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Motion with Memory of a Self-Propelled Object

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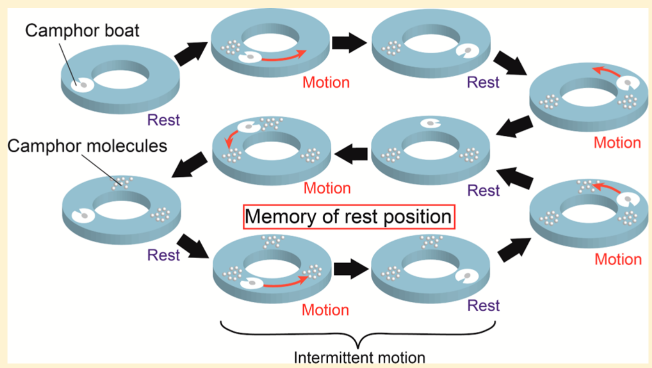
Supporting Information

ABSTRACT: The concept of self-propelled objects is important for the understanding of biological mobility, as well as for the development of autonomous devices in medicine and engineering. In this study, a simple self-propelled object, driven by a difference in surface tension, was found to exhibit intermittent self-motion (alternately in motion and at rest) in an annular water channel, with resting positions and features of motion in subsequent cycles remaining almost the same as those previously visited; that is, memories of the resting positions and features of motion were observed. The occurrence of the memory phenomenon was found to depend on the relationship between the resting time and the period for one lap of the annular channel. The mechanism of memory is discussed in terms of the distribution of surface-active molecules and local surface tension at the resting positions.



■ INTRODUCTION

Studies of self-motion that mimics bacterial motion on a small scale are very important not only for understanding the mechanism of biological motion in living organisms, such as energy transduction, chemotaxis, and collective motion, but also for the development of autonomous motors that can perform inspection, manipulation, and transport functions in the fields of medicine and engineering.[1−5]

Several artificial self-propelled systems have been studied under almost isothermal and chemical nonequilibrium conditions.[6−10] Although most investigations have focused on the ability to control the speed and direction of motion, systems in which behavior changes depending on the physicochemical environment have not yet been successfully developed.

We have previously investigated various types of mode-switching self-motion in which the driving force is the gradient of the surface tension (e.g., mode change depending on internal[11] and external[12−14] boundaries, synchronization between two motors,[15−17] and motion coupled with chemical reactions).[18−20]

In this study, for a camphor boat that exhibited unidirectional intermittent motion while floating in an annular water channel, we found that the features of motion were influenced by those of previous motion; that is, motion with memory was observed. The mechanism of this motion with memory is discussed in terms of the distribution of camphor molecules, the surface tension at the rest position, and the water level near the camphor disk.

■ EXPERIMENTAL SECTION

(+)-Camphor was purchased from Wako Pure Chemical Industries (Kyoto, Japan) and a camphor disk (diameter, 3 mm; thickness, 1 mm; mass, 5 mg) was prepared using a pellet die set for Fourier transform infrared (FTIR) spectrometry. A camphor boat was prepared by attaching a camphor disk to the center of a polyester plastic disk (thickness, 0.1 mm; diameter, 10 mm) with a V-shaped edge to induce unidirectional motion, and then the camphor disk was brought into contact with the water surface, as shown in Figure 1. As the geometry of the boat was sensitive to the speed of motion, the V-shaped edge was

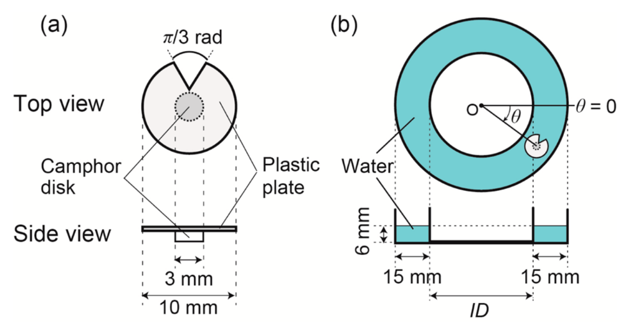


Figure 1. Schematic illustration of (a) a camphor boat and (b) an annular water channel used in this study. In b, ID and O are the inner diameter and the center of the channel, respectively.

