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Emergent Complexity in a Light-Driven Self-Oscillatory Crystal: A Molecular Perspective on Autonomous Behavior and Stimulus-Modulated Motion

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ABSTRACT: Living organisms are molecular systems with self-sustained dynamics via energy conversion through molecular cooperation, resulting in highly complex macroscopic behaviors. Construction of such autonomous macroscopic dynamics at a molecular system level remains one of the central challenges in the field of chemistry. Looking further ahead, constructing motile systems that can receive external information and adapt their autonomous behavior represents the next frontier towards newly functional molecular devices such as microrobots. In this study, we focused on a light-driven self-oscillatory crystal that exhibits continuous flipping motion under constant light irradiation. We experimentally evaluated the oscillation frequency of the crystal under polarized light, confirmed the validity of our previously proposed mechanism, and clarified the requirements for self-oscillation. Based on this mechanism, we constructed a mathematical model that demonstrates the motion of the crystal itself. The model revealed that diverse oscillatory behaviors at the macroscopic level can arise from differences in the energy acceptance capability, even when the underlying molecular-level processes are identical. Furthermore, we found that the oscillatory behavior depended on the state generated by the previously applied light. This finding suggests that a memory effect also contributes to the adaptive and complex motion of the crystal.

Introduction

The bottom-up construction of molecular machines to create a life-like autonomous architecture represents a longstanding challenge in the fields of molecular science and nanotechnology.¹⁻⁴ A fundamental characteristic of such architectures is their self-repetitive mechanical work at the macroscopic level,^{5,6} as well as in their potential for self-replication and intelligent behavior.⁷⁻¹¹ An inanimate chemical system will generally achieve a balanced state of chemical reactions, known as equilibrium or a stationary state, in which the system maintains a static composition determined by kinetic coefficients.^{10,12} For example, under stimulus application, stimulus-responsive materials are transiently deformed to the balanced state. Therefore, to achieve repeated deformation, researchers typically repeat the application of stimuli designed to alternate the reaction velocity.¹³⁻²⁸ In contrast, some researchers have successfully exhibited continuous dynamics of stimulus-responsive materials without modulation of the stimulus. One of these methods is the application of a self-shadowing mechanism, in which the receiving rate of the stimulus is self-modulated by the deformation of the subjected material. By employing this mechanism, White et al. developed high-frequency oscillation of an azobenzene elastomer immobilized on an object,²⁹ and Broer et al. demonstrated directional crawling of a frame-fixed azobenzene polymer.³⁰ Numerous studies using this highly versatile mechanism have been reported to date.³¹⁻⁵⁰ Similarly, continuous dynamics through the switching of heat flow caused by object deformation have been reported.

⁵¹⁻⁵³ The key for the emergence of such continuous dynamics is the position of the energy source relative to the deformed structure,⁵⁴⁻⁵⁶ including further examples of polarized light-driven continuous motions.^{57,58} In these studies, it remains uncertain whether continuous motion can be achieved when energy is incident from all directions.⁵⁹ This raises an important point: although energy is a scalar quantity, the expression of autonomy often depends on directional interactions. Notably, there are systems in which autonomy is achieved through energy conversion independent of the relative position of the energy sources. Chemically oscillating hydrogels illustrate such behavior.^{60,61} One important advancement in this area is the construction of a self-oscillating gel system with a constant period independent of temperature that combines the functions of a chemically oscillating gel and a thermo-responsive gel.⁶² In parallel, the bottom-up construction of molecular assemblies with continuous dynamics has been realized via autocatalytic processes with time-delayed feedback at both the flask level⁶³⁻⁶⁵ and the molecular assembly level,^{66,67} despite the absence of mechanical work.

Previously, we reported the light-driven self-sustained oscillation of a cocrystal composed of the azobenzene derivative 6-[4-(phenylazo)phenoxy]hexanoic acid (**1**) and oleic acid in a ~3:2 molar ratio, demonstrating an example of the nonself-shadowing type of light-driven self-oscillation.⁶⁸⁻⁷⁰ In our first paper, we revealed that the frequency of the self-sustaining oscillation is proportional to the incident light intensity.⁶⁸ This finding indicates that the actual mechanism is not a self-shadowing mechanism,

although there are some dissenting opinions.^{54, 58} Rather, the presence of two diffraction peaks in the *in-situ* X-ray diffraction (XRD) pattern under light irradiation suggests that a crystalline phase transition alters the photoisomerization rate, thereby playing a key role in driving the self-oscillation behavior (Fig. 1).⁶⁸ An advantage of this mechanism is that conditions related to relative directionality, such as the position of the energy source, are not a critical requirement, unlike the other reported continuously moving photomechanical materials working under directional light. Therefore, regardless of whether it adopted a “standing” or “lying” orientation with respect to the incident light, our crystal continued to flip (Movie S1 in the Electronic Supporting Information (ESI)). Furthermore, the underwater self-propulsion of the crystal arose from mechanical forces acting on the surrounding medium and overcame Purcell’s theorem, which states that small flappers cannot swim in water. Unlike general light-responsive materials,⁷¹⁻⁷⁵ this propulsion was governed not by the direction of incident light but by the object’s anisotropic shape during deformation.⁷⁰ Conversely, when a directional energy source was used, the original self-sustaining oscillation of the object was disturbed because the reaction probability was affected by the directionality. Indeed, we have previously reported that the shapes of the repetitive motion vary in response to changes in the polarization angle.⁶⁹ In that paper, we also reported the single-crystal structure of a polymorph of **1**. Its powder XRD pattern closely resembles that of the cocrystal, although the single-crystal structure of the cocrystal itself remains undetermined. Based on the single-component crystal structure containing six crystallographically independent azobenzene molecules, we concluded that the cocrystal consisted of four crystallographically independent azobenzene molecules and two crystallographically independent oleic acid molecules (Fig. 2). We hypothesize that one of the azobenzene molecules acts as the oscillation generator, while another regulates the flipping behavior.

In the present study, the frequency of self-oscillation of the same cocrystal under polarized light was examined, and the origin of the polarized-light-triggered variation in the frequency was determined with the support of a model derived from the reaction kinetics. Thus, we established the validity of the proposed mechanism that the isomerization reaction is reversed by the phase transition, as suggested in our previous paper.⁶⁸ Additionally, by extending the model to crystalline structures, we demonstrated that one reason real crystals exhibit diverse behaviors—despite identical molecular-level mechanisms—is the inhomogeneity of the energy supply. Furthermore, we discovered a novel type of hysteresis in autonomous dynamics due to the “remembering” information from the previous external operation. These characteristics of multimolecular cooperative systems were realized through the combination of autonomous systems and nonautonomous molecular behaviors. We hope that this paper will serve as a starting point for considering what it truly means for us, as chemists, to pursue the construction of autonomous molecular systems.

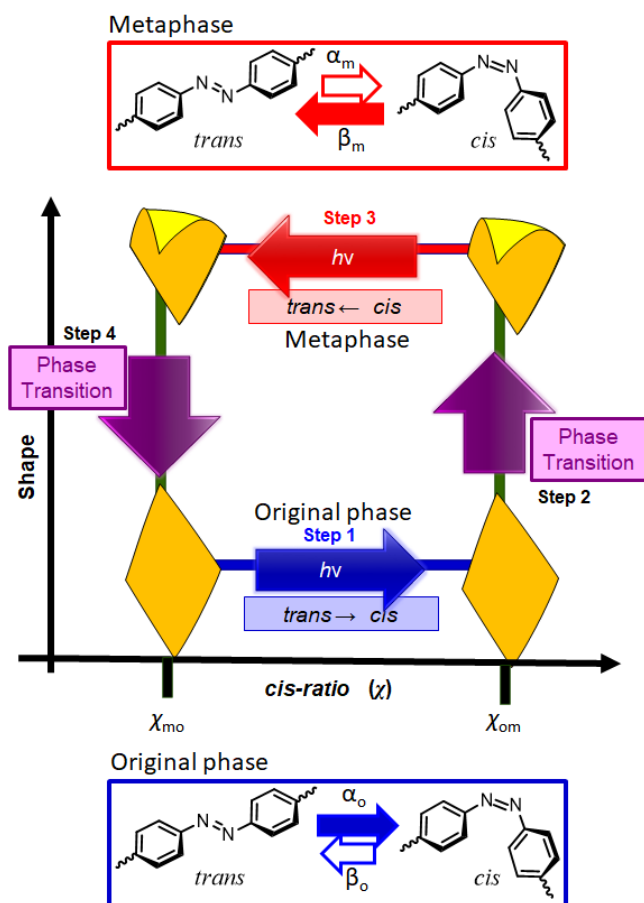


Figure 1. Schematic illustration of the proposed mechanism of limit-cycle self-oscillation of the cocrystal composed of **1** and oleic acid under continuous blue-light irradiation.⁶⁸

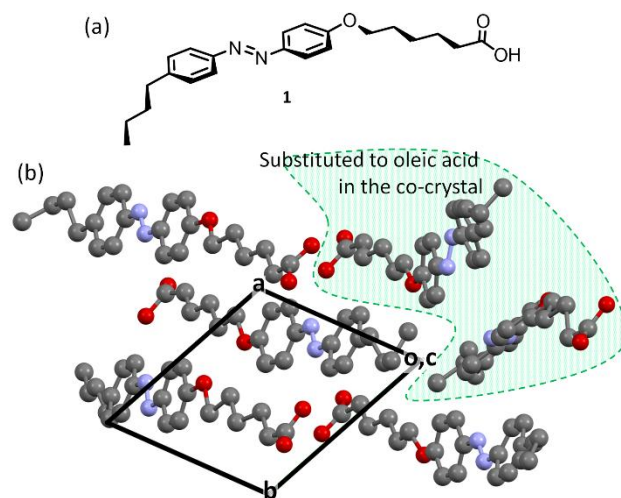


Figure 2. Schematic illustration of (a) the chemical formula of **1** and (b) the unit cell of single crystals of **1**, which crystallizes in the space group P_1 (the crystallographic data are available from the Cambridge Crystallographic Data Centre (CCDC1833362)); the hydrogen atoms in **1** have been omitted for clarity. The structure of the cocrystals between **1** and oleic acid was tentatively assigned to be the same as that illustrated above, except for the two encircled molecules of **1**, which lack effective dipole-dipole interactions around the ether oxygen and are thus presumed to be replaced by oleic acid.⁶⁹

Methods

Preparation of the cocrystal

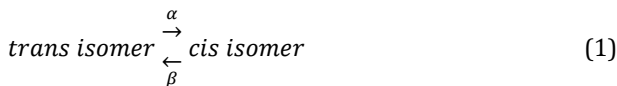
Cocrystals of **1** and oleic acid were prepared according to a literature procedure,⁶⁹ and the compound identification data matched those reported previously.⁷⁶ In brief, a mixed dispersion of 1 mg of the *trans* isomer of 6-[4-(phenylazo)phenoxy]hexanoic acid (**1**) and 1.3 mg of sodium oleate in 1 mL of phosphate-buffered solution (pH = 7.5; 75 mM) was ultrasonicated at 55 °C for 0.5 h and incubated at 25 °C for more than one day to obtain a dispersion of cocrystals. The dispersion was placed on a glass slide and sealed for observation.

