the motion control of ‘LC’ droplets using light in surfactant solutions for the first time.[31] (N-(4-methoxybenzylidene)-4’-butylaniline (MBBA) was utilized both as an LC and a photo-active molecule, which was photo-isomerized. Inhomogeneous UV light illumination with an oblique angle was used to induce the dissolution of molecules triggered by photo-isomerization, which resulted in a surface tension gradient. The Marangoni flow induced inside the droplets resulted in MBBA droplets rolling on a substrate toward the light source.

MBBA acts as both an LC and a photo-active molecule, meaning that the whole region of the droplet is subject to the photo-isomerization reaction. Therefore, this strategy of motion control could potentially be applied to other LC systems, which would have a range of applications, such as drug delivery or microfluidic control. A non-photoresponsive LC droplet could be mobilized for use in various applications. Therefore, we utilized the host/guest interaction by doping azo dyes into an LC droplet made of 4-Cyano-4’-pentylbiphenyl (5CB). In this case, only a part of the molecules in the LC droplet were photo-excited. Surprisingly, we could still induce motion and control the motion direction of the host/guest LC systems just by changing the functional group of the guest dyes. The detailed mechanism of this motion control is discussed.

Experiment

LC droplets were prepared using a micro-fluidic device.[32] A diagram and picture are shown in

Fig. S1 in the supplementary information (SI). A square glass capillary (inner dimensions: 0.90 × 0.90 mm^2) was attached to a glass slide, and a tapered cylindrical glass capillary (inner diameter: 0.70 mm, outer diameter: 0.87 mm) was inserted into it. A taper with a diameter of 50 μm was prepared using a micropipette puller (P-1000, Sutter Instrument). The inner LC fluid was introduced from the inlet side of the square glass capillary to the outlet side and sheared by the outer fluid introduced from another side of the square glass capillary. The inner and outer fluids were introduced by two syringe pumps. The LC droplets were formed in the inlet of the tapered cylindrical capillary.

4-cyano-4-pentylbiphenyl (5CB, nematic phase: 22.5–35°C) was used as a host LC. (Fig. 1(a)). Two different guest dyes were used as photo-responsive molecules and mixed with the host LC for the inner fluid. The dyes were 4-butyl-4’-hydroxyazobenzene (BHAB) and 4-butyl-4’-methoxyazobenzene (BMAB), which have different functional groups, as shown in Fig. 1(b)(c). Sodium dodecylsulfate (SDS, 0.3 wt%, 25°C) dissolved in pure water was used as a surfactant solution and the outer fluid. The critical micellar concentration C_{CMC} was 0.13 wt% for SDS. BMAB was synthesized via the methylation of BHAB. BHAB (8.0 mmol), iodemethan (32 mmol), and KOH (9.4 mmol) were dissolved in ethanol (8 ml), and the mixture was heated at 50°C for 6 h while stirring. The solid product (BMAB) was recrystallized using hexane after evaporation.

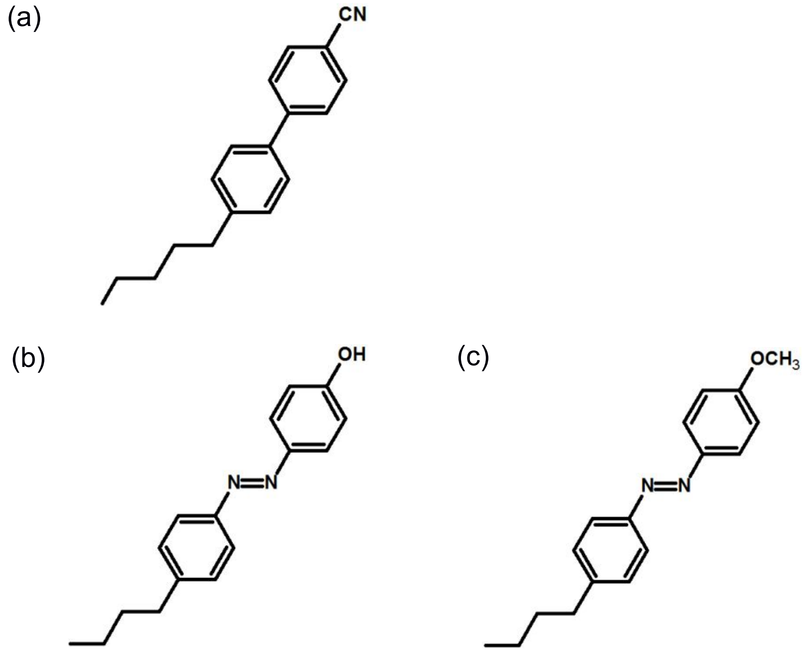

Fig. 1 Molecular structures of the host LC (a) and the doped dyes (b),(c): (a) 4-cyano-4’-pentylbiphenyl (5CB), (b) 4-Butyl-4’-hydroxyazobenzene (BHAB), (c) 4-Butyl-4’-methoxyazobenzene (BMAB).