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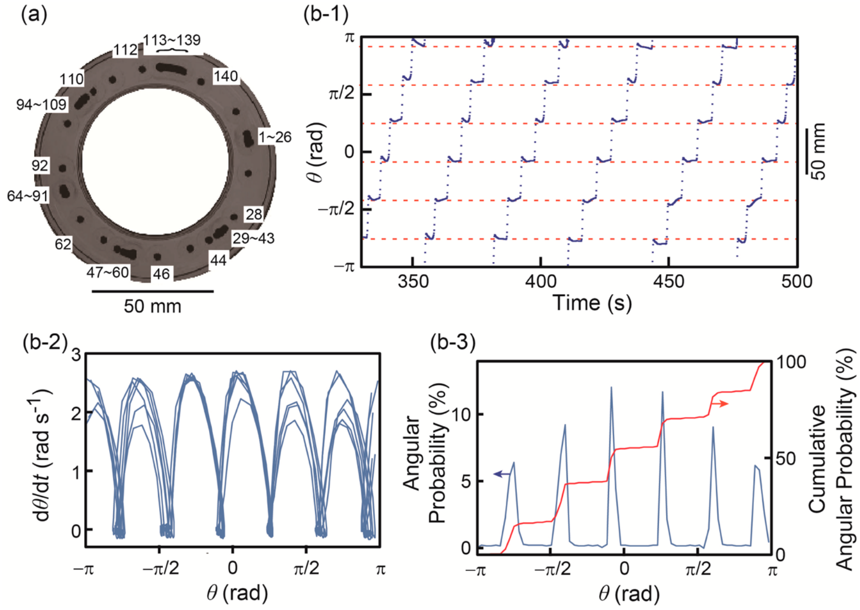

Figure 2. Experimental results on (a) superimposed photographs (time interval = 0.2 s, water channel = 1); (b-1) time series of θ for self-motion of the camphor boat (blue dotted line, time interval = 0.1 s), (b-2) relation between position and angular velocity, θ vs $d\theta/dt$; and (b-3) histogram of the probability of the camphor boat (blue line) locating at an angle θ (resolution = 0.1 rad) and the cumulative probability for $\theta = -\pi$ to π rad (red line) for channel 1. Black dots in panel a indicate the positions of the center of the boat for one cycle of motion. The red dotted lines in panel b-1 parallel to the horizontal axis are separated by distances equivalent to PD/6 and are close to the resting positions of the camphor boat. The histogram was prepared using the data in panel b-1. The corresponding video is shown in the Supporting Information.