Observation method

For microscopic observation, an inverted fluorescence microscope (TE2000 system, Nikon, Japan) equipped with an epifluorescence module (C-HGFI, Nikon, Japan) for light illumination from the bottom side of the sample was used. This microscope consisted of a precentered fiber illuminator with a mercury lamp, a turret for filter units for light excitation, a polarizer, and a Nikon Plan Fluor ELWD 20× (NA0.45) objective lens. In the turret, Nikon filter cube units, UV-1A ($\lambda_{\text{ex}} = 365 \pm 5$ nm), V-1A ($\lambda_{\text{ex}} = 400 \pm 20$ nm), BV-1A ($\lambda_{\text{ex}} = 435 \pm 10$ nm), B-2A ($\lambda_{\text{ex}} = 470 \pm 20$ nm), B-3A ($\lambda_{\text{ex}} = 455 \pm 35$ nm), and G-2A ($\lambda_{\text{ex}} = 535 \pm 25$ nm), were used. The excitation photon number was $6 \times 10^{15}/\text{s}$ for polarized light and $2 \times 10^{16}/\text{s}$ for unpolarized light, as measured using a power meter (LP1 Mobiken, Sanwa, Japan). The light intensity was controlled using neutral density filters and a neutral density-control dial on the epifluorescence module. As the second light source, a custom-made light-excitation unit was added to the upper side of the microscope, as shown in Fig. S1 in ESI. An IR cut-off filter, a 435-nm bandpass filter (ASAHI Spectra, Japan), and a 455-nm dichroic mirror (provided by Nikon as a part of the BV-1A filter unit) were equipped to the unit. The second light source was used in experiments in which the light irradiation conditions were switched during the course of the observation. The observations were conducted using either the polarization microscopy method or the differential interference contrast microscopy method. A charge-coupled device (CCD) camera (STC-TC152USB, Sentechn, Japan) was used to record movies at 19.26 fps, and Image-Pro Premier software (Media Cybernetics, USA) was used for movie analysis. When more than one oscillation mode was present, the frequency was measured for the long-period oscillation mode. The frame rate of the movies in ESI were processed to be 23.98 fps by using Adobe Premier Pro software (USA). To monitor the temperature-dependent behavior, a homemade temperature controller with a platinum resistance thermometer and a CCD camera (Detect, HAS-220, Japan) were used.

Kinetic equations for a self-oscillatory unit in a crystal

Using the expression for reversible photoisomerization between the *trans* isomer and the *cis* isomer of azobenzene (eq (1)), the coarse-grained reaction rate eq (2) and eq (3) can be established.



$$\frac{d}{dt}\chi = \alpha - (\alpha + \beta)\chi \quad (2)$$

$$\Delta\chi = \int_{t_0}^{t_1} \frac{d}{dt}\chi dt = \int_{t_0}^{t_1} (\alpha - (\alpha + \beta)\chi) dt \quad (3)$$

In these expressions, α is the sum of the photoisomerization and thermal isomerization coefficients for *trans*-to-*cis* isomerization, β is the corresponding sum for *cis*-to-*trans* isomerization, χ is the fraction of the *cis* isomer, and $\Delta\chi$ is the difference in χ between time t_0 and time t_1 . Each kinetic coefficient for photoisomerization is multiplied by the quantum yield of isomerization (Φ), the excitation probability, and the light intensity (I).

In the self-oscillating crystal with the mechanism shown in Fig. 1, the kinetic parameters differ between the original phase and the metaphase. Herein, we consider the behavior of the generator molecule. The phase transitions are triggered when χ , the *cis*-isomer fraction, reaches the respective threshold (χ_{om} and χ_{mo} for the original-phase-to-metaphase transition and the metaphase-to-original-phase transition, respectively). When DT_o and DT_m are defined as the duration times of the original phase and the metaphase, respectively, $\Delta\chi_{tt}$, which is the difference in χ between the two thresholds, can be expressed as shown in eq (4) and eq (5), which are derived from eq (3):

$$\Delta\chi_{tt} = \int_0^{DT_o} \frac{d}{dt}\chi dt = \int_0^{DT_o} (\alpha_o - (\alpha_o + \beta_o)\chi) dt \quad (4)$$

$$-\Delta\chi_{tt} = \int_0^{DT_m} \frac{d}{dt}\chi dt = \int_0^{DT_m} (\alpha_m - (\alpha_m + \beta_m)\chi) dt \quad (5)$$

where the subscripts o and m indicate the original phase and the metaphase, respectively. The periodic time is the sum of DT_o and DT_m if the phase transitions occur quickly enough; thus, the frequency (F) can be expressed as eq (6):

$$F = \left(\frac{1}{DT_o + DT_m} \right) \quad (6)$$

The calculations were performed using MATLAB software (Mathworks, USA) on a desktop computer.

Kinetic equations under polarized light

In general, the excitation probability is proportional to $|\mathbf{M}|^2 \cos^2\Delta\theta$, where $\Delta\theta$ denotes the angle between the polarization direction of the incident light and the molecular transition dipole moment.⁷⁷ Therefore, α and β can be expressed as shown in eq (7) and eq (8):

$$\alpha(\theta_p) = A \cos^2(\theta_t - \theta_p) \times I + k_+ \quad (7)$$

$$\beta(\theta_p) = B \cos^2(\theta_c - \theta_p) \times I + k_- \quad (8)$$

where θ_p is the polarization angle of the light, which is irradiated from the vertical direction, θ_t and θ_c are the azimuth angles of the transition moment of the *trans*-isomer and *cis*-isomer, respectively, I is the incident light intensity, and A and B are constants that depend on the elevation angle of $\mathbf{M}$.

Mathematical four-dimensional model representing the light-driven self-oscillation with introduction of the first-order phase-transition model

To reproduce the crystal structure, hexagonal structures with triangular lattices were employed (Fig. 3).^{78, 79} The numbers of nodes forming the three sides of the hexagonal structure were (6, 6, 29), (8, 8, 21), (9, 9, 17), or (10, 10, 15), with the total numbers of the nodes being 333, 349, 336, or 347, respectively. The fraction of metaphase (ϕ_i), *cis*-isomeric ratio (χ_i), and coordinates ($r_i = (x_i, y_i, z_i)$) were

defined in each node, with the time evolutions calculated using the equations shown below. In the numerical simulations, each triangle in the crystal was colored according to the values of these variables averaged over the three nodes of the triangle.

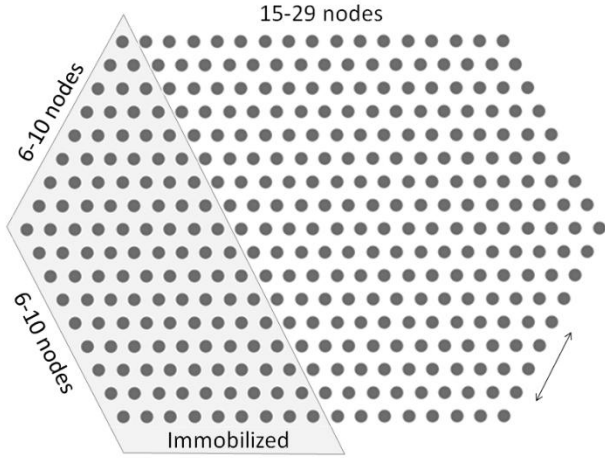


Figure 3. The crystal model used in the numerical calculations. The isomer fraction, phase-state fraction, and spontaneous curvature at each node (shown as ●) as well as the elastic interactions between the nodes were calculated. The value of K_{bend} was halved for edges parallel to the arrow.

Reaction velocities

In the present model, we introduced the following exponential relationships between the kinetic coefficients and the metaphase fraction (ϕ_i), which is defined between 0 and 1:

$$\alpha(\phi_i) = 7.5 \times 10^{-5} \times \exp(-5\phi_i) \times CS \times I + k_+ \quad (9)$$

$$\beta(\phi_i) = 7.5 \times 10^{-6} \times \exp(5\phi_i - 0.5) \times CS \times I + k_- \quad (10)$$

In this study, it was assumed that collimated light is emitted from the lower side of the object (in the Z-axis direction). In this case, the light-receiving area was the projected area of the triangle from the Z-axis direction to the XY plane. CS is the factor that adjusts the change in the light-receiving area of each triangle depending on the direction of light irradiation. It is noteworthy that stable oscillations will occur even if light irradiation is assumed to be isotropic, i.e., $CS = 1$. In this model, we employed 10^{-9} and 10^{-6} for k_+ and k_- , respectively. Using these kinetic coefficients, eq (2) for the *cis*-isomeric ratio χ_i is modified as

$$\frac{d\chi_i}{dt} = \alpha(\phi_i) - (\alpha(\phi_i) + \beta(\phi_i))\chi_i. \quad (11)$$

Landau theory for the first-order phase transition

Referring to the mean-field model of Landau theory, we employed eq (12) and eq (13) for the pseudo energy function (f_i) to indicate the stability of the phase.

$$f_i(\phi_i, \chi_i) = \frac{\Lambda(\chi_i)}{2} \phi_i^2 - \frac{b}{4} \phi_i^4 + \frac{c}{6} \phi_i^6 \quad (12)$$

$$\Lambda(\chi_i) = L \times (\chi_{PT} - \chi_i) \quad (13)$$

In the present study, we employed 1.5, 0.3, 1.6, and 2.0 for the quantities of L , χ_{PT} , b , and c , respectively. We also considered the diffusive interaction between the adjacent nodes, with the interaction strength $D_\phi = 0.01$ and the

slowness of the dynamics represented by the parameter $\varepsilon_\phi = 0.01$. ϕ_i is given by eq (14):

$$\frac{1}{\varepsilon_\phi} \frac{d\phi_i}{dt} = D_\phi \sum_j (\phi_j - \phi_i) - \frac{\partial f_i}{\partial \phi_i}. \quad (14)$$

Mechanical interaction between nodes

For each node, we assumed that the spontaneous curvature at each edge of the lattice depends on the metaphase fraction ϕ_i . Assuming the stretching energy between two nodes and the bending energy between two triangles, the change in coordinates of node r_i is governed by eq (15):

$$\frac{d\mathbf{r}_i}{dt} = -\frac{\partial}{\partial \mathbf{r}_i} (V_{str} + V_{bend}) \quad (15)$$

where the summation of V_{str} and V_{bend} is taken over the pairs of nodes (i, j) forming edges (eq. (16-17)).

$$V_{str} = \frac{K_{spring}}{2} \sum_{(i,j) \in edges} (|\mathbf{r}_i - \mathbf{r}_j| - l_0)^2 \quad (16)$$

$$V_{bend} = K_{bend} \sum_{(i,j) \in edges} [1 - \cos(\Psi_{i,j} - v(\phi_i + \phi_j))] \quad (17)$$

The lattice constant l_0 is set to 1.0. The spring constants for these potentials (K_{spring} and K_{bend} , the values of which are set to 20 and 8, respectively) were also defined. The variable $\Psi_{i,j}$ is the bending angle between the two adjacent triangles sharing edge (i, j), which is computed based on the positions of the four nodes on the two triangles. The stable value of $\Psi_{i,j}$ is assumed to be proportional to the sum of the metaphase fractions ϕ_i and ϕ_j , and the proportionality constant v is set to 0.05. In addition, to reproduce the fact that the bending was parallel to a side of the crystal, we introduced an asymmetric factor to the bending rigidity in such a way that all edges parallel to a given axis (indicated by the arrow in Fig. 3) were assigned the half value of K_{bend} .