The setup for the motion observation is shown in Fig. S2 in the SI. A rubber spacer with an open space was sandwiched between two coverslips, and an SDS solution including LC droplets was pipetted into the open space. The cell was placed on an inverted optical microscope (IX71, OLYMPUS), and the behavior of the LC droplets under light illumination was observed. The boundary of the droplet was not clear under cross-Nicole or bright-field conditions, so the analyzer angle was adjusted to make it clearer. A non-polarized UV-LED (Execure LH-1V, HOYA, Center wavelength: 360 nm) was used as a UV light source with an intensity of 58 mW/cm^2 unless otherwise stated. The light was irradiated at an oblique angle of 40 degrees from the top of the microscope. The LC droplets were dissolved for hours without light illumination. In one example, an LC droplet (diameter: 100 μm) in 0.3 wt% SDS solution was dissolved completely about 7 h, and it did not affect the observation of the light-induced change. Considering the pKa of phenol (~10), BHAB was not deprotonated in the surfactant solution (pH ~7).

Results and discussion

Figure 2(a) and (b) show the trajectories of the droplets with different dye doping with the UV light on and off. The optically induced motion of the dye-doped LC droplets in the SDS solution was similar to that observed previously for MBBA droplets.[31] No motion was observed without SDS in the outer solution. The BHAB-doped 5CB droplet moved away from the UV light source, while the BMAB-doped 5CB droplet moved toward it. In both cases, the droplets started to move once the UV light was turned on, and they rolled on a substrate without floating. They kept moving during the irradiation and stopped when the light was turned off. The light-induced motion was repeated when the UV light was turned on and off again (Movies S1 and S2 in the SI). No motion was observed without dye doping.

Under the cross-Nicole observation, the droplet shows a typical “radial” pattern. This is because the LC molecules were aligned perpendicular to the interface due to the anchoring condition. The anchoring condtion depends on the SDS concentration, and it changed to the perpendicular condition for the higher concentrations.[33] As was observed for an MBBA droplet,[31] the “radial” pattern changed into “escaped radial” pattern,[34] because the concentration of the surfactant molecules were less at the interface due to solubilization and the anchoring condtion was changed from the perpendicular to parallel condition at the light irradiated position.

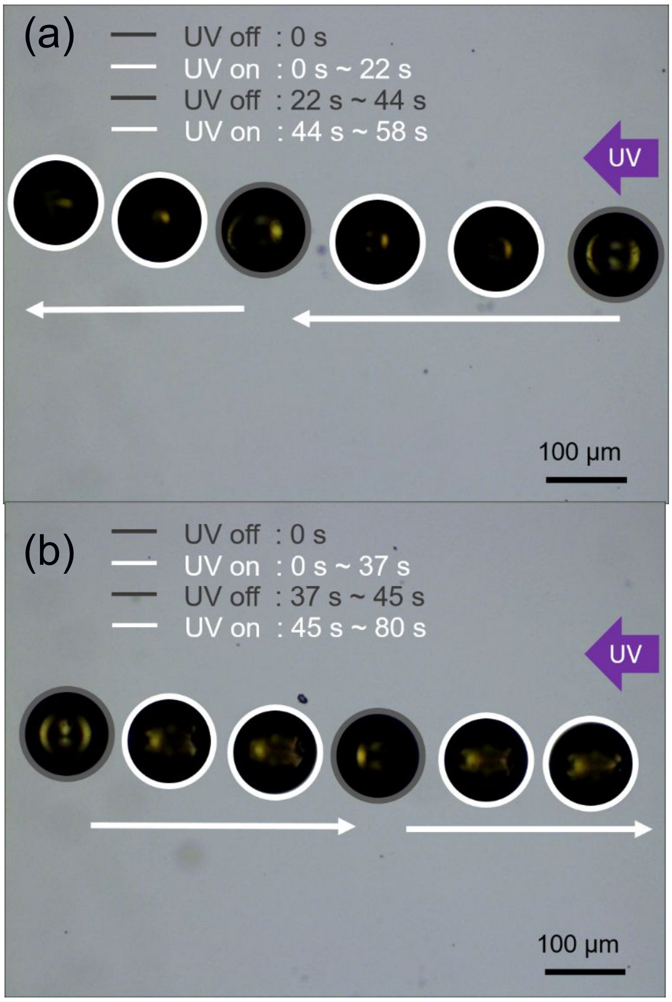

Fig. 2 The trajectory of LC droplets during with the UV light on and off for (a) BHAB-doped and (b) BMAB-doped 5CB droplets. The white circles indicate the positions of the droplet during the UV irradiation, while gray circles indicate the positions when the UV light was turned off. Using a polarized microscope, the analyzer angle was adjusted to make the boundary clearer.