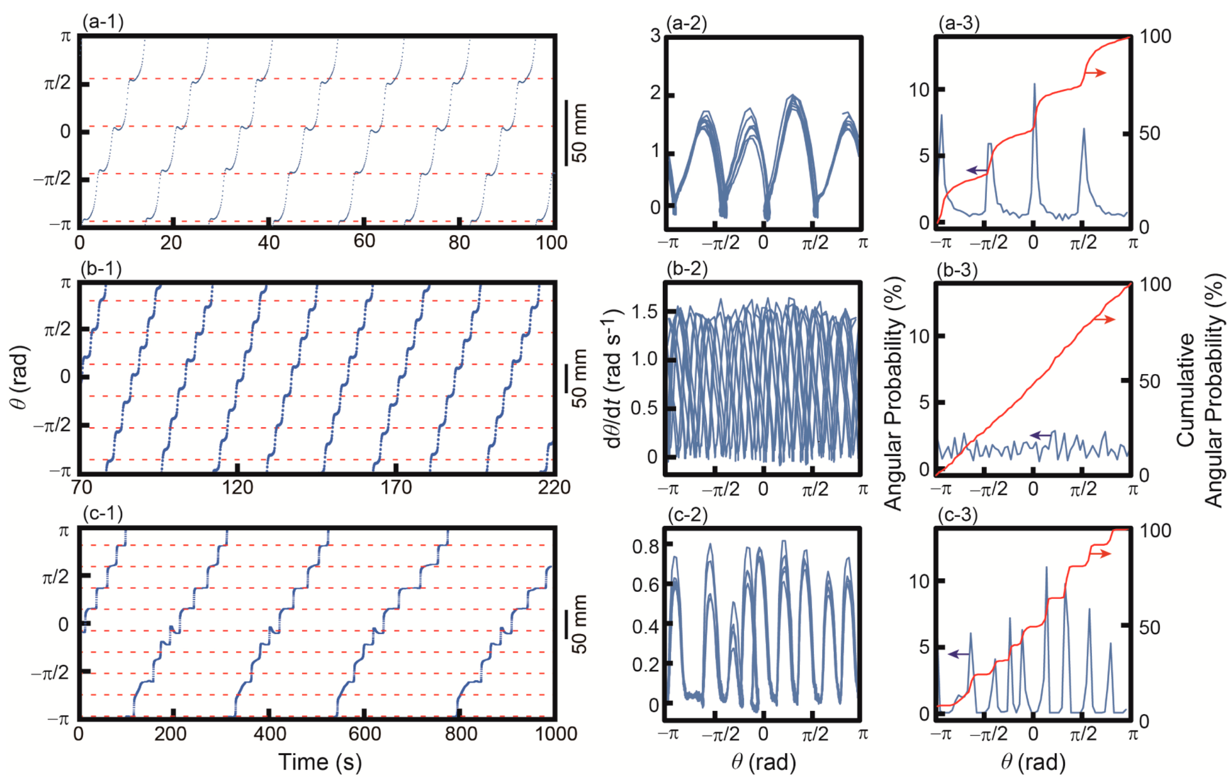

Figure 3. Experimental results of (1) the time series of θ for self-motion of the camphor boat (blue dotted line, time interval = 0.1 s); (2) the relation between position and angular velocity, θ vs $d\theta/dt$; and (3) the histogram of the probability of the camphor boat (blue line) locating at an angle θ (resolution = 0.1 rad) and the cumulative probability from $\theta = -\pi$ to π rad (red line) for different water channels [(a) channel 2, (b,c) channel 3]. The camphor boat used in panel c was modified from those used in panels a and b and that in Figure 2 by changing the position of the camphor disk under the plastic film. The red dotted lines in panels a−c parallel to the horizontal axis are separated by distances equal to PD/4, PD/6, and PD/9, respectively. The histograms in panels a-3, b-3, and c-3 were prepared using the data in panels a-1, b-1, and c-1, respectively.

carefully prepared. The 15-mm-wide annular water channel was made by combining two Petri dishes of different sizes. We used three water channels, as shown in Figure 1b: channel 1 with an inner diameter (ID) of 64 mm and peripheral length in the center of the channel (PL) of 248 mm, channel 2 with ID = 31 mm and PL = 145 mm, and channel 3 with ID = 90 mm and PL = 330 mm. The angle θ, as defined in Figure 1b, was used to analyze the features of the boat's motion. Water was poured into the water channel to a depth of ~6 mm. The movement of the camphor boat was monitored with a digital video camera (HDR-CX560 V, SONY, Tokyo, Japan; minimum time resolution = 1/30 s) in an air-conditioned room at 298 ± 2 K and then analyzed using an image-processing system (ImageJ, National Institutes of Health, Bethesda, MD). The surface tension was measured with a surface tensiometer (CBVP-A3, Kyowa Interface Science Co. Ltd., Saitama, Japan). To quantify the concentration of camphor dissolved in the water phase, the absorbance was measured by UV/vis spectroscopy (UV-1650PC, Shimadzu Co., Kyoto, Japan). The concentration of camphor was evaluated based on the absorbance at 284 nm and the use of a calibration curve. The water level was measured with a laser confocal displacement meter (LT9010M, Keyence, Osaka, Japan).

