

Supporting Information for “Self-Propelled Motion of a Coumarin Disk
Characteristically Changed in Couple with Hydrolysis on an Aqueous Phase”

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1. Detailed method for the preparation of a coumarin disk

The method for preparing a coumarin disk is schematically illustrated in detail in Fig. S1.

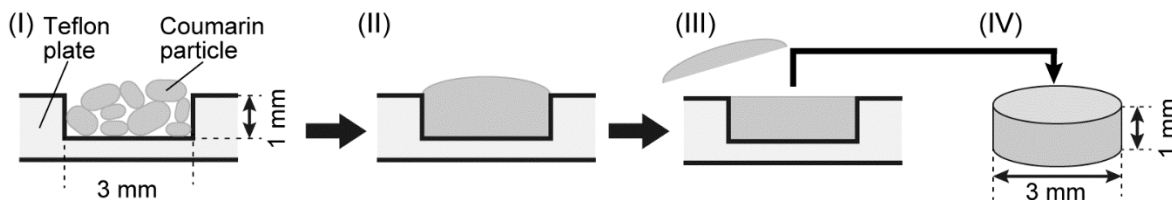


Figure S1. Illustration of coumarin disk preparation (I–III: side view, IV: overhead view). (I) Coumarin particles were filled in a hole in a Teflon plate. (II) Particles were melted by heating, and the melted coumarin was cooled at 298 ± 2 K. (III) Coumarin protruding from the hole was removed to obtain a coumarin disk. (IV) The solid coumarin disk was removed from the hole.

2. Movies of experimental results in Fig. 1

Movie S1. Movie of continuous motion in Fig. 1a (10× speed)

Movie S2. Movie of continuous motion in Fig. 1b (10× speed)

Movie S3. Movie of oscillatory motion in Fig. 1c (10× speed)

Movie S4. Movie of oscillatory motion in Fig. 1d (10× speed)

3. Other analyses of motion of a coumarin disk as a function of initial concentration of Na_3PO_4

To distinguish between continuous and oscillatory motion, the average speed of motion was analyzed for different initial concentrations of Na_3PO_4 ($[\text{Na}_3\text{PO}_4]_0$), as shown in Fig. S2. In this study, we regard the threshold value of the average speed between continuous and oscillatory

motion as 4 mm s^{-1} . An increase in the period of the oscillation between rest and motion reduces the average speed of the oscillatory motion. In reality, the period of the oscillation was similar to the resting time. The speed of a coumarin disk in Fig. 1a was also expressed as a speed distribution, as shown in Fig. S3.

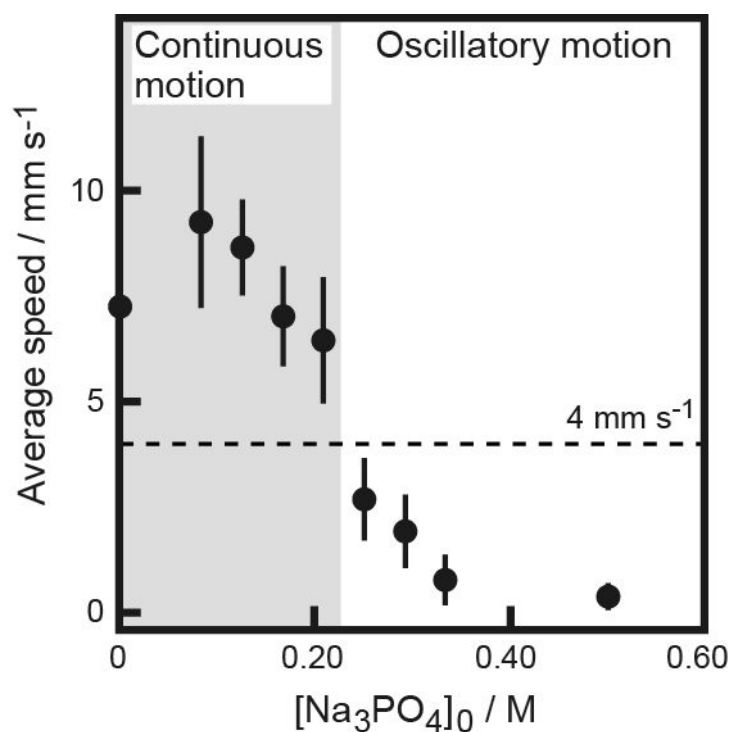


Figure S2. Average speed of motion of a coumarin disk as a function of $[\text{Na}_3\text{PO}_4]_0$.