The dependence of the velocity of the LC droplets on the UV light intensity was investigated. The velocity increased linearly with the UV light intensity at lower intensity, but the increase was slight nonlinearly for larger intensities for either type of LC droplet, as shown Fig. 3 (a) and (b). The motion process involves complicated forces at higher intensity, but a detailed analysis is beyond the scope of this paper and will be studied in the future.

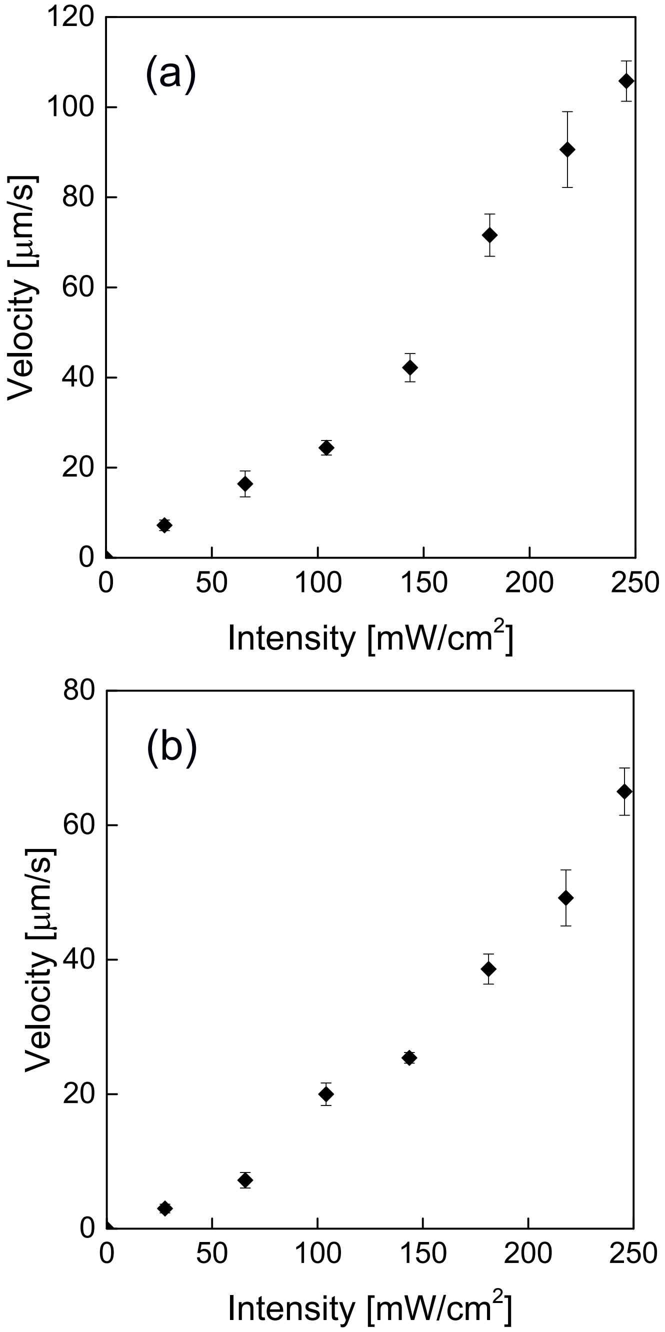

Fig. 3 The velocity dependence of the LC droplet on the UV light intensity for (a) BHAB-doped and (b) BMAB-doped 5CB droplets. The velocity was calculated from the sequence of images obtained during UV irradiation.

In a previous study, the droplet motion was explained by the Marangoni convective flow inside the droplet. The flow inside the two types of the LC droplets was observed, as shown in Movies S3 and S4 in the SI. In both cases, a self-sustained unidirectional convective flow was observed inside the LC droplet during the UV irradiation. It is noted that the droplet was observed from the bottom side by an inverted optical microscope, and the convection flow clearly occurred from the top to bottom and from the bottom to the top side. Interestingly, the convection flow occurred in the opposite direction for the BHAB-doped and BMAB-doped droplets. Obviously, this opposite convective flow must be the cause of the difference in the direction of motion for the two types of droplets. In a previous report,[31] it is supposed that the convective flow inside the LC droplet was induced by the surface tension gradient generated by the photo-induced solubilization of LC molecules into the surfactant solution, and a similar process is expected during the motion in these cases.