RESULTS

When a camphor boat was placed on the water channel, unidirectional intermittent motion (alternating between motion and rest) started. For water channel 1 (ID = 60 mm), the camphor boat settled at almost the same rest positions for almost equal intervals after several cycles (Figure 2; see also Video S1 in the Supporting Information). Thus, the rest position was determined by the previous position; that is, memory of the rest position was observed. The rest time and period were 3.9 ± 1.2 s and 28.9 ± 3.1 s, respectively. The maximum migration distance between rest positions (L_{max}) was 42.0 ± 3.5 mm, which was close to PL/n (= 41.3 mm), where PL is the peripheral length in the center of the channel and n is the number of rest positions (here, n = 6). Slow backward motion was observed when the camphor boat moved slightly beyond the previous rest position (Figure 2b-1), and the camphor boat stopped upon reaching the previous rest position. This memory of the rest position in intermittent motion was maintained for at least 10 cycles.

To characterize the movement with respect to θ, the relationship between θ and the angular velocity (dθ/dt) for individual cycles is shown in Figure 2b-2. These characteristics (e.g., acceleration and deceleration) were reproduced at almost the same position in each cycle. Based on the data in Figure 2b-1, a histogram of the probability that the camphor boat is located at θ was created, as shown in Figure 2b-3. Six peaks at almost equivalent intervals of θ can clearly be seen, and the cumulative probability increased stepwise with θ.

Next, we examined the influence of the peripheral length of the water channel by using channels 2 (ID = 30 mm) and 3 (ID = 90 mm). For channel 2, motion with memory was also observed at n = 4 with an equivalent interval in each cycle (Figure 3a-1). The resting time and period were 1.7 ± 0.3 s and 13.7 ± 0.3 s, respectively, and L_{max} was 36.5 ± 2.0 mm, which was close to PL/4 (= 36.1 mm). The θ versus dθ/dt plot and histogram for channel 2 were similar to those for channel 1 (Figure 3a-3). Slow backward motion was also observed for channel 2. In contrast, motion with memory was not observed for channel 3, which was longer than channel 1, as shown in Figure 3b. The rest time and period in Figure 3b were 1.8 ± 0.2 s and 17.3 ± 0.8 s, respectively. The motion of the camphor boat depicted in the θ versus dθ/dt plot was independent of the cycle (Figure 3b-2), a uniform distribution was observed in the histogram, and the cumulative probability increased linearly with θ (Figure 3b-3). The difference between motion with and without memory can be distinguished based on the histograms shown in Figures 2 and 3; i.e., motion with memory exhibits a cumulative probability that depends in a stepwise manner, rather than linearly, on θ. Backward motion was hardly observed in channel 3 (Figure 3b).

To consider the effect of the rest time on motion with memory, the attached position of a camphor disk was shifted away from the V-shaped edge of the plastic plate. It was noted that the rest time increased with an increase in the distance between the edge of the camphor boat and the camphor disk.[14] The rest time and period of one cycle of the modified camphor boat in channel 3 were 24.2 ± 8.3 s and 224.2 ± 31.1 s, respectively, and motion with memory was observed, even in this longer water channel (Figure 3c). The experimental conditions and results are summarized in Table 1.