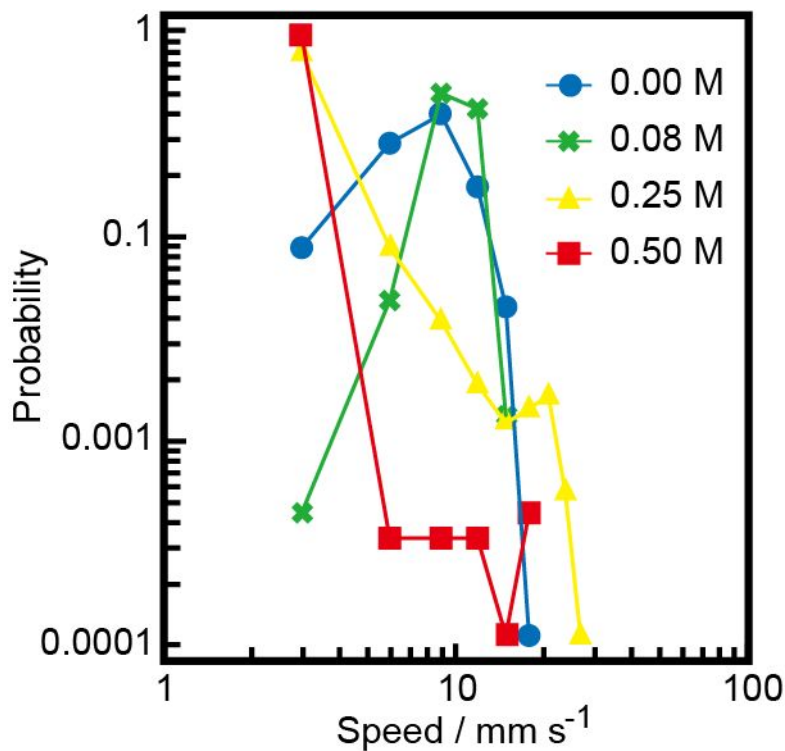


Figure S3. Speed distribution of motion of a coumarin disk as a function of $[\text{Na}_3\text{PO}_4]_0$.

4. Phosphate buffering action

The concentration of OH^- under the equilibrium condition can easily be calculated as follows. Owing to conservation of phosphate ions, $[\text{PO}_4^{3-}]$ and $[\text{HPO}_4^{2-}]$ can be described by the following equations.

$$[\text{PO}_4^{3-}] = [\text{Na}_3\text{PO}_4]_0 - [\text{OH}^-] + 10^{-7}, \quad (\text{S1})$$

$$[\text{HPO}_4^{2-}] = [\text{Na}_3\text{PO}_4]_0 - [\text{PO}_4^{3-}] = [\text{OH}^-] - 10^{-7}. \quad (\text{S2})$$

Here, $[\text{H}_2\text{PO}_4^-]$ and $[\text{H}_3\text{PO}_4]$ are neglected because $[\text{PO}_4^{3-}]$, $[\text{HPO}_4^{2-}] \gg [\text{H}_2\text{PO}_4^-]$, $[\text{H}_3\text{PO}_4]$. The equilibrium constant between PO_4^{3-} and HPO_4^{2-} , K_{a3} , can be described as follows:

$$K_{a3} = \frac{[\text{PO}_4^{3-}][\text{H}^+]}{[\text{HPO}_4^{2-}]} = \frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}][\text{OH}^-]}K_w. \quad (\text{S3})$$