Thus, each node in the hexagonal lattice is characterized by the three variables (χ_i , ϕ_i , r_i), and their time evolution is determined by eq (11), (14), and (15), respectively. These three equations are interrelated as follows. First, eq (11) is influenced by eq (15), since macroscopic shape changes affect the functions $\alpha(\phi)$ and $\beta(\phi)$, defined by eq (9-10), via the factor CS . Second, eq (14) is governed by eq (11) through modification of the Landau potential by the χ_i values (eq (12-13)). Finally, eq (15), which describes the mechanical motion of the crystal, is affected by eq (14) through variations in the ϕ_i values, which appear in V_{bend} (eq (17)).

The calculations were performed on a desktop workstation (HPC5000, HPC Systems, Japan). In mathematical models, parameters are inherently relative. In this study, we selected parameter sets that enhance the clarity of behavioral trends in visualized simulations and minimize discretization errors. It is noteworthy that the use of different parameter values from those in the previously introduced model does not affect the essence of the discussion. This study aimed to model and understand the experimental results rather than to optimize the parameters for the exact reproduction of those results. The number of calculated steps was 4×10^5 , and the value of time was 4×10^3 , in general, with time step $\Delta t = 0.01$. For the analysis of light-intensity dependence, the calculated steps were extended.

Results and Discussion

1. Phase diagram for the emergence of dynamics with the reaction coefficients as the axes

In general, particularly in solution-phase conditions, the reversible photoisomerization of the azobenzene derivative described in eq (1) in the Methods section yields a photostationary state with an expected *cis*-isomeric ratio (χ_{pss}) given by the expression $\alpha/(\alpha+\beta)$. Because the kinetic coefficients, α and β , generally depend on the surrounding conditions of the molecule, the χ_{pss} value is shifted based on the conditions, such as the dielectric properties of the solvent. Even in the case of crystals, the kinetic coefficient varies with the surrounding conditions. In this section, we discuss the photoisomerization behavior of the generator azobenzene molecule in a “unit” in the self-oscillatory crystal. Because a crystal may be too large to analyze its dynamic behavior from nanoscale physicochemical dynamics, we focused on a small unit in a crystal that shows the crystalline phase transition. This unit corresponds to the “primary unit” in section 6 of the Results and Discussion.

First, we considered the *cis*-isomer-increasing process of the unit under light irradiation. If the expected χ_{pss} is less than the phase-transition threshold (χ_{om} in Fig. 1), χ never reaches χ_{om} , and the subjected unit never shows phase transition (Case A in Fig. 4a). In this case, the unit remains at the photostationary state. On the other hand, if the expected χ_{pss} is greater than χ_{om} , the unit undergoes the phase transition before it reaches the photostationary state (Case B in Fig. 4a). Next, we considered the *trans*-isomer-increasing process. Because of the phase transition, the kinetic coefficients are different from those in the *cis*-isomer-increasing process. In the *trans*-isomer-increasing process, phase transition occurs only if the expected χ_{pss} is less than χ_{mo} (Fig. 4b); otherwise, the unit turns into a photostationary state or an undiscussed state (Case C in Fig. 4a). In summary, as illustrated in Fig. 4c, we could predict the phase diagram showing the dynamic behavior.

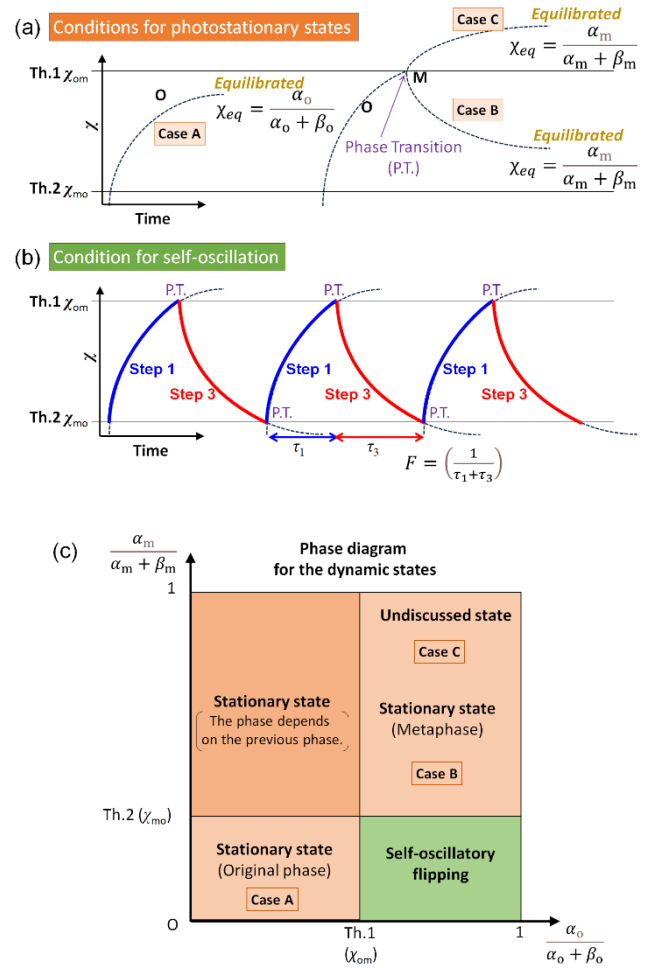


Figure 4. Schematic illustrations showing the conditions for light-driven self-oscillation. (a) Reaction rate conditions leading to photostationary states. (b) Reaction rate conditions leading to light-driven self-oscillation. (c) A phase diagram representing the dynamic states of the crystal based on the reaction rate conditions. Abbreviation: Th, threshold.

The values of the photoisomerization rate coefficients depend on the wavelength of the excitation light. Therefore, the availability of self-oscillation must depend on the excitation wavelength. Indeed, in the previously reported experiments, upon unpolarized light irradiation, we observed self-oscillatory dynamics if the light color was blue or blue-violet, while we did not observe them with irradiation of green light ($\lambda = 535 \pm 25$ nm), violet light ($\lambda = 400 \pm 20$ nm), nor ultraviolet light ($\lambda = 365 \pm 5$ nm).⁶⁸ Under green light irradiation, where α_o is expected to be small, we did not observe any bending of the crystal; while under violet or ultraviolet light, where β_m is expected to be small, we observed deformation followed by melting of the crystal.

2. Theoretical expectation of polarized light angle dependency of self-oscillation

If the excitation light is polarized, α and β also depend on the relative angle of the polarization against the transition moment of the subjected molecule, as shown in eq (7-8). The expected χ_{pss} values at each phase, i.e., $\alpha_o/(\alpha_o + \beta_o)$ and $\alpha_m/(\alpha_m + \beta_m)$, depend on the relative polarization angle;

notably, if the thermal isomerization is negligible, these values can range continuously from 0 to 1. This fact means that the kinetic parameters among the change in polarization angle between 0° and 180° are displayed as a closed line on the phase diagram of the dynamics, as shown in Fig. 5a as well as Fig. S2a and S3a in ESI. If the line crosses the self-oscillatory region once, the polar plot shows two lobes, each resembling a pear (Fig. 5b and c, Fig. S2a and b in ESI, and Fig. S3a and b in ESI) or heart (Fig. S3c in ESI). If it crosses twice, the plot exhibits four lobes in a samara-like arrangement (Fig. 5d, Fig. S2c in ESI, and Fig. S3a and c in ESI). It is noteworthy that the polar plots of light-triggered deformation of materials generally exhibit two symmetrical lobes with a rounded, leaf-like shape, since the excitation probability of a molecule as a function of the light polarity is proportional to $|M|^2 \cos^2 \Delta\theta$.⁷⁷

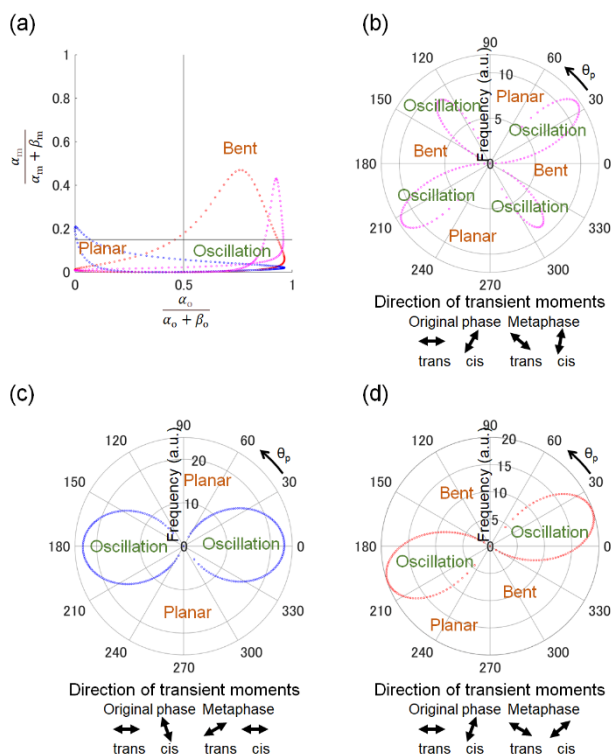


Figure 5. Three examples of the polarization angle dependence of self-oscillation predicted by the simple model based on the rate equations. The relative values of A and B in eq (7-8) were 30 and 12 for the original phase and 1 and 50 for the metaphase, respectively. We employed k_+ and k_- values of 10^{-3} and 1, respectively. The values of θ_t (original phase), θ_c (original phase), θ_t (metaphase), and θ_c (metaphase) were set to $[0^\circ, 60^\circ, -40^\circ, 80^\circ]$ (magenta), $[0^\circ, -70^\circ, -30^\circ, 0^\circ]$ (blue), and $[0^\circ, 70^\circ, -30^\circ, 40^\circ]$ (red), respectively. The angles are illustrated as double arrows in panels b, c, and d. Calculations were performed in 1° increments. Herein, we set χ_{om} and χ_{mo} as 0.5 and 0.15, respectively. In the phase diagram (a), the magenta case, which enters the self-oscillatory region twice in the phase diagram, exhibits a four-lobe polarization angle dependence, as shown in (b). In contrast, the blue and red cases, which enter the region only once, are expected to show a two-lobe polarization angle dependence as shown in (c and d). From this theoretical approach, it is expected that in the case of four-lobe polarization angle dependence, bent and planar stationary

states will be observed on opposite sides of the region of self-oscillation. On the other hand, in the case of two-lobe polarization angle dependence, it is predicted that the bent and planar stationary states may be adjacent to each other, or only the stationary planar state may be observed. Further examples are shown in Fig. S2 and S3 in ESI.