Table 1. Experimental Conditions and Results

ID (mm)	PL (mm)	L_{max} (mm)	t_p (s)	t_r (s)
30	145	36.5 ± 2.0	13.7 ± 0.3	1.7 ± 0.3
60	248	42.0 ± 3.5	28.9 ± 3.1	3.9 ± 1.2
90	330	41.4 ± 1.2	17.3 ± 0.8	1.8 ± 0.2
90	330	19.0 ± 3.8	224.2 ± 31.1	24.2 ± 8.3

To clarify the effect of rest time on motion with memory, the rest time (t_r) versus the period of one cycle (t_p) is shown in Figure 4. Because of the definitions of t_p and t_r, no data were obtained at $t_p \leq nt_r$. In Figure 4, the average values of t_r for individual cycles are plotted, because $t_p > nt_r$ sometimes does not hold for rest states in which t_r is considerably longer than the average value. Based on the experimental results, we found

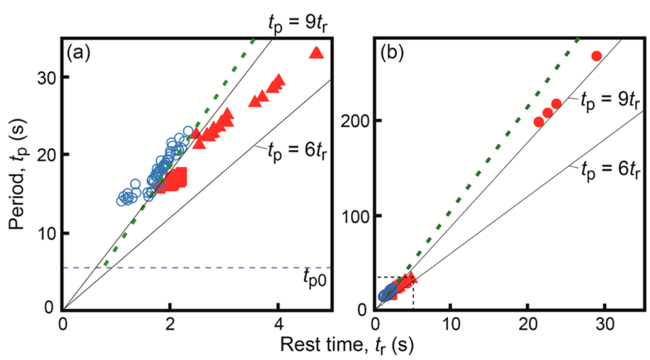

Figure 4. Relationship between the rest time of intermittent motion (t_r) and the period of one cycle of the camphor boat (t_p) when motion with (solid symbols) or without memory (empty circles) was observed. The horizontal blue dotted line (t_{p0}) in panel a is the period within which the camphor boat completes one lap of channel 2. The triangles, squares, and circles show data for channels 1−3, respectively. Because n = 6 for channel 1 and n = 9 for channel 3, the lines $t_p = 6t_r$ and $t_p = 9t_r$ are considered boundary lines. The green dotted line denotes the threshold between motion with and without memory based on the experimental results. Panel a is an enlarged view of the area enclosed in the dotted square in the lower quadrant of panel b.

an empirical boundary between motion with and without memory.

To investigate the influence on the motion of the dissolution of camphor during the rest period and the diffusion of camphor during one lap, the time series of surface tension was measured. The time series of surface tension is shown in Figure 5, when a camphor disk was moved by hand. When the camphor disk was moved toward a platinum wire and settled just below it for 3 s, the surface tension decreased to 52 mN m^{-1}. When the camphor disk was moved away from the platinum wire, the surface tension increased with time. Here, the period (20 s) and rest time (3 s) under the condition of motion with memory in Figure 4 were reflected in the periods of states IV and V and that of state III, respectively, in Figure 5. The water level at a fixed position was measured by changing the position of the camphor disk to clarify the relationship between the surface tension and water level, as shown in Figure 6.

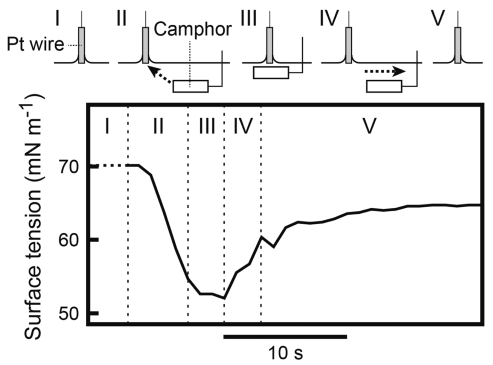

Figure 5. Experimental results for the time series of the surface tension. In this experiment, a platinum wire was placed in contact with the water surface to measure the surface tension (state I). A camphor disk sinking in the water slowly moved toward the Pt wire (state II). The effect of Marangoni flow was eliminated by sinking the camphor disk into the bulk phase. The camphor disk was fixed just below the Pt wire for 3 s (state III). The camphor disk was then moved away from the Pt wire (state IV).