To determine whether the solubilization was promoted by the UV irradiation, the changes in the UV/Vis absorption spectrum were observed for the SDS solution outside the LC droplets under UV irradiation. In this experiment, an SDS solution (0.3 wt%, 20 mL) containing an LC droplet (volume: 20 μL) was prepared in a vial. Every 30 seconds during the UV irradiation, 0.5 mL of the outer SDS solution was sampled. >10 min after the sampling, the collection of the samples was measured by the spectrometer. It was assumed that all the dyes in the solutions had been already changed into the trans state because no visible light absorption, corresponding to the cis-isomer,[35] was not observed. The UV/Vis absorption spectra for the different times of UV light duration are shown in Fig. 4 for LC droplets doped with BHAB and BMAB. The UV/Vis absorption spectra of the 5CB

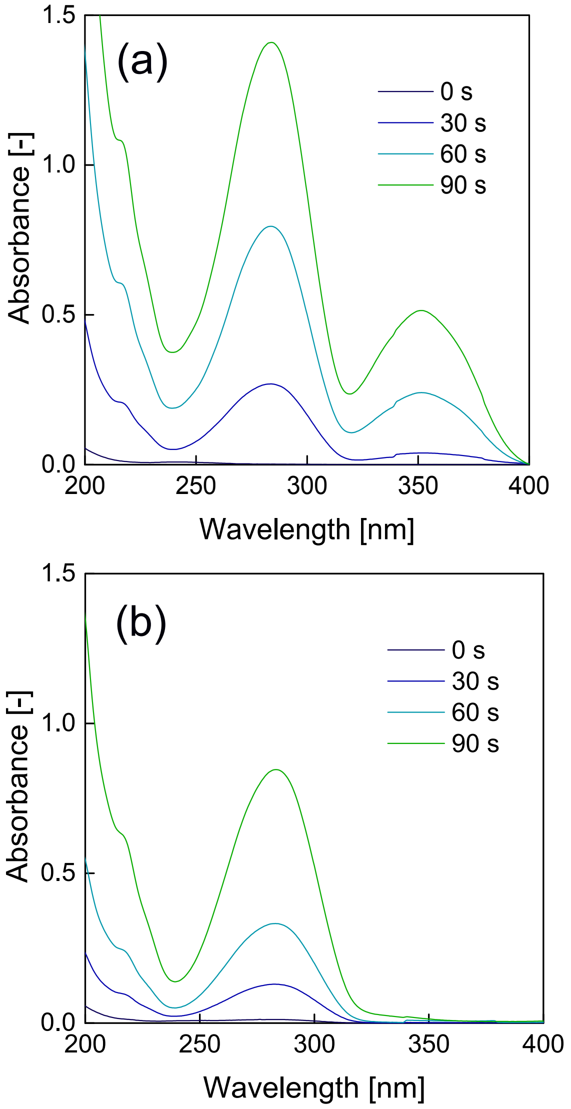

Fig. 4 The temporal change of the UV/Vis absorption spectrum of the SDS solution including an LC droplet was monitored during the UV irradiation for (a) BHAB-doped, (b) BMAB-doped 5CB droplets. A sample solution was pipetted out from the outside SDS solution each time for the absorption spectrum measurement.

and SDS dyes are provided in Fig. S3 for reference. The absorption peaks of 5CB and BHAB/BMAB are around 280 and 350 nm, respectively. Thus, it is understood that 5CB was solubilized into the outer SDS solution in both cases, but the dye was solubilized for only the BHAB droplet. This result indicates different solubilities of the guest dyes under UV irradiation.

The different solubility suggested that there were different effects of the dyes at the LC/water interface under UV irradiation. To understand the behavior of the dyes during the solubilization, the initial conditions of the dyes must be clarified. The affinity of the dyes at the LC/solution interfaces was examined by studying the dependence of the contact angle on the concentration of the doped dyes. For this purpose, a dye-doped LC was dropped onto the bottom of a petri-dish containing an SDS solution. The petri-dish surface was processed with a hydrophobic treatment to keep the LC droplet attached to the bottom surface. An LC droplet with a volume of 20 μL and a 0.3 wt% SDS solution were used for the observation. The dye concentrations were 1, 3, and 5 wt% in the LC droplets. The contact angle was measured for each droplet. A lower contact angle indicates lower interfacial tension, which indicates that the dyes prefer to adsorb at the LC/solution interface.