In terms of a qualitative discussion, the shape of the polar plot can also be understood as stated below. If the polarization angle is perpendicular to the transition moment of the *trans* isomer in the original phase, *trans*-to-*cis* photoisomerization at the original phase is prohibited. If the polarization angle is perpendicular to the transition moment of the *cis* isomer in the metaphase, *cis*-to-*trans* photoisomerization at the metaphase is prohibited. Due to the two forbidden angles, the shape becomes four lobes or heart-shaped two lobes; and if the forbidden angles are close each other, or depending on the relationship between the threshold values and the reaction rate constants, it becomes a two-lobe shape.

3. Polarized light angle dependency of self-oscillation

A crystal composed of the *trans* isomer of **1** and oleic acid was placed on a glass slide as an aqueous dispersion. The excitation light ($\lambda_{ex} = 435$ nm) was applied vertically (i.e., perpendicular to the face of the glass slide), and its polarization azimuth was defined with respect to the micrographic view. The azimuth angles presented in this paper as experimental data were modified by the corresponding angles in case the crystals rotated during the experiment. The crystals oscillated in the vertical direction; the oscillation was detected as the repeated observation of an in-focus flat object and an out-of-focus bent object, or as the brightness change of the object. In this experiment, we first exposed the crystal to unpolarized light ($\lambda_{ex} = 435$ nm) for 5 s to standardize the conditions, and then we measured the oscillation frequency under polarized light ($\lambda_{ex} = 435$ nm). The results without preillumination of unpolarized light are discussed in the next section. The frequency of the resulting self-oscillation under polarized blue-light irradiation was visualized as a polar plot, with the azimuth angle of the polarized light indicated.

The results of various experiments are shown in Fig. 6 and 7, as well as Fig. S4 and S5 in ESI. Since the shape of the crystal varied greatly, the polarization-angle dependence was also different for each crystal. Of note, the dependencies can be classified into two groups: the two-lobe type and the four-lobe type, as expected theoretically. Furthermore, even in cases in which the flipping frequency was similar for different light-polarization angles, the time profile of the flipping was different. For example, Fig. 6c presents the time profile of the flipping motion of the same crystal under 100° - and 170° -polarized light. The duration ratio of the planar shape to the oscillation period (Dr) was 0.41 at 170° and 0.56 at 100° . Other examples are shown in Fig. 7c as well as Fig. S4 and S5 in ESI. The polarization angle dependency of Dr was also reproduced by the theoretical model (Fig. S2 and S3 in ESI).

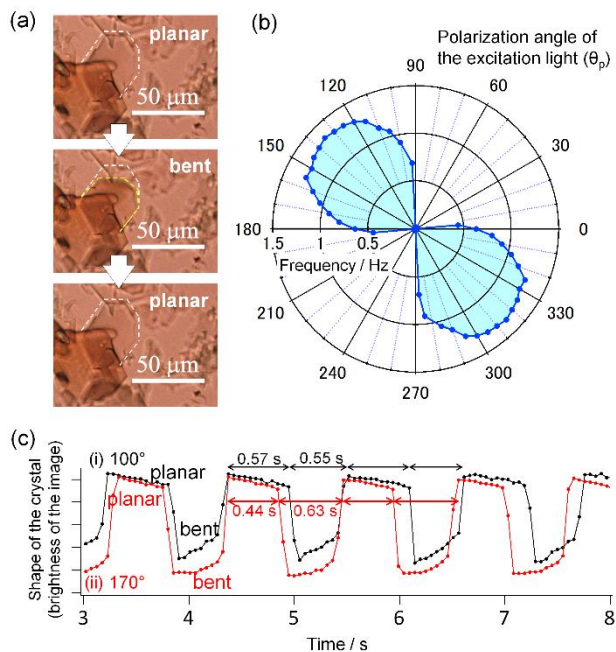


Figure 6. (a) Sequential microscopic images (interval: 0.42 s) of the oscillatory flipping of the crystal under blue-light ($\lambda_{\text{ex}} = 435$ nm) excitation with a polarization angle of 140° . The dashed lines are guides for the eye. (b) Frequency of the self-oscillation of a crystal under blue-light polarization ($\lambda_{\text{ex}} = 435$ nm), obtained after irradiation with unpolarized blue light ($\lambda_{\text{ex}} = 435$ nm) for 5 s. The frequency resolution is approximately 0.05 Hz due to the frame speed of the video used to generate this image (for details, see Movie S2 in the Electronic Supporting Information (ESI)). (c) Time profiles of the self-oscillation under light with a polarization angle of 100° and 170° , respectively. The vertical axis is the brightness of a part of the crystal in the video used to generate this image (for details, see Movie S2 in ESI) and indicates the state of the crystal.

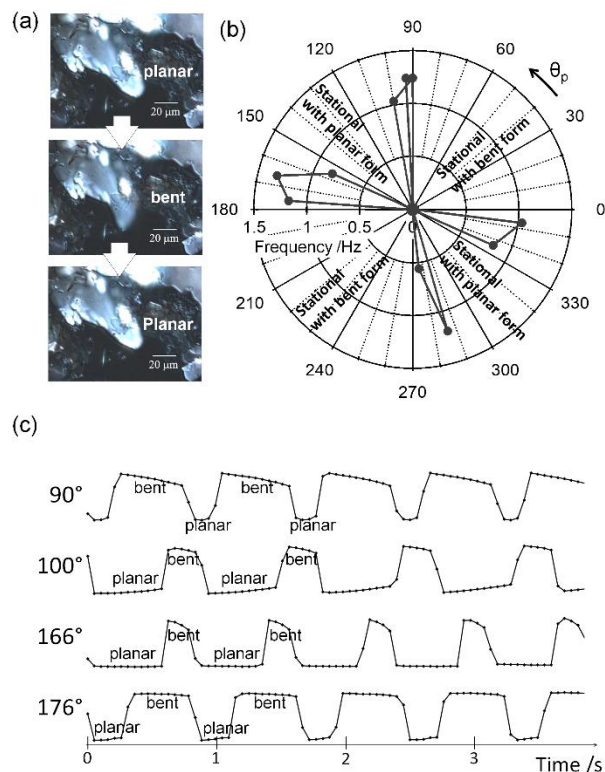


Figure 7. (a) Sequential microscopic images (interval: 0.36 s) of the oscillatory flipping of a tilted crystal under blue-light excitation ($\lambda_{\text{ex}} = 435$ nm) with a polarization angle of 90° . (b) Frequency of the self-oscillation of the crystal under blue-light polarization, obtained after irradiation with unpolarized blue light ($\lambda_{\text{ex}} = 435$ nm) for 5 s. The frequency resolution is approximately 0.05 Hz due to the frame speed of the video (for details, see Movie S5 in ESI). (c) Time profiles of the oscillations under light with a polarization angle of 90° , 100° , 166° , and 176° .

4. Hysteresis due to the history of the polarized-light rotation

Next, we experimentally measured the flipping frequency of the crystal used for the measurements in Fig. 6 while rotating the polarization angle by 5° every 5 s, without preillumination of unpolarized light during the experiment. As shown in Fig. 8 and Fig. S6 in ESI, the oscillation frequency differed depending on whether the polarization angle was rotated clockwise or counterclockwise. Similar behavior was also observed in another crystal; the polarized light dependency showed a four-lobe shape (Fig. 9). The behavior is unexplainable from the models shown above. Therefore, the presence of a molecule or a subsystem that stores the previously received information is required.

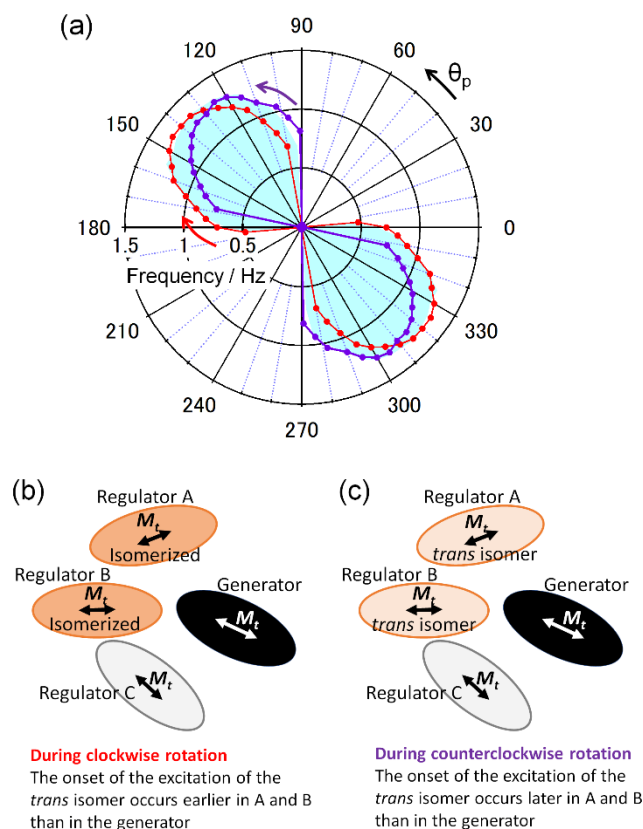


Figure 8. (a) Frequency of the self-oscillation of the crystal shown in Fig. 6 when the polarization angle of the blue light was changed stepwise in increments or decrements of 5° (for details, see Movies S3 and S4 in ESI). The red line and the purple line represent the results for clockwise and counterclockwise rotations, respectively. The cyan-colored area indicates the results shown in Fig. 6. (b and c) Schematic illustrations explaining the hysteresis observed with the polarization rotation of the excited light. In the crystal, azobenzene molecules (represented as ellipses) of different symmetries are present, each with a transition moment in a different direction (represented as arrows in the ellipses). The rotation direction of the polarization angle determines the order in which the azobenzene molecules are photoexcited, causing the state of the crystal to vary with the rotational direction. In short, when the generator's transition dipole moment aligns with the polarization direction, the crystal components differ between (b) and (c) due to the difference in the rotational direction of the polarized light. Additional data are shown in Fig. S6 in ESI.

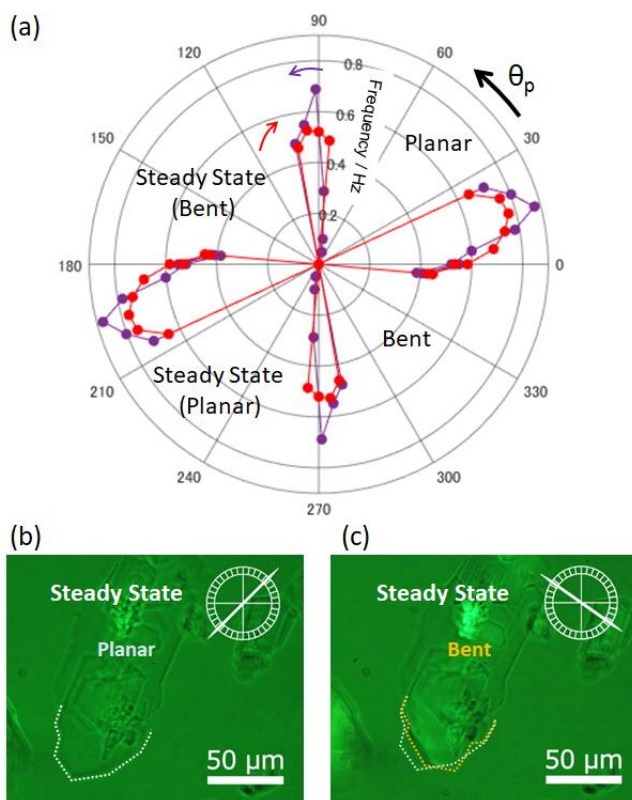


Figure 9. (a) Frequency of the self-oscillation of a crystal when the polarization angle of 435-nm light was changed stepwise (Movies S6 and S7 in ESI). The red and purple lines represent the results for clockwise and counterclockwise rotation, respectively. (b, c) Micrographs of the corresponding crystal under 435-nm-polarized-light irradiation, the angles of which were 45° and 135° , respectively. Under these conditions, the crystal did not show self-oscillation but formed a planar shape and a bent shape, respectively. Under oscillation conditions, the crystal deformed between the two shapes. The dashed lines are for easy visualization: white outlines the planar shape, and yellow outlines the bent shape. The micrographs appear green due to the use of a green filter to block the blue light in the observation light. Dependence on light intensity is also shown in Fig. S8 in ESI.