Therefore, using Eqs. S1–S3, $[\text{OH}^-]$ can be calculated as follows:

$$\begin{aligned} K_{a3}[\text{OH}^-]([\text{OH}^-] - 10^{-7}) &= K_w([\text{Na}_3\text{PO}_4]_0 - [\text{OH}^-] + 10^{-7}) \\ [\text{OH}^-]^2 - \left(-\frac{K_w}{K_{a3}} + 10^{-7}\right)[\text{OH}^-] - \frac{K_w}{K_{a3}}([\text{Na}_3\text{PO}_4]_0 + 10^{-7}) &= 0 \\ [\text{OH}^-] &= \frac{1}{2} \left\{ -\frac{K_w}{K_{a3}} + 10^{-7} + \sqrt{\left(\frac{K_w}{K_{a3}} - 10^{-7}\right)^2 + 4\frac{K_w}{K_{a3}}([\text{Na}_3\text{PO}_4]_0 + 10^{-7})} \right\}. \end{aligned} \quad (\text{S4})$$

When the coumarin simultaneously undergoes hydrolysis, the amount of OH^- consumed by hydrolysis equals the amount of *o*-coumaric acid produced. Therefore, Eqs. S1 and S2 can be rewritten as follows:

$$[\text{PO}_4^{3-}] = [\text{Na}_3\text{PO}_4]_0 - [\text{OH}^-] + 10^{-7} - w_b, \quad (\text{S5})$$

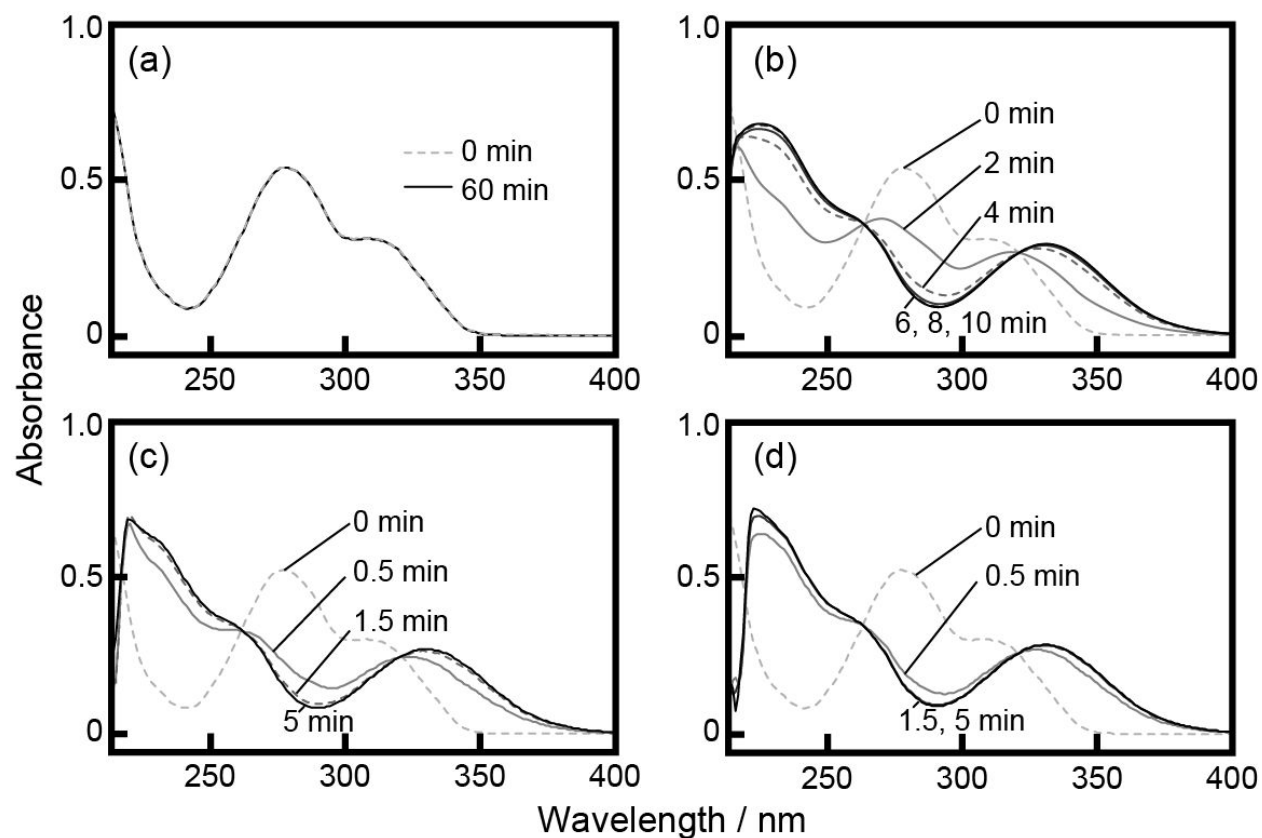
$$[\text{HPO}_4^{2-}] = [\text{Na}_3\text{PO}_4]_0 - [\text{PO}_4^{3-}] = [\text{OH}^-] - 10^{-7} + w_b, \quad (\text{S6})$$