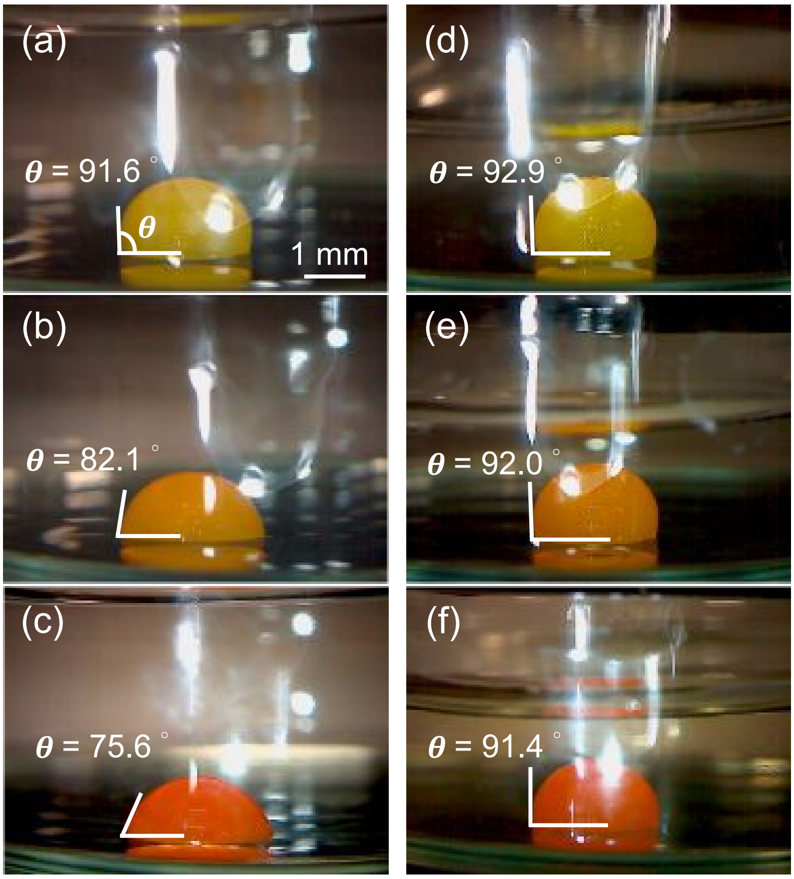

Fig. 5 Pictures of the LC droplets with different concentrations of doped dyes: (a)-(c) BHAB-doped 5CB droplets with 1, 3, and 5 wt% of the doped dye, respectively, (d)-(f) BMAB-doped 5CB droplets with 1, 3, and 5 wt% of the doped dye, respectively. The contact angle was measured for each droplet. LC droplets were attached on the bottom of a petri-dish that was hydrophobically treated.

Pictures of the droplets for different concentrations of dyes are shown in Fig 5. In the case of the BHAB-doped droplet, the contact angle decreased as the dye concentration increased, but it did not change much for the BMAB droplet. The results indicate that BHAB molecules can stay at the interface under static conditions due to the amphiphilic ability, while BMAB molecules remain inside the droplet due to the hydrophobic property.

Next, the dynamic position change of the dyes during the UV irradiation was investigated through the dynamic change of the interfacial tension.[36] The pendant drop method (DMs-401, Kyowa Kaimen Kagaku) was used to monitor the change in interfacial tension of the LC droplet. Samples were prepared by dropping a pendant drop (20 μL) of dye-doped LC from a syringe needle in a cell filled with an SDS solution (0.3 wt%). A sequence of pendant drop images was acquired by a camera every second, and the interfacial tension was calculated from the shape by fitting with the Young-Laplace equation.

Figure 6(a) and (b) show the changes in interfacial tension by the UV irradiation for the BHAB- and BMAB-doped LC droplets. The UV light was turned on 5 seconds after starting the measurement. The interfacial tension increased immediately after the UV irradiation in the case of the BHAB-doped 5CB, but it was decreased by the UV irradiation in the case of BMAB-doped 5CB. The results indicate the desorption of molecules from the LC/water interface and the adsorption of molecules onto the LC/water interface by the UV irradiation, respectively. These opposite trends of the different dyes for the LC/solution interface are responsible for the opposite convective flow.