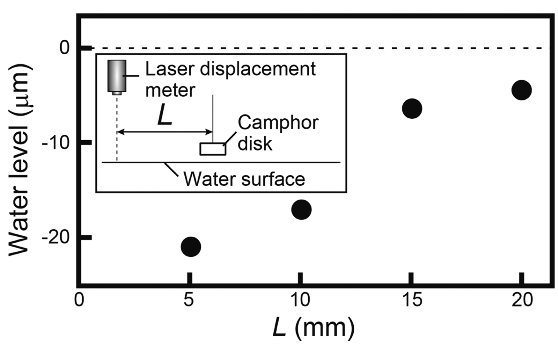

Figure 6. Experimental results for the dependence of the water level on the length L, which is defined in the inset.

The water level was lowered by 21 μm, at a distance of $L = 5$ mm from a camphor disk. We now consider the motion with memory of a camphor boat for which the driving force arises from differences in the surface tension based on the experimental results and related articles.[11−17,21−23] The experimental results with the three channels suggest that a longer rest time and a shorter period per cycle play important roles in motion with memory. A longer rest time increases the amount of camphor dissolved in the water phase. A shorter period per cycle reduces the diffusion and sublimation of camphor in the rest position. As a result, a higher concentration of camphor in the rest position can decrease the velocity of the camphor boat because a higher concentration induces a lower surface tension. The number of rest times per lap is determined by the migration length of one intermittent motion and the peripheral length of the channel.

The data presented in Figure 4 suggest that the relationship between the rest time and the period of one cycle plays an important role in determining whether motion with or without memory occurs, regardless of the size of the water channel.

The surface tension is significantly decreased to 52 mN m^{-1} when the camphor is fixed for a few seconds, which corresponds to the rest time (Figure 5). This surface tension value can stop camphor motion. Twenty seconds after the camphor disk is moved away from the Pt wire, the surface tension increases to 62 mN m^{-1}. This suggests that the surface tension is 62 mN m^{-1} after the period of one cycle. We previously reported that this value of the surface tension is close to the threshold value to stop motion.[24]

A decrease in the water level around the camphor disk induces backward motion (Figure 6). Marangoni flow[10,25,26] or the change in the contact angle at the water/glass interface is generated by the difference in surface tension at the rest position. As a result, the water level may decrease around this position. The camphor boat moves backward when it overshoots the previous rest position because the water level is kept lower as a result of the remaining difference in surface tension. Based on a measurement of absorbance for the aqueous solution around the fixed camphor, the concentration of camphor was ∼5 mM. This value suggests that the concentration of camphor must be significantly high to suppress self-motion because the surface tension for a 5 mM camphor solution is ∼58 mN m^{-1}.

■ DISCUSSION

A suggested mechanism for motion with memory is shown in Figure 7. Camphor molecules from the solid disk dissolve in the water phase and accumulate at the base of the plastic plate (state I).[14] In this state, the camphor boat does not move because the surface tension is balanced around the camphor boat. As the underside of the plastic plate becomes saturated with accumulated camphor molecules, which ultimately reach the V-shaped edge of the plastic plate (left side of the plastic

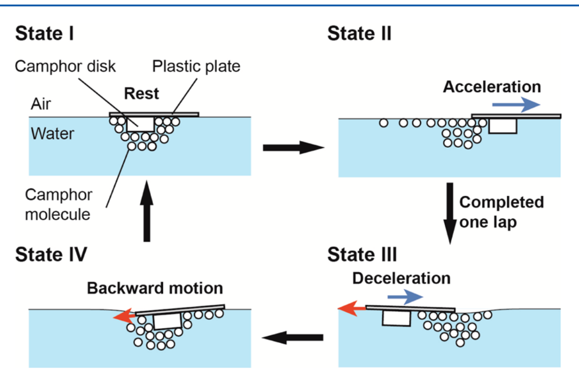

Figure 7. Schematic illustration of the mechanism of the memory function for self-motion (side view). Motion with memory is generated by the repetition of states I−IV.