Based on the crystal structure reported in our previous paper (Fig. 2),⁶⁹ we hypothesized that the *cis*-isomeric ratio of the regulator molecules, which varies with the polarized light supplied, changes the frequency of the self-oscillation driven by the generator molecules. The direction of each transition moment of the regulator azobenzene molecules and the generator azobenzene molecules is different. Therefore, the rotational direction of the polarization angle determines whether the regulator molecules begin to accept the light polarization efficiently before or after the generator molecules do (Fig. 8b and c). This is caused by a difference in the *cis*-isomeric ratio of the regulator molecules, which depends on the history of the rotational direction and consequently changes the characteristics of the crystal. If we regard the *trans* isomer and the *cis* isomer as different molecules, the crystal obtained after clockwise versus counterclockwise rotation of polarized light is one with different components, despite the fact that the object

is identical. Thus, the frequency inherently depends on the rotational direction of the polarization.

However, to directly confirm these hypotheses, it would be desirable to quantify the *cis*-isomeric ratio of molecules with specific orientations in the crystal. Nevertheless, given the currently available analytical techniques, it is difficult to carry out such measurements. Despite these limitations, experimental observations support the hypothesis. As evidenced by the results and as expected based on the above discussion, the frequency of self-oscillation generally reflects the history of an external operation, i.e., the rotation of the polarization angle of the excitation light. Indeed, hysteresis was observed in all cases, despite the variations in its expression from crystal to crystal (Fig. S4 and S7 in ESI). Furthermore, as shown in Fig. S4e-h, the presence of hysteresis was reproducible, even though the specific behavioral phenotype was not always identical. Importantly, the idea that the presence of molecules with different crystallographic symmetries contributes to hysteresis during polarization rotation is not limited to the case of single-crystal phases. For example, the existence of twin structures also implies the presence of molecules with orientations different from those of the generator molecules in the targeted phase, which could similarly underlie the hysteresis and the resulting behavioral complexity.

5. Memory effects on the patterned dynamics under unpolarized light illumination

The memory effect due to the polarization-light hysteresis also modulates the self-oscillatory behavior under unpolarized light irradiation. Fig. 10 (Movie S8 in ESI) and Fig. 11 (Movie S10 in ESI) show the self-oscillation behavior under unpolarized light irradiation following a 2-s irradiation of polarized light. As shown in Fig. 10, the frequency became slow during the first 4 s only when the preillumination of 165°-polarized light was applied, and it recovered by keeping the light irradiation. This finding indicates that the behavior was influenced by the prestimulus, albeit for a short period of time. For a crystal with a complex structure, we also found that the temporal pattern was modulated by the preillumination of 470-nm polarized light. An example is shown in Fig. 11. If the angle of the preilluminated polarized light was 90°, 150°, or 180°, the crystal repeatedly changed into five shapes, [A→B→C→D→E→], after induction periods under unpolarized 435-nm light. On the other hand, if the angle of the preilluminated polarized light was 120°, the crystal repeated the change among three shapes, [F→G→H→], after an induction period under unpolarized 435-nm light. Here, we do not discuss whether forms A, C, and F; forms B, D, and G; and forms E and H are the same structures or not, although the outlines are similar.

Herein, we present two examples of modulation by preillumination with polarized light. In both cases as well as in other experiments, this modulation of subsequent dynamics was observed when the polarization angle was between 20° and 25° relative to the crystal's long axis. This fact supports the aforementioned assumption that preisomerization of a specific azobenzene molecule in the crystal plays a key role in the modulation.

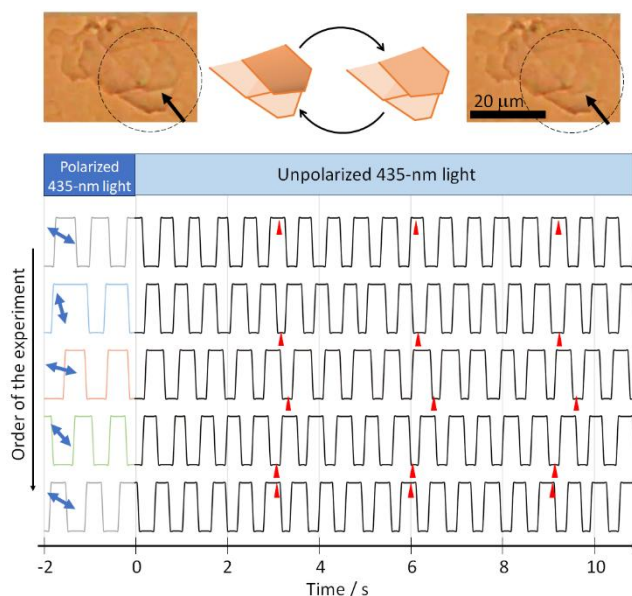


Figure 10. Self-oscillation patterns of a crystal under unpolarized light irradiation after being exposed to polarized light for 2 s. The patterns in the graph represent the binarized brightness of an area of the crystal, and the raw data are shown in Movie S8 and Fig. S9 in ESI. Blue arrows indicate the angle of the polarized light (from top to bottom: 150°, 105°, 165°, 135°, and 150°, respectively). Red triangles are shown every five cycles of each oscillatory pattern. The direction of the long side of the flipping crystal in the picture is from the top left to the bottom right.

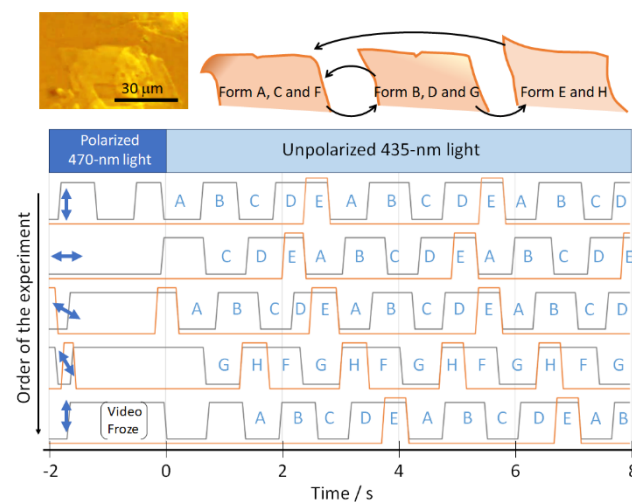


Figure 11. Self-oscillation patterns of a crystal under unpolarized light irradiation after exposure to polarized light for 2 s. The patterns in the graph represent the binarized brightness or brightness change in two areas of the crystal, and the raw data are shown in Movie S9 and Fig. S10 in ESI. Blue arrows indicate the angle of the polarized light (from top to bottom: 90°, 180°, 150°, 120°, and 90°, respectively). The direction of the long side of the flipping crystal in the picture is from the top left to the bottom right.

6. Model for demonstrating the flipping dynamics

The crystal-level motion was reproduced by a phenomenological model of a deformable two-dimensional lattice moving in

three-dimensional space. The model presented here integrates kinetic equations, the Landau mean-field theory for the first-order phase transition, and internal elastic interactions. As demonstrated below, it effectively captures the system's dynamics. The crystal structure, comprising 10^{13} molecules, is represented as a hierarchical arrangement, as shown in Fig. 12. A two-dimensional crystal was regarded as an assembly of 3×10^2 crystalline domains consisting of primary units of the crystalline phase composed of several unit cells, the phase transition of which was triggered by the photoisomerization of azobenzene and by the cooperative effects derived from the state of the surrounding crystalline phase. This model does not impose a strict limit on the number of primary units or unit cells, provided it is sufficiently large; for example, each can be considered to contain 10^5 units. The *cis*-isomeric ratio for triggering the first-order phase transition of the unit was defined as χ_{PT} , and the phase transitions occurred after χ of the unit crosses the value χ_{PT} . The cooperative factor was considered according to the Landau mean-field theory: the ratio of the meta-phase units in a domain (ϕ_i) can be expressed as eq (14) with a diffusion term. Fig. 13a shows an example of the functions for the phase stability under a self-oscillatory condition, and the trajectory of (χ_i, ϕ_i) is drawn in Fig. 13b. According to the model, we hypothesized that each domain has a spontaneous curvature proportional to the ϕ value, and we also employed elastic interactions between domains to demonstrate the mechanical deformation behavior (eq (15)).

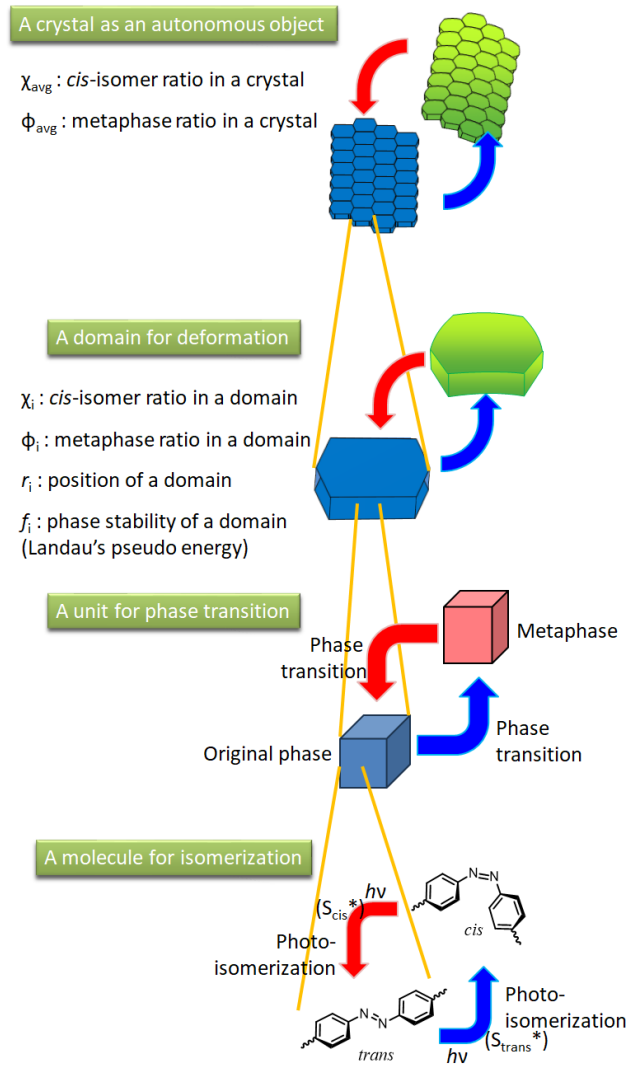


Figure 12. Hierarchical structure of the molecular system assumed in the mathematical model. Each domain (i) is treated as a subsystem, and the variation in the ratio of the original phase and the metaphases within it (ϕ_i) is determined using the mean-field model inspired by Landau's first-order phase-transition model, with ϕ as the order parameter and the *cis*-isomeric ratio (χ_i) as the trigger parameter. Additionally, the assumption that the spontaneous curvature of the domain is proportional to ϕ is introduced, and the deformation of the higher-order structure, the crystal, is modeled through elastic interactions between domains.