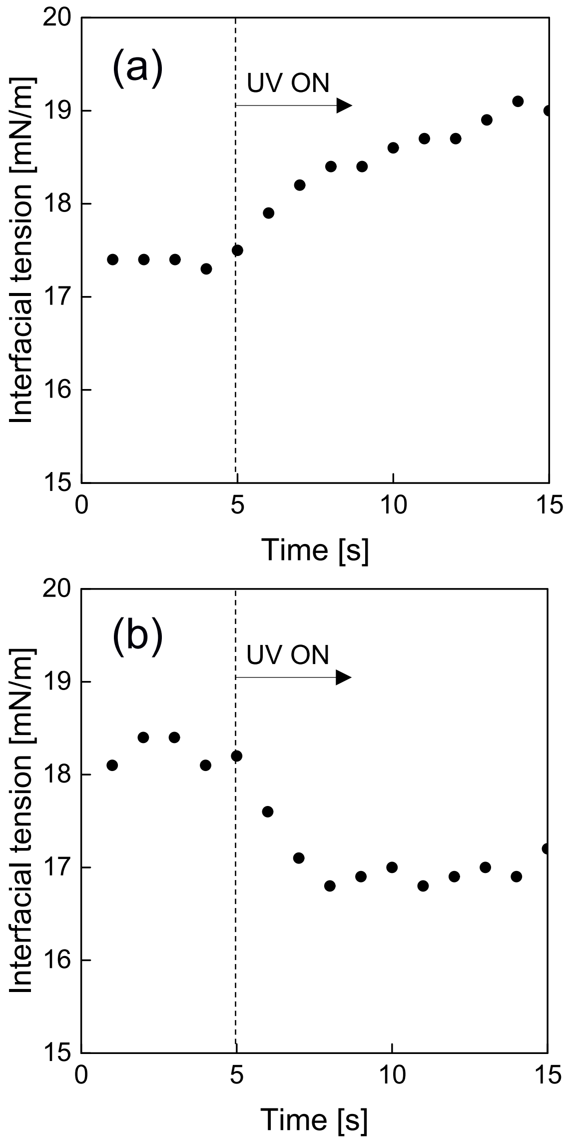

Fig. 6 The change in dynamic interfacial tension by the UV irradiation for (a) BHAB-doped and (b) BMAB-doped 5CB droplets. The UV light was turned on 5 seconds after the measurement started. The interfacial tension was measured by the pendant-drop method.

Based on the measurements and observations, we propose the following mechanism for the BHAB/BMAB-doped 5CB droplets, as shown in Fig 7. For the BHAB-doped 5CB, a part of the dye molecules initially remains adsorbed at the LC/water interface (Fig. 7(a)) based on the static interfacial tension measurements. These dye molecules are subject to photo-isomerization by the UV irradiation. The dynamic interfacial tension measurements and the UV/Vis monitoring of the surfactant solution indicate that the 5CB was solubilized into the surfactant solution and that the dye molecules were solubilized into the solution (Fig. 7(a)).

The desorption of dye molecules from the interface increased the interfacial tension on the side of UV irradiation, which resulted in a gradient of the interfacial tension. This is the origin of the convective flow inside the LC droplet (Fig. 7(b)). The flow direction on the top surface of the droplet moved away from the UV light source, as shown in Movie S3 in the SI. The droplet then experienced counter-clockwise torque, which induced rolling motion and moved the droplet away from the UV light source.