plate in Figure 7), the camphor molecules are released to the water surface, and thus, the surface tension at this point decreases, and the camphor boat begins to accelerate in the opposite direction (state II). The boat then loses its driving force as a result of the loss of camphor molecules and is decelerated by resistance due to the viscosity of the water. The number of camphor molecules on water is reduced by sublimation, but those dissolved during the rest time remain at the rest position. When the camphor boat has completed one lap of the water channel and approaches a previous rest position, it decelerates as a result of a local decrease in the surface tension due to the presence of camphor molecules (state III). In the experimental results, the camphor disk would overshoot and then return to the previous position. The decrease in the water level around the camphor disk induces backward motion, as indicated by the red arrow in the figure (state IV). Thus, the camphor boat slowly moves forward or backward to the minimum water level around the previous rest position, where the forces around the camphor boat are balanced. The main factor of the memory function is the existence of a local area at lower surface tension, and the lowest surface level can lead to stopping at the same position as previously visited.

■ CONCLUSIONS

In this study, memory of the rest position in intermittent motion in an annular water channel was observed, and the mechanism of this phenomenon was discussed in terms of the surface tension and the kinetics of camphor molecules in water. A longer rest time and shorter period of a cycle induce motion with memory. In addition, backward motion is also important for ensuring that the boat returns to the previous rest position. Although the difference in surface tension around the camphor boat might be related to backward motion, this mechanism has not yet been fully elucidated. This point will be explored further in future studies and should provide a more comprehensive understanding of the mechanism of motion with memory. The present experimental system can be regarded as a self-organized hierarchical system composed of the water surface and the water phase: this hierarchical system can predict future motion based on the hierarchical condition resulting from previous movement.

■ ASSOCIATED CONTENT

Supporting Information

Video of self-propelled motion with memory. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Ismagilov, R. F.; Schwartz, A.; Bowden, N.; Whitesides, G. M. Autonomous Movement and Self-Assembly. *Angew. Chem., Int. Ed.* **2002**, *41*, 652−654.

(2) Paxton, W. F.; Sundararajan, S.; Mallouk, T. E.; Sen, A. Chemical Locomotion. *Angew. Chem., Int. Ed.* **2006**, *45*, 5420−5429.

(3) Hong, Y.; Velegol, D.; Chaturvedi, N.; Sen, A. Biomimetic Behavior of Synthetic Particles: From Microscopic Randomness to Macroscopic Control. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1423−1435.

(4) Kolmakova, G. V.; Yashin, V. V.; Levitan, S. P.; Balazs, A. C. Designing Communicating Colonies of Biomimetic Microcapsules. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 12417−12422.

(5) Shepherd, R. F.; Ilievski, F.; Choi, W.; Morin, S. A.; Stokes, A. A.; Mazzeo, A. D.; Chen, X.; Wang, M.; Whitesides, G. M. Multigait Soft Robot. *Proc. Natl. Acad. Sci. U.S.A.* **2011**, *108*, 20400−20403.

(6) Ikezoe, Y.; Washino, G.; Uemura, T.; Kitagawa, S.; Matsui, H. Autonomous Motors of a Metal−Organic Framework Powered by Reorganization of Self-Assembled Peptides at Interfaces. *Nat. Mater.* **2010**, *11*, 1081−1085.

(7) Toyota, T.; Maru, N.; Hanczyc, M. M.; Ikegami, T.; Sugawara, T. Self-Propelled Oil Droplets Consuming "Fuel" Surfactant. *J. Am. Chem. Soc.* **2009**, *131*, 5012−5013.

(8) Bassik, N.; Abebe, B. T.; Gracias, D. H. Solvent Driven Motion of Lithographically Fabricated Gels. *Langmuir* **2008**, *24*, 12158−12163.

(9) Fournier-Bidoz, S.; Arsenault, A. C.; Manners, I.; Ozin, G. A. Synthetic Self-Propelled Nanorotors. *Chem. Commun.* **2005**, 441−443.

(10) de Gennes, P. G.; Brochard-Wyart, F.; Quéré, D. *Capillarity and Wetting Phenomena: Drops, Bubbles, Pearls, Waves*; Springer: New York, 2004.