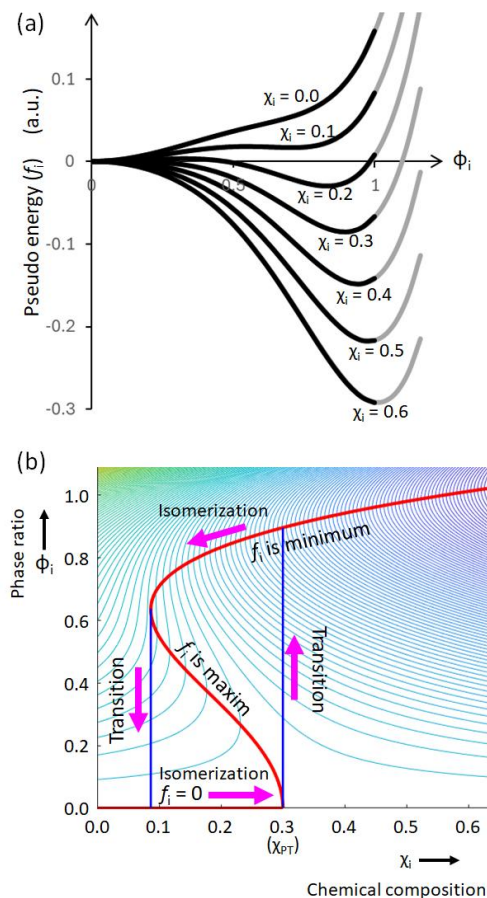


Figure 13. Shape of the pseudo energy function shown as eq (12), where ϕ_i is defined in the range of 0 to 1. (a) The cross section of the contour graph of f_i (b). When χ_i is between 0 and 0.086, the minimum of the function is at $\phi_i = 0$. On the other hand, when χ_i is greater than 0.3, the function has a minimum around $\phi_i = 0.9$. When χ_i lies between these values, the function is of the double-minimum type, and the phase state depends on the reaction history.

Fig. 14 and Movie S10 show examples of the behaviors calculated by the model. Herein, we employed $I = 1$. The parameter differences among the models shown in Fig. 14 are only in the outline of the crystal, while all other parameters, including the kinetic coefficients, are the same. We successfully reproduced the oscillatory flipping motion of each object visually, with changes in the *cis*-isomeric ratio and the metaphase fraction. Notably, the average ϕ value never reaching 1 indicates that the formation of a single-phase crystal is not a prerequisite for oscillation. Furthermore, the model revealed that the oscillation frequency depends on the physical shape of the crystal. These variations stem from the relative position of each node with respect to the incident light. The temporal patterns remained consistent when calculations assumed isotropic energy acceptance, i.e. CS in eq (9-10) is 1 (Movies S11). In the actual system, the shape exhibited even greater diversity; therefore, a mathematical model like this should not be expected to fully predict the spatiotemporal patterns of each crystal. However, the analysis of the mathematical model provides us with insights into the characteristics of the phenomena.

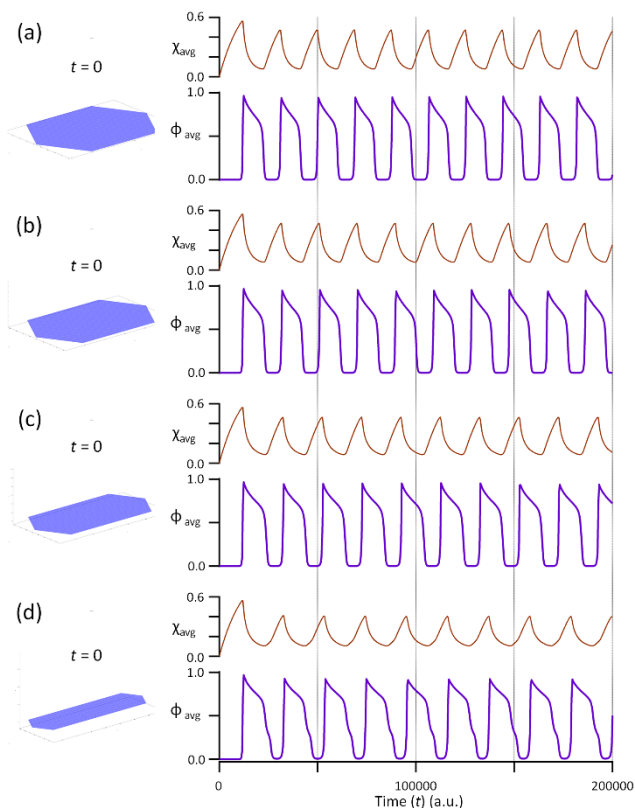


Figure 14. Differences in the time profiles in the calculated results due to variations in the outline shape. The calculations were performed with progressively elongated shapes from panels (a) to (d), while keeping all other parameters identical. As the shape became more elongated, the oscillation period increased. As shown in panel (d), the motion continued without returning to a planar shape and transitioned into a stable periodic motion after a computation time of 3×10^5 a.u. (Movie S10 in ESI).

One of the successes of the model is that behaviors that are different from those observed in stimulus-responsive materials were well visualized (Fig. 15). In planar crystals, although the system initially started with a higher *trans*-isomeric ratio, the state with a higher *cis*-isomeric ratio persisted for a longer duration. Moreover, at the time of the start of deformation to the curved shape followed by the phase transition, the *cis*-isomeric ratio started to decrease, and the state with a small *cis*-isomeric ratio continued in the curved crystal. Then, immediately after the phase transition to the original phase, the *cis*-isomeric ratio started to increase and deformation of the crystal to the planar shape occurred (Movie S12 in ESI). This behavior—marked by a time lag between molecular-level changes and macroscopic responses—fundamentally differs from that of stimulus-responsive materials, where the molecular state is typically closely coupled to the material's deformation.⁸⁰

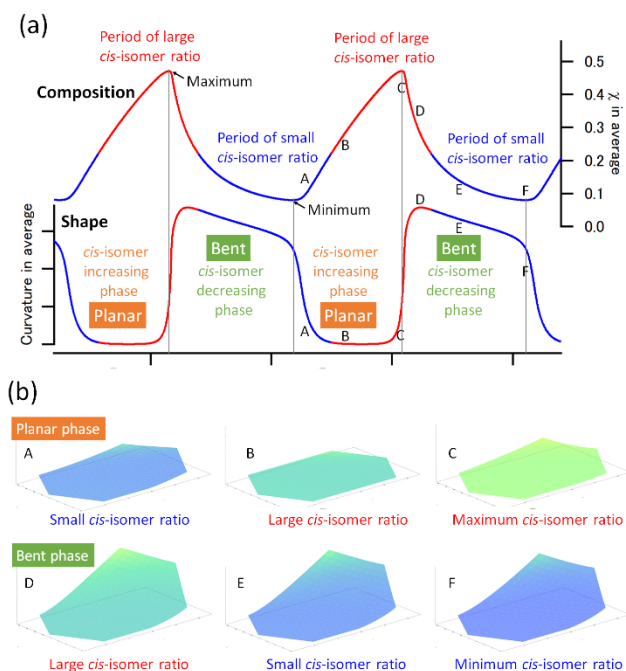


Figure 15. Analysis of the mathematical model results shown in Fig. 14b. (a) The time profile of the composition and curvature of the crystal. Red and blue indicate that the *cis*-isomeric ratio (χ_{avg}) is greater or less than 0.22, respectively. (b) Snapshots of the calculated shapes of the crystal at different

cis-isomeric ratios according to the time profile (A-F). The colors represent the χ -value (blue, green, and greenish yellow indicate ~ 0.1 , ~ 0.3 , and ~ 0.5 , respectively). The results indicate that the shape does not directly depend on the chemical composition; rather, the shape influences the variation in composition.

7. Light-intensity dependence and temperature effect

Fig. 16 shows the light-intensity dependence of self-oscillation, with Fig. 16a depicting an experimental result⁸¹ and Fig. 16b and c displaying the calculated result using the four-dimensional model. The slope for the inverse value of duration of step 1 (DT_0) is greater than 1, while that of step 3 (DT_m) is less than 1, since thermal isomerization affects deceleration in step 1 and acceleration in step 3. The experimental results closely align with the theoretical expectation, confirming its validity. According to the model, self-oscillation does not occur under lower-intensity light conditions because thermal isomerization prevents the *cis*-isomer ratio from reaching the threshold value for phase transition (Fig. 16c). The contribution of the thermal isomerization may lead to the assumption that DT_0 becomes longer at higher temperatures. Indeed, the ratio of DT_0 to the oscillation period (Dr) became longer, as shown in Table 1; however, the DT_0 and DT_m values decreased at higher temperatures. This effect is likely due to the thermal properties of the crystal: at higher temperatures, looser molecular packing enhances the efficiency of molecular isomerization.

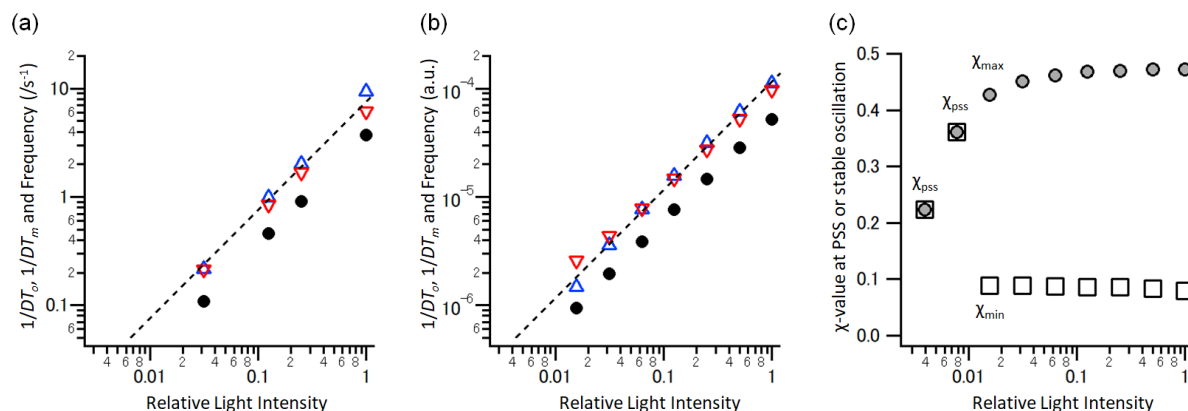


Figure 16. Light-intensity dependence of self-oscillation. (a) Experimental data^{68,81} and (b) the expected relationship calculated by the model. The markers $\triangle$, ∇ , and $\bullet$ are inverse values of DT_0 , DT_m , and frequencies, respectively. The dashed lines are an eye-guide with a slope of 1. (c) Expected χ -values (χ_{pss} indicates the photostationary state, and χ_{max} and χ_{min} represent the oscillatory state) calculated by the model.