where w_b is the bulk concentration of *o*-coumaric acid, which reflects the progress of coumarin hydrolysis. Finally, $[\text{OH}^-]$ can be written in Eq. 1 in the main text as follows.

$$[\text{OH}^-] = \frac{1}{2} \left\{ -\frac{K_w}{K_{a3}} + 10^{-7} - w_b + \sqrt{\left(\frac{K_w}{K_{a3}} - 10^{-7} + w_b\right)^2 + 4\frac{K_w}{K_{a3}}([\text{Na}_3\text{PO}_4]_0 + 10^{-7} - w_b)} \right\}. \quad (1)$$

5. Evaluation of k_1 and k_{-1} based on the experimental results

To evaluate the reaction rates for coumarin hydrolysis, k_1 and k_{-1} , the time series for the absorbance of 50 μM coumarin was measured at different $[\text{Na}_3\text{PO}_4]_0$ values ($= 0, 0.08, 0.13, 0.17, 0.21, 0.25, 0.29, 0.33, 0.40, \text{ and } 0.50 \text{ M}$), as shown in Fig. S3. At $[\text{Na}_3\text{PO}_4]_0 = 0 \text{ M}$, the spectrum did not change during a 60 min measurement. Therefore, we regard Fig. S4a as the spectrum of coumarin. For a mixture of coumarin and Na_3PO_4 ($[\text{Na}_3\text{PO}_4]_0 = 0.08 \text{ to } 0.50 \text{ M}$), the spectrum of the mixture changed with time and converged within 10 min. Thus, hydrolysis reached the equilibrium condition within 10 min in these cases. Here, we focus on the absorbance at 242 nm to estimate the concentrations of coumarin and *o*-coumaric acid. The absorbance increased with $[\text{Na}_3\text{PO}_4]_0$, and a sigmoidal curve was obtained (Fig. S5). Therefore, we assumed that the spectrum of the solution at $t \sim 5 \text{ min}$ and $[\text{Na}_3\text{PO}_4]_0 = 0.50 \text{ M}$ is that of *o*-coumaric acid.



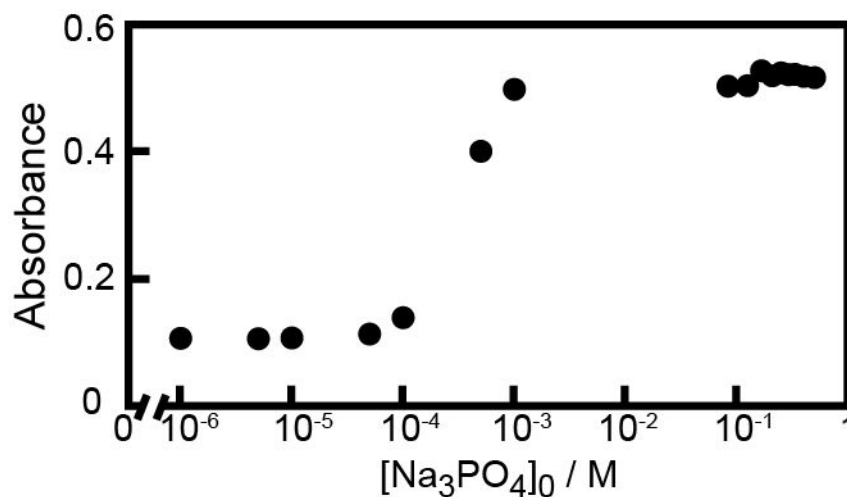


Figure S5. Absorbance at 242 nm of 50 μM coumarin aqueous solutions as a function of $[\text{Na}_3\text{PO}_4]_0$ under the equilibrium condition.