(11) Nakata, S.; Iguchi, Y.; Ose, S.; Kuboyama, M.; Ishii, T.; Yoshikawa, K. Self-Rotation of a Camphor Scraping on Water: New Insight into the Old Problem. *Langmuir* **1997**, *13*, 4454−4458.

(12) Hayashima, Y.; Nagayama, M.; Nakata, S. A Camphor Grain Oscillates while Breaking Symmetry. *J. Phys. Chem. B* **2001**, *105*, 5353−5357.

(13) Nakata, S.; Murakami, M. Self-Motion of a Camphor Disk on an Aqueous Phase Depending on the Alkyl Chain Length of Sulfate Surfactants. *Langmuir* **2010**, *26*, 2414−2417.

(14) Suematsu, N. J.; Ikura, Y.; Nagayama, M.; Kitahata, H.; Kawagishi, N.; Murakami, M.; Nakata, S. Mode-Switching of the Self-Motion of a Camphor Boat Depending on the Diffusion Distance of Camphor Molecules. *J. Phys. Chem. C* **2010**, *114*, 9876−9882.

(15) Nakata, S.; Doi, Y.; Kitahata, H. Synchronized Sailing of Two Camphor Boats in Polygonal Chambers. *J. Phys. Chem. B* **2005**, *109*, 1798−1802.

(16) Kohira, M. I.; Hayashima, Y.; Nagayama, M.; Nakata, S. Synchronized Self-Motion of Two Camphor Boats. *Langmuir* **2001**, *17*, 7124−7129.

(17) Nakata, S.; Doi, Y.; Kitahata, H. Synchronized Motion of a Mobile Boundary Driven by a Camphor Fragment. *J. Colloid Interface Sci.* **2004**, *279*, 503−508.

(18) Nagayama, M.; Yadome, M.; Murakami, M.; Kato, N.; Kirisaka, J.; Nakata, S. Bifurcation of Self-Motion Depending on the Reaction Order. *Phys. Chem. Chem. Phys.* **2009**, *11*, 1085−1090.

(19) Iida, K.; Suematsu, N. J.; Miyahara, Y.; Kitahata, H.; Nagayama, M.; Nakata, S. Experimental and Theoretical Studies on the Self-Motion of a Phenanthroline Disk Coupled with Complex Formation. *Phys. Chem. Chem. Phys.* **2012**, *12*, 1557−1563.

(20) Nakata, S.; Matsuda, Y.; Ikura, Y. S.; Takeda, A.; Izumi, S. Mode Change in the Self-Motion of a Benzoquinone Disk Coupled with a NADPH System. *ChemPhysChem* **2012**, *13*, 520−524.

(21) Tomlinson, C. On the Motions of Camphor on the Surface of Water. *Proc. R. Soc. London* **1860**, *11*, 575−577.

(22) Rayleigh, L. Measurements of the Amount of Oil Necessary in Order to Check the Motions of Camphor upon Water. *Proc. R. Soc. London* **1889**, *47*, 364−367.

(23) Ikura, Y. S.; Tenno, R.; Kitahata, H.; Suematsu, N. J.; Nakata, S. Suppression and Regeneration of Camphor-Driven Marangoni Flow with the Addition of Sodium Dodecyl Sulfate. *J. Phys. Chem. B* **2011**, *116*, 992−996.
(24) Nakata, S.; Matsuo, K. Characteristic Self-Motion of a Camphor Boat Sensitive to Ester Vapor. *Langmuir* **2005**, *21*, 982−984.
(25) Scriven, L. E.; Sternling, C. V. The Marangoni Effects. *Nature* **1960**, *187*, 186−188.
(26) Bekki, S.; Vignes-Alder, M.; Nakache, E.; Adler, P. M. Solutal Marangoni Effect. *J. Colloid Interface Sci.* **1990**, *140*, 492−506.