Table 1. Examples of the temperature-dependent temporal pattern observed in a crystal

Run	Temp.	Period /s	DT_o /s	DT_m /s	Dr
1	20°C	0.73	0.40	0.32	0.55
2	25°C	0.68	0.41	0.27	0.60
3	30°C	0.59	0.37	0.22	0.63
4	25°C	0.64	0.39	0.25	0.61
5	20°C	0.77	0.45	0.32	0.58

Conclusions

In this paper, we analyzed the self-oscillation of a crystal under blue-polarized light irradiation, verified the validity of the inferred reaction mechanism, and constructed a four-dimensional mathematical model based on the proposed mechanism to study the hierarchical self-organized behavior characteristics exhibited by light-driven self-oscillating crystals. The results revealed that the frequency of light-driven self-oscillation varies with both the polarization angle of the incident light and its rotational direction. Since the self-oscillation arose from multiple photoexcitation processes, the range of polarization angles over which it occurred differed from typical photochemical conditions: the dependence on the polarization angle exhibited either a two-lobe or four-lobe pattern, as confirmed by both the theoretical analysis and the experimental results. These distinct patterns correspond to whether the closed trajectory in the phase diagram intersects the self-oscillation region once or twice. Importantly, this theoretical framework suggests that light-driven self-oscillation is a more generalizable phenomenon, potentially occurring in a wide range of molecular-oriented assemblies that undergo photoisomerization-induced phase transitions—a well-established phenomenon in chemistry.^{82–86} Under unpolarized light irradiation, the state on the phase diagram corresponds to a specific point determined by the light's wavelength. In contrast, when polarized light is used, the state varies from the left to the right and from the bottom to the top of the phase diagram, depending on the polarization angle. By selecting the appropriate combination of wavelength and polarization angle, self-oscillatory behavior can be induced in other materials.

Conversely, our crystal demonstrated stable self-oscillation under unpolarized blue light. This stability was disrupted by the light polarity; and under certain conditions, oscillation ceased. This finding contrasts with many other stimulus-responsive materials, where anisotropic deformation is induced when energy is supplied with directional bias.

Although the experimentally observed dynamics appear to be complex, we still believe that the fundamental mechanism underlying self-oscillation remains simple, as depicted in Fig. 1. Indeed, a model derived from this proposed mechanism was able to closely reproduce the

observed self-oscillatory behavior. On the other hand, due to the interplay between chemical processes and physical properties, a complete prediction of the spatiotemporal patterns is inherently difficult, and determining precise parameter values remains an unresolved challenge. Even with a complete understanding of the underlying molecular-level chemical processes, fully predicting the system's behavior remains impossible. Minor fluctuations in kinetic parameters, energy acceptance rates, or threshold values—often stemming from variations in molecular alignment—can lead to significant differences in behavior. This limitation is likely an intrinsic characteristic of autonomous molecular systems, which operate in close association with chaotic systems.

Throughout this theoretical investigation, we assumed that the chemical reactions between the two isomers proceed in both the forward and reverse directions, although the system does not reach equilibrium. While the photoisomerization reaction proceeds through an irreversible process via the excited state, we did not attribute the emergence of light-driven self-oscillation to this irreversibility. Instead, the system is kept under a steady energy flow, within which a phase transition occurs before the intrinsic chemical reactions reach equilibrium. This phase transition alters the reaction rates, shifting the equilibrium point. By repeating this process, a chemical reaction system that never reaches equilibrium is realized. Although photochemical reactions were used in the experiments, the observed phenomena could also arise in thermally driven chemical reactions, and the constructed model is applicable to those reactions as well.

Furthermore, since the information on light polarization is stored as the isomeric composition of the regulatory molecules, the spatial and temporal patterns of self-oscillation were found to depend on the sequence of the external light-irradiation operations. These results indicate that the memory of external operations is retained at the molecular level, modulating the autonomous dynamics of the crystal. In this process, molecules other than those actively driving oscillation—namely, nonoscillatory molecules within the crystal or those in the twin structure, or both—are inferred to play a role in memory and modulation. This concept contributes to the realization of short-term memory in life-like autonomous materials. These findings not only highlight a molecular-level mechanism for short-term memory in autonomous systems but also suggest that autonomous systems and biological systems share fundamental design principles. Just as biological organisms rely on the cooperation of active molecular motors and passive sensors, our study demonstrates how self-governing behavior and adaptive modulation can emerge from molecular systems under nonequilibrium conditions.

ASSOCIATED CONTENT

The supporting information is available free of charge via the Internet at <http://pubs.acs.org>.

Figures S1–S10 (PDF)

Movies S1–S17 (MP4)

The code used in the simulation is available at <https://doi.org/10.5281/zenodo.16874633>

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Author Contributions

Y. Kageyama designed and performed the experimental studies and mathematical analysis for the reaction kinetics and prepared the manuscript. Y. Kobayashi designed the mathematical four-dimensional model, and T.S. and Y. Kageyama optimized the model and performed the calculations. M.M., T.I. N.T. and D.Y. assisted with the experiments, and M.M. also supported the movie analysis.

Notes

The authors declare no competing financial interests.

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REFERENCES

- (1) Feynman, R. Infinitesimal machinery. *J. Microelectromechanical Syst.* **1993**, *2* (1), 4-14. DOI: 10.1109/84.232589.
- (2) Lehn, J.-M. Perspectives in Chemistry—Steps towards Complex Matter. *Angew. Chem. Int. Ed.* **2013**, *52* (10), 2836-2850. DOI: 10.1002/anie.201208397.
- (3) Iino, R.; Kinbara, K.; Bryant, Z. Introduction: Molecular Motors. *Chem. Rev.* **2020**, *120* (1), 1-4. DOI: 10.1021/acs.chemrev.9b00819.
- (4) Sugawara, T.; Matsuo, M.; Toyota, T. “Life” as a dynamic supramolecular system created through constructive approach. *Bul. Chem. Soc. Jpn.* **2025**, *98* (1) uoae134. DOI: 10.1093/bulcsj/uoae134.
- (5) Kageyama, Y. Catalyst: Advancing nonequilibrium chemistry by clarifying misconceptions. *Chem* **2025**, *11* (8) 102455. DOI: 10.1016/j.chempr.2025.102455.
- (6) Nie, Z.-Z.; Wang, M.; Yang, H. Self-sustainable autonomous soft actuators. *Commun. Chem.* **2024**, *7* (1), 58. DOI: 10.1038/s42004-024-01142-1.
- (7) Szostak, J. W.; Bartel, D. P.; Luisi, P. L. Synthesizing life. *Nature* **2001**, *409* (6818), 387-390. DOI: 10.1038/35053176.
- (8) Lehn, J.-M. Perspectives in Chemistry—Aspects of Adaptive Chemistry and Materials. *Angew. Chem. Int. Ed.* **2015**, *54* (11), 3276-3289. DOI: <https://doi.org/10.1002/anie.201409399>.
- (9) Semenov, S. N.; Kraft, L. J.; Ainla, A.; Zhao, M.; Baghbanzadeh, M.; Campbell, V. E.; Kang, K.; Fox, J. M.; Whitesides, G. M. Autocatalytic, bistable, oscillatory networks of biologically relevant organic reactions. *Nature* **2016**, *537* (7622), 656-660. DOI: 10.1038/nature19776.
- (10) Kageyama, Y. Robust Dynamics of Synthetic Molecular Systems as a Consequence of Broken Symmetry. *Symmetry* **2020**, *12* (10), 1688. DOI: 10.3390/sym12101688.
- (11) Murata, S.; Toyota, T.; Nomura, S.-i. M.; Nakakuki, T.; Kuzuya, A. Molecular Cybernetics: Challenges toward Cellular Chemical Artificial Intelligence. *Adv. Funct. Mater.* **2022**, *32* (37), 2201866. DOI: <https://doi.org/10.1002/adfm.202201866>.
- (12) Aprahamian, I.; Goldup, S., Non-equilibrium Steady States in Catalysis, Molecular Motors, and Supramolecular Materials: Why Networks and Language Matter *J. Am. Chem. Soc.* **2023**, *145* (26) 14169–14183. DOI: 10.1021/jacs.2c12665.
- (13) Shang, Y.; Wang, J.; Ikeda, T.; Jiang, L. Bio-inspired liquid crystal actuator materials. *J. Mater. Chem. C* **2019**, *7* (12), 3413-3428, 10.1039/C9TC00107G. DOI: 10.1039/C9TC00107G.
- (14) Lin, X.; Wang, X.; Zeng, L.; Wu, Z. L.; Guo, H.; Hourdet, D. Stimuli-Responsive Toughening of Hydrogels. *Chem. Mater.* **2021**, *33* (19), 7633-7656. DOI: 10.1021/acs.chemmater.1c01019.
- (15) Zhao, Y.; Hua, M.; Yan, Y.; Wu, S.; Alsaid, Y.; He, X. Stimuli-Responsive Polymers for Soft Robotics. *Annu. Rev. Control Robot. Auton. Syst.* **2022**, *5* (1), 515-545. DOI: 10.1146/annurev-control-042920-014327.
- (16) Xu, L.; Wagner, R. J.; Liu, S.; He, Q.; Li, T.; Pan, W.; Feng, Y.; Feng, H.; Meng, Q.; Zou, X.; et al. Locomotion of an untethered, worm-inspired soft robot driven by a shape-memory alloy skeleton. *Sci. Rep.* **2022**, *12* (1), 12392. DOI: 10.1038/s41598-022-16087-5.
- (17) Jiao, D.; Zhu, Q. L.; Li, C. Y.; Zheng, Q.; Wu, Z. L. Programmable Morphing Hydrogels for Soft Actuators and Robots: From Structure Designs to Active Functions. *Acc. Chem. Res.* **2022**, *55* (11), 1533-1545. DOI: 10.1021/acs.accounts.2c00046.
- (18) Zhang, Y.; Gong, Y.; Li, B.; Ma, R. M.; Che, Y.; Zhao, J. Light - Driven Continuous Twist Movements of Microribbons. *Small* **2019**, *15* (7). DOI: 10.1002/sml.201804102.
- (19) Shinohara, S.; Seki, T.; Sakai, T.; Yoshida, R.; Takeoka, Y. Photoregulated wormlike motion of a gel. *Angew. Chem. Int. Ed.* **2008**, *47* (47), 9039-9043. DOI: 10.1002/anie.200803046.
- (20) Takashima, Y.; Hayashi, Y.; Osaki, M.; Kaneko, F.; Yamaguchi, H.; Harada, A. A Photoresponsive Polymeric Actuator Topologically Cross-Linked by Movable Units Based on a [2]Rotaxane. *Macromolecules* **2018**, *51* (12), 4688-4693. DOI: 10.1021/acs.macromol.8b00939.
- (21) Takashima, Y.; Hatanaka, S.; Otsubo, M.; Nakahata, M.; Kakuta, T.; Hashidzume, A.; Yamaguchi, H.; Harada, A. Expansion-contraction of photoresponsive artificial muscle regulated by host-guest interactions. *Nat. Commun.* **2012**, *3* (1), 1270. DOI: 10.1038/ncomms2280.
- (22) Zhu, S.; Wei, Y.; Chen, K.; Wu, W.; Zhao, H.; Wei, R.; Tian, B.; Huang, X.; Wang, T.; Wang, N.; et al. Multistimulus-Responsive Copolymers of Azobenzene Derivatives with Excellent Elastic Deformation Ability. *Cryst. Growth Des.* **2024**, *24* (10), 4065-4076. DOI: 10.1021/acs.cgd.3c01500.
- (23) Peng, J.; Yang, J.; Zhao, Y.; Li, A.; Shu, Y. Superelastic and Photomechanical Behavior of Acylhydrazone Derivative Crystals.