According to the Lambert–Beer law and equilibrium between coumarin and *o*-coumaric acid (see Scheme 1), the relationship between the absorbance at a wavelength and the concentrations of coumarin (u_b) and *o*-coumaric acid (w_b) is described as follows.

$$\frac{u_b}{w_b} = \frac{(A_{ca} - A)}{(A - A_c)}, \quad (S7)$$

where A is the absorbance of a mixture of coumarin and *o*-coumaric acid, A_c is the absorbance of coumarin (concentration: $u_{b0} = 50 \text{ } \mu\text{M}$), and A_{ca} is the absorbance of *o*-coumaric acid (concentration: $w_{b0} = 50 \text{ } \mu\text{M}$). In fact, we selected a wavelength of 242 nm and used the absorbance of the coumarin solution at $t = 5 \text{ min}$ and $[\text{Na}_3\text{PO}_4]_0 = 0.50 \text{ M}$ as A_{ca} , and the absorbance of the

coumarin solution without Na_3PO_4 as A_c . According to the conservation law (see Eq. 3), Eq. S7 can be rewritten as follows.

$$w_b = \frac{(A - A_c)}{(A_{ca} - A_c)} u_{b0}. \quad (\text{S8})$$

Eq. S8 indicates that u_b and w_b can be evaluated by measuring the absorbance.

Next, we describe the derivation of k_1 and k_{-1} using the measured absorbance. The kinetics of w_b is described in Eq. S9 on the basis of hydrolysis of coumarin in an aqueous solution.

$$\frac{dw_b}{dt} = k_1[\text{OH}^-]u_b - k_{-1}w_b. \quad (\text{S9})$$

Eq. S9 can be rewritten as follows.

$$\begin{aligned} \frac{dw_b}{dt} &= -(k_1[\text{OH}^-] + k_{-1})w_b + k_1[\text{OH}^-]u_{b0} \\ &= -\tau w_b + \beta, \end{aligned} \quad (\text{S10})$$

where $\tau = k_1[\text{OH}^-] + k_{-1}$, and $\beta = k_1[\text{OH}^-]u_{b0}$. If $[\text{OH}^-]$ is constant, both τ and β are constants. Eq. S11 is obtained by integrating Eq. S10.

$$w_b = \frac{\beta}{\tau}(1 - e^{-\tau t}). \quad (\text{S11})$$

Eq. S11 shows that w_b converges to β/τ at $t = +\infty$. That is, β/τ can be obtained experimentally as

$\frac{(A - A_c)}{(A_{ca} - A_c)} u_{b0}$ at $t = +\infty$. In fact, $\beta/\tau = 50 \mu\text{M}$ at $[\text{Na}_3\text{PO}_4]_0 \geq 0.13 \text{ M}$.

Eq. S12 is obtained from Eq. S11.

$$\ln\left[1 - \frac{\tau}{\beta}w_b(t)\right] = -\tau t. \quad (\text{S12})$$

We use Eq. S13 to evaluate τ and β experimentally.

$$-\ln\left[1 - \left(\frac{\tau}{\beta}\right)\left(\frac{A - A_c}{A_{ca} - A_c}\right)u_{b0}\right] = \tau t. \quad (\text{S13})$$

Figure S6 shows a graph of $-\ln\left[1 - \left(\frac{\tau}{\beta}\right)\left(\frac{A - A_c}{A_{ca} - A_c}\right)u_{b0}\right]$ vs. t at $u_{b0} = 50 \mu\text{M}$ and $[\text{Na}_3\text{PO}_4]_0 = 0.08 \text{ M}$. Using this graph, τ can be obtained for each $[\text{Na}_3\text{PO}_4]_0$ value (0.08, 0.13, 0.17, 0.21, 0.25, 0.29, 0.33, 0.40, and 0.50 M). Finally, k_1 and k_{-1} were obtained as $0.385 \pm 0.011 \text{ M}^{-1} \text{ s}^{-1}$ and $(1.32 \pm 0.75) \times 10^{-4} \text{ s}^{-1}$, respectively, from the τ value corresponding to each $[\text{Na}_3\text{PO}_4]_0$ value.