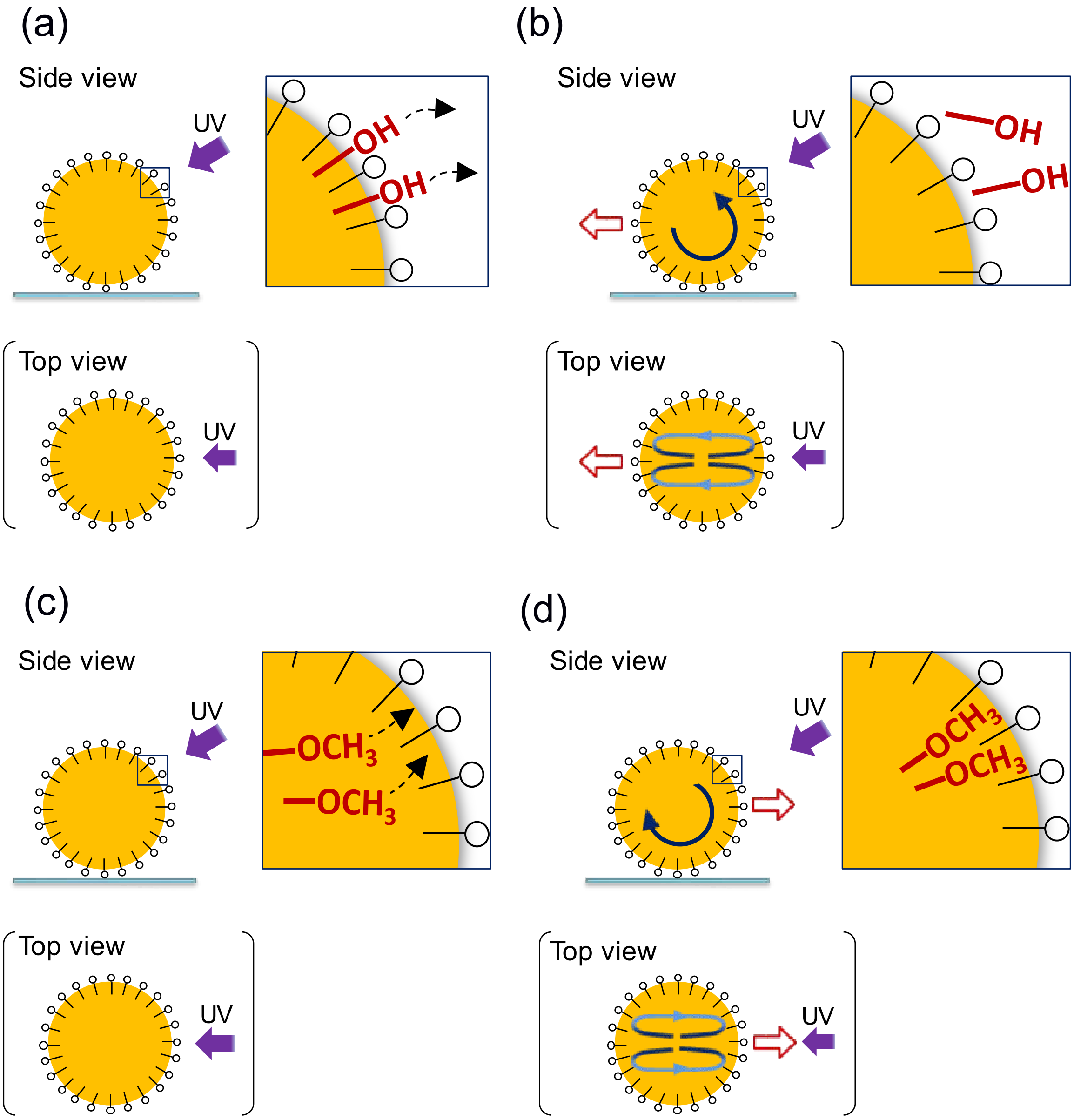

Fig. 7 Diagram of the proposed motion mechanism of BHAB-doped (a,b) and and BMAB-doped (c,d) liquid crystal droplet. The bright blue arrow in the top view indicates flow on the top side of droplet.

On the other hand, BMAB molecules were initially inside the LC droplet (Fig. 7(c)) according to the static interfacial tension measurements. The dynamic interfacial tension decreased during the UV illumination and the UV/Vis monitoring, which suggested that the dye molecules moved to the

LC/solution interface from the inside (Fig. 7(c)). The adsorption of the dye molecules onto the interface decreased the interfacial tension on the side of UV irradiation, which is the opposite of the trend in the case of BHAB. This interfacial tension gradient caused a convective flow (Fig. 8(d)). Movie S4 in the SI shows that the convection flow moved toward the UV light source on the top surface of the droplet. As a result, the droplet had a clockwise torque, which induced motion toward the UV light source.

Additionally, it is mentioned how the liquid crystal phase influenced the motion. The behavior of a droplet in the isotropic phase was investigated under the same experimental conditions except for the temperature. The droplet was 5CB doped with BHAB. The result is shown in Movie S5 in the SI. At room temperature, the droplet was in the nematic phase, but the phase changed to the isotropic phase when increasing the temperature, which was recognized by the change in the pattern of the droplet in the middle of the movie. After the phase change into the isotropic state, UV light was illuminated, but motion did not occur.

Next, the behavior of an oil droplet doped with BHAB was also studied under similar experimental conditions, and the result is shown in Movie S6. The droplet showed a sudden motion upon illumination with UV light, but the movement was random, and directional motion could not be maintained. These results show that the LC state was necessary for the photo-induced motion, possibly because the directional flow is maintained by the long-range molecular interaction of the LC.

Conclusion

We successfully controlled the photo-induced motion of dye-doped LC droplets in a surfactant solution with a concentration higher than the CMC. We controlled the direction of motion by simply changing the functional groups of guest dyes, which resulted in movement toward and away from the light source. This motion was explained by the Marangoni flow caused by the photo-induced desorption from the LC/solution interface or the adsorption of dye molecules onto it. This is a new demonstration of optically induced motion for LC droplets and could lead to further applications involving the motion control of active matter. The motion of any LC droplets could be controlled using this light-based strategy, which could be applied for drug delivery, microscopic extraction, and the condensation and detection of chemicals, especially for microfluidic applications.

Acknowledgments

The research was financially supported by the Institute of Science and Engineering, Chuo University, JST PRESTO (#JPMJPR1675), and the Science Research Promotion Fund from the Promotion and Mutual Aid Corporation for Private Schools of Japan. We are grateful to Prof. H. Suzuki at Chuo University for the surface tension measurements.

References

1 C. Jin, C. Krüger and C. C. Maass, *PNAS*, 2017, **114**, 5089–5094.

2 S. Sánchez, L. Soler and J. Katuri, *Angewandte Chemie International Edition*, 2015, **54**, 1414–1444.

3 Y. Xiao, S. Zarghami, K. Wagner, P. Wagner, K. C. Gordon, L. Florea, D. Diamond and D. L. Officer, *Advanced Materials*, 2018, **0**, 1801821.

4 H. Hess, G. D. Bachand and V. Vogel, *Chemistry – A European Journal*, 2004, **10**, 2110–2116.

5 L. Deprez and P. de Buyl, *Soft Matter*, 2017, **13**, 3532–3543.

6 S. Jiang, Q. Chen, M. Tripathy, E. Luijten, K. S. Schweizer and S. Granick, *Advanced Materials*, 2010, **22**, 1060–1071.