- Cryst. Growth Des.* **2024**, *24* (12), 5269-5275. DOI: 10.1021/acs.cgd.4c00501.
- (24) Lakshmipathi, M.; Sk, A. I.; Kundu, P. K.; Tothadi, S.; Ghosh, S. Mechanically Elastic and Light-Induced Bending of Acylhydrazones-Based Photoswitch Crystal. *Cryst. Growth Des.* **2023**, *23* (7), 4939-4945. DOI: 10.1021/acs.cgd.3c00196.
- (25) Hazarika, P. J.; Gupta, P.; Gunnam, A.; Thakuria, R.; Nangia, A. K.; Nath, N. K. Flexible Chlorinated Azine Molecular Crystals and Their Photothermally Driven Actuation. *Cryst. Growth Des.* **2023**, *24* (2), 763-773. DOI: 10.1021/acs.cgd.3c01193.
- (26) Rogó, M.; Zeng, H.; Xuan, C.; Wiersma, D. S.; Wasylczyk, P. Light-Driven Soft Robot Mimics Caterpillar Locomotion in Natural Scale. *Adv. Opt. Mater.* **2016**, *4* (11), 1689-1694. DOI: <https://doi.org/10.1002/adom.201600503>.
- (27) Palagi, S.; Mark, A. G.; Reigh, S. Y.; Melde, K.; Qiu, T.; Zeng, H.; Parmeggiani, C.; Martella, D.; Sanchez-Castillo, A.; Kapernaum, N.; et al. Structured light enables biomimetic swimming and versatile locomotion of photoresponsive soft microrobots. *Nat. Mater.* **2016**, *15* (6), 647-653. DOI: 10.1038/nmat4569.
- (28) Huang, C.; Lv, J.-a.; Tian, X.; Wang, Y.; Yu, Y.; Liu, J. Miniaturized Swimming Soft Robot with Complex Movement Actuated and Controlled by Remote Light Signals. *Sci. Rep.* **2015**, *5* (1), 17414. DOI: 10.1038/srep17414.
- (29) White, T. J.; Tabiryan, N. V.; Serak, S. V.; Hrozhyk, U. A.; Tondiglia, V. P.; Koerner, H.; Vaia, R. A.; Bunning, T. J. A high frequency photodriven polymer oscillator. *Soft Matter* **2008**, *4* (9), 1796-1798. DOI: 10.1039/b805434g.
- (30) Gelebart, A. H.; Jan Mulder, D.; Varga, M.; Konya, A.; Vantomme, G.; Meijer, E. W.; Selinger, R. L. B.; Broer, D. J. Making waves in a photoactive polymer film. *Nature* **2017**, *546* (7660), 632-636. DOI: 10.1038/nature22987.
- (31) Zhang, H.; Zeng, H.; Eklund, A.; Guo, H.; Priimagi, A.; Ikkala, O. Feedback-controlled hydrogels with homeostatic oscillations and dissipative signal transduction. *Nat. Nanotechnol.* **2022**, *17* (12), 1303-1310. DOI: 10.1038/s41565-022-01241-x.
- (32) Yamada, M.; Kondo, M.; Mamiya, J.; Yu, Y.; Kinoshita, M.; Barrett, C.; Ikeda, T. Photomobile polymer materials: Towards light-driven plastic motors. *Angew. Chem. Int. Ed.* **2008**, *47* (27), 4986-4988. DOI: 10.1002/anie.200800760.
- (33) Serak, S.; Tabiryan, N.; Vergara, R.; White, T. J.; Vaia, R. A.; Bunning, T. J. Liquid crystalline polymer cantilever oscillators fueled by light. *Soft Matter* **2010**, *6* (4), 779-783. DOI: 10.1039/b916831a.
- (34) Suzuki, M.; Nakano, H. Moving Fragments of Photochromic Molecular Glass of 4-[Bis(9,9-dimethylfluoren-2-yl)amino]-4'-cyanoazobenzene. *J. Photopolym. Sci. Technol.* **2012**, *25* (2), 159-160. DOI: 10.2494/photopolymer.25.159.
- (35) Uchida, E.; Azumi, R.; Norikane, Y. Light-induced crawling of crystals on a glass surface. *Nat. Commun.* **2015**, *6*, 7310. DOI: 10.1038/ncomms8310.
- (36) Gelebart, A. H.; Vantomme, G.; Meijer, E. W.; Broer, D. J. Mastering the Photothermal Effect in Liquid Crystal Networks: A General Approach for Self-Sustained Mechanical Oscillators. *Adv. Mat.* **2017**, *29* (18). DOI: 10.1002/adma.201606712.
- (37) Vantomme, G.; Gelebart, A. H.; Broer, D. J.; Meijer, E. W. A four-blade light-driven plastic mill based on hydrazone liquid-crystal networks. *Tetrahedron* **2017**, *73* (33), 4963-4967. DOI: 10.1016/j.tet.2017.06.041.
- (38) Vantomme, G.; Gelebart, A. H.; Broer, D. J.; Meijer, E. W. Self-sustained actuation from heat dissipation in liquid crystal polymer networks. *J. Polym. Sci. A Polym. Chem.* **2018**, *56* (13), 1331-1336. DOI: doi:10.1002/pola.29032.
- (39) Zeng, H.; Lahikainen, M.; Liu, L.; Ahmed, Z.; Wani, O. M.; Wang, M.; Yang, M.; Priimagi, A. Light-fuelled freestyle self-oscillators. *Nat. Commun.* **2019**, *10* (1), 5057. DOI: 10.1038/s41467-019-13077-6.
- (40) Zhao, Y.; Xuan, C.; Qian, X.; Alsaid, Y.; Hua, M.; Jin, L.; He, X. Soft phototactic swimmer based on self-sustained hydrogel oscillator. *Sci. Robot.* **2019**, *4* (33), eaax7112. DOI: doi:10.1126/scirobotics.aax7112.
- (41) Yang, L.; Chang, L.; Hu, Y.; Huang, M.; Ji, Q.; Lu, P.; Liu, J.; Chen, W.; Wu, Y. An Autonomous Soft Actuator with Light-Driven Self-Sustained Wavelike Oscillation for Phototactic Self-Locomotion and Power Generation. *Adv. Funct. Mat.* **2020**, *30* (15), 1908842. DOI: 10.1002/adfm.201908842.
- (42) Hu, Z.; Li, Y.; Lv, J.-a. Phototunable self-oscillating system driven by a self-winding fiber actuator. *Nat. Commun.* **2021**, *12* (1), 3211. DOI: 10.1038/s41467-021-23562-6.
- (43) Wang, J.; Song, T.; Zhang, Y.; Liu, J.; Yu, M.; Yu, H. Light-driven autonomous self-oscillation of a liquid-crystalline polymer bimorph actuator. *J. Mat. Chem. C* **2021**, *9* (37), 12573-12580. DOI: 10.1039/D1TC02891J.
- (44) Zibaei, R.; Zakerhamidi, M. S.; Korram, S.; Ranjkesh, A. Effects of polarized light on the optical and self-oscillation behaviors of liquid crystal network polymers. *J. Mat. Chem. C* **2021**, *9* (41), 14908-14915. DOI: 10.1039/D1TC03870B.
- (45) Wang, J.; Yang, B.; Yu, M.; Yu, H. Light-Powered Self-Sustained Oscillators of Graphene Oxide/Liquid Crystalline Network Composites Showing Amplitude and Frequency Superposition. *ACS Appl. Mat. Interfaces* **2022**, *14* (13), 15632-15640. DOI: 10.1021/acsami.2c00680.
- (46) Deng, Z.; Zhang, H.; Priimagi, A.; Zeng, H. Light-Fueled Nonreciprocal Self-Oscillators for Fluidic Transportation and Coupling. *Adv. Mater.* **2024**, *36* (12), 2209683. DOI: 10.1002/adma.202209683.
- (47) Sun, Y.; Men, Y.; Liu, S.; Wang, X.; Li, C. Liquid crystalline elastomer self-oscillating fiber actuators fabricated from soft tubular molds. *Soft Matter* **2024**, *20* (21), 4246-4256. DOI: 10.1039/D4SM00134F.
- (48) Xu, L.; Xu, Y.; Li, L.; Qiu, C.; Ling, Y.; Hu, Y.; Chang, L.; Peng, Q.; He, X. MXene-Based Soft Actuators With Phototropic Self-Sustained Oscillation for Versatile Applications in Micro Robotics. *Adv. Funct. Mat.* **2025**, *35* (4), 2414338. DOI: 10.1002/adfm.202414338.
- (49) Bartholomew, A. K.; Stone, I. B.; Steigerwald, M. L.; Lambert, T. H.; Roy, X. Highly Twisted Azobenzene Ligand Causes Crystals to Continuously Roll in Sunlight. *J. Am. Chem. Soc.* **2022**, *144* (37), 16773-16777. DOI: 10.1021/jacs.2c08815.
- (50) Lam, K.; Carta, V.; Almtiri, M.; Bushnak, I.; Islam, I.; Al-Kaysi, R. O.; Bardeen, C. J. Solar-Powered Molecular Crystal Motor Based on an Anthracene-Thiazolidinedione Photoisomerization Reaction. *J. Am. Chem. Soc.* **2024**, *146* (28), 18836-18840. DOI: 10.1021/jacs.4c05566.
- (51) Ge, F.; Zhao, Y. A new function for thermal phase transition-based polymer actuators: autonomous motion on a surface of constant temperature. *Chem. Sci.* **2017**, *8* (9), 6307-6312. DOI: 10.1039/C7SC01792H.
- (52) Pilz da Cunha, M.; Peeketi, A. R.; Mehta, K.; Broer, D. J.; Annabattula, R. K.; Schenning, A. P. H. J.; Debije, M. G. A self-sustained soft actuator able to rock and roll. *Chem. Commun.* **2019**, *55* (74), 11029-11032. DOI: 10.1039/C9CC05329H.
- (53) Kato, H.; Horii, Y.; Watanabe, C.; Sasaki, T.; Ichiiyanagi, K.; Noguchi, M.; Fujimori, H.; Yamamoto, T.; Suzuki, H.; Hirai, Y.; et al. Molecular Thermal Engine Based on a Highly Flexible Elastic Crystal