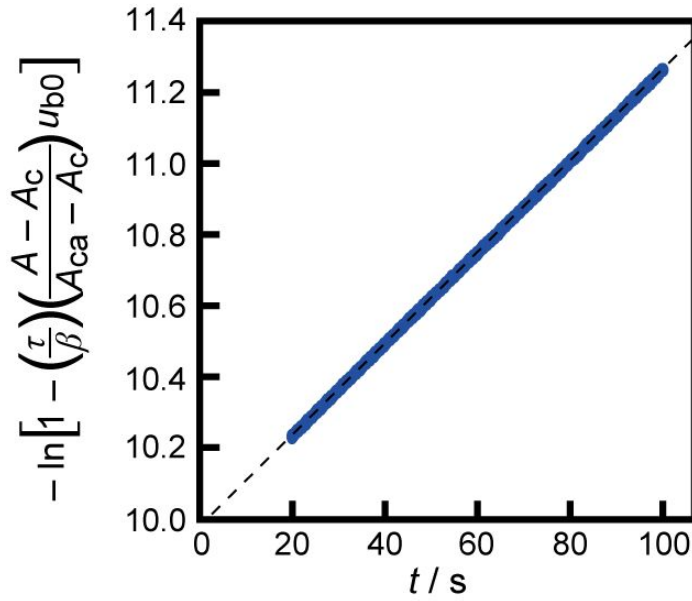


Figure S6. $-\ln\left[1 - \left(\frac{\tau}{\beta}\right)\left(\frac{A - A_c}{A_{ca} - A_c}\right)u_{b0}\right]$ versus t . The values of the constants are $u_{b0} = 50 \mu\text{M}$, $[\text{Na}_3\text{PO}_4]_0 = 0.08 \text{ M}$, and $\beta/\tau = 47.2 \mu\text{M}$.

Using the derived k_1 and k_{-1} , we calculated the time variation of w_b , as shown in Fig. S7. The calculated results are fitted to the experimental results for every $[\text{Na}_3\text{PO}_4]_0$ value (data not shown).