7 A. Walther and A. H. E. Müller, *Chemical Reviews*, 2013, **113**, 5194–5261.

8 L. Hong, S. Jiang and S. Granick, *Langmuir*, 2006, **22**, 9495–9499.

9 S. J. Ebbens and J. R. Howse, *Langmuir*, 2011, **27**, 12293–12296.

10 R. Dong, Q. Zhang, W. Gao, A. Pei and B. Ren, *ACS Nano*, 2016, **10**, 839–844.

11 Q. Zhang, R. Dong, Y. Wu, W. Gao, Z. He and B. Ren, *ACS Appl. Mater. Interfaces*, 2017, **9**, 4674–4683.

12 N. Sugai, Y. Nakai, Y. Morita and T. Komatsu, *ACS Appl. Nano Mater.*, 2018, **1**, 3080–3085.

13 S. Kobayakawa, Y. Nakai, M. Akiyama and T. Komatsu, *Chemistry – A European Journal*, 2017, **23**, 5044–5050.

14 T. Lopez-Leon and A. Fernandez-Nieves, *Colloid Polym Sci*, 2011, **289**, 345–359.

15 A. Fernández-Nieves, V. Vitelli, A. S. Utada, D. R. Link, M. Márquez, D. R. Nelson and D. A. Weitz, *Physical Review Letters*, 2007, **99**, 157801.

16 F. C. Keber, E. Loiseau, T. Sanchez, S. J. DeCamp, L. Giomi, M. J. Bowick, M. C. Marchetti, Z. Dogic and A. R. Bausch, *Science*, 2014, **345**, 1135.

17 P. Guillamat, Ž. Kos, J. Hardoüin, J. Ignés-Mullol, M. Ravnik and F. Sagués, *Science Advances*, 2018, **4**, eaao1470.

18 I. Muševič, *Materials (Basel)*, , DOI:10.3390/ma11010024.

19 O. D. Lavrentovich, I. Lazo and O. P. Pishnyak, *Nature*, 2010, **467**, 947–950.

20 I. Lazo and O. D. Lavrentovich, *Philos Transact A Math Phys Eng Sci*, , DOI:10.1098/rsta.2012.0255.

21 C. Peng, T. Turiv, Y. Guo, Q.-H. Wei and O. D. Lavrentovich, *Science*, 2016, **354**, 882.

22 K. Peddireddy, P. Kumar, S. Thutupalli, S. Herminghaus and C. Bahr, *Langmuir*, 2012, **28**, 12426–12431.

23 S. Herminghaus, C. C. Maass, C. Krüger, S. Thutupalli, L. Goehring and C. Bahr, *Soft Matter*, 2014, **10**, 7008–7022.

24 C. Krüger, C. Bahr, S. Herminghaus and C. C. Maass, *Eur. Phys. J. E*, 2016, **39**, 64.

25 C. Krüger, G. Klös, C. Bahr and C. C. Maass, *Phys. Rev. Lett.*, 2016, **117**, 048003.

26 T. Yamamoto and M. Sano, *Soft Matter*, 2017, **13**, 3328–3333.

27 M. Suga, S. Suda, M. Ichikawa and Y. Kimura, *Phys. Rev. E*, 2018, **97**, 062703.

28 L. Wang and Q. Li, *Advanced Functional Materials*, 2016, **26**, 10–28.

29 J. Fan, Y. Li, H. K. Bisoyi, R. S. Zola, D. Yang, T. J. Bunning, D. A. Weitz and Q. Li, *Angewandte Chemie International Edition*, 2015, **54**, 2160–2164.

30 Y. Dogishi, S. Endo, Y. W. Sohn and K. Katayama, *Entropy*, 2017, **19**, 669.

31 Y. Dogishi, Y. Sakai, W. Y. Sohn and K. Katayama, *Soft Matter*, 2018, **14**, 8085–8089.

32 A. S. Utada, E. Lorenceau, D. R. Link, P. D. Kaplan, H. A. Stone and D. A. Weitz, *Science*, 2005, **308**, 537–541.

33 S. Kulkarni and P. Thareja, *Journal of Adhesion Science and Technology*, 2016, **30**, 1371–1390.

34 O. O. Prishchepa, A. V. Shabanov and V. Ya. Zyryanov, *Phys. Rev. E*, 2005, **72**, 031712.

35 J.-H. Sung, S. Hirano, O. Tsutsumi, A. Kanazawa, T. Shiono and T. Ikeda, *Chem. Mater.*, 2002, **14**, 385–391.

36 J. D. Berry, M. J. Neeson, R. R. Dagastine, D. Y. C. Chan and R. F. Tabor, *Journal of Colloid and Interface Science*, 2015, **454**, 226–237.n

LC droplets could be mobilized and direction-controlled by the structure of photo-respon
molecules.