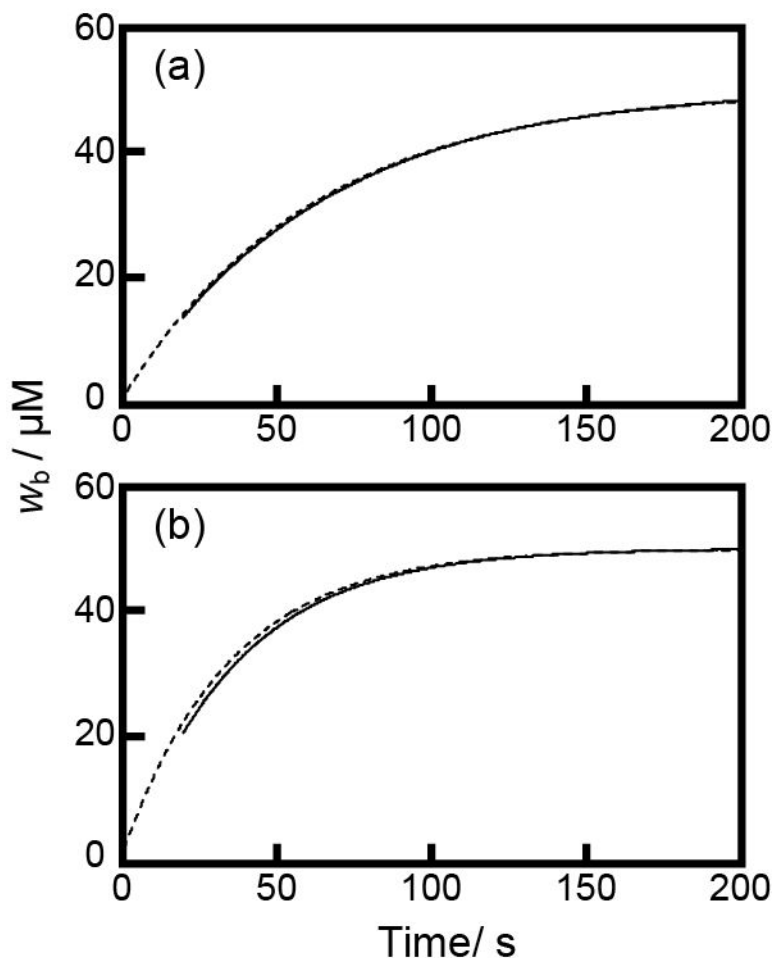


Figure S7. Time series of w_b obtained from numerically calculated (dotted line) and experimental values (thick line) of the coumarin concentration obtained from the absorbance at different $[\text{Na}_3\text{PO}_4]_0$ values [(a) 0.13 and (b) 0.33 M]. $k_1 =$ (a) 0.388 and (b) 0.386 $\text{M}^{-1} \text{s}^{-1}$. $k_{-1} =$ (a) 5.51×10^{-6} , (b) $4.56 \times 10^{-5} \text{s}^{-1}$. The initial coumarin concentration was 50 μM .

6. Kinetics of surface coumarin concentration during hydrolysis

To consider hydrolysis of coumarin on the water's surface, we assumed that the surface concentrations of coumarin (u), *o*-coumaric acid (w), and OH^- ($[\text{OH}^-]_s$) were proportional to their

bulk concentrations ($u_b, w_b, [\text{OH}^-]$), namely, $u = K_{H1}u_b, w = K_{H2}w_b$, and $[\text{OH}^-]_s = K_{H3}[\text{OH}^-]$,

where K_{H1}, K_{H2} , and K_{H3} are constants. The kinetics of hydrolysis can be written as follows:

$$\frac{du_b}{dt} = -k_1[\text{OH}^-]u_b + k_{-1}w_b, \quad (\text{S14})$$

$$\frac{du}{dt} = -\frac{k_1}{K_{H3}}[\text{OH}^-]_s u + \frac{K_{H1}}{K_{H2}}k_{-1}w, \quad (\text{S15})$$

$$\frac{du}{dt} = -k_1[\text{OH}^-]u + k_{-1}w. \quad (\text{S16})$$

Here, we use the bulk concentration of OH^- for technical reasons and assume that $K_{H1} \approx K_{H2}$.

7. Effect on the area of the water surface

Figure S8 shows the time series of the speed of motion for the smaller water chamber (diameter: 70 mm) at different concentrations of Na_3PO_4 . The motion for the smaller water chamber was suppressed in comparison with the diameter of 145 mm. However, the reproducibility was wrong for the smaller water chamber, e.g., either continuous or oscillatory motion (period: ~ 30 s) was observed for 0 M Na_3PO_4 .

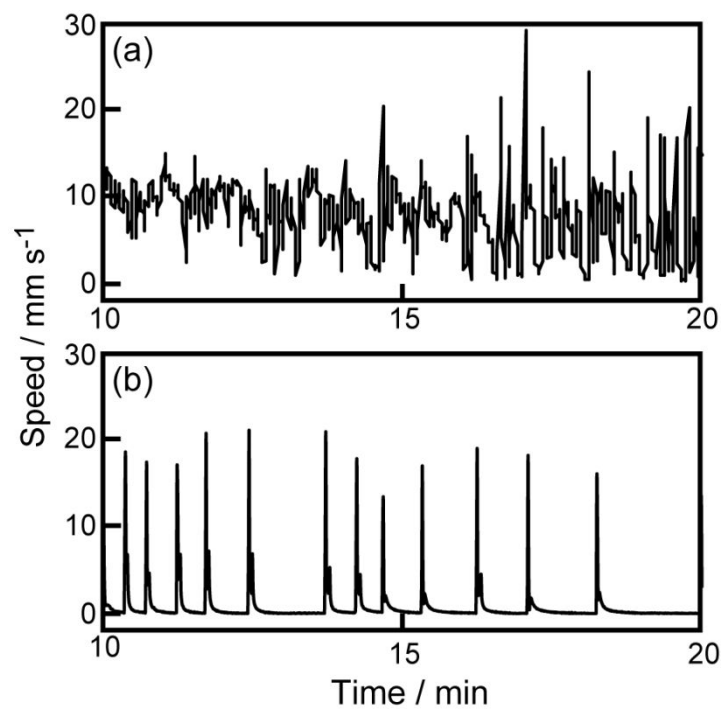


Figure S8. Time series of speed of the coumarin disk at different $[\text{Na}_3\text{PO}_4]_0$ values [(a) 0 and (b) 0.08 M] for the smaller water chamber (diameter: 70 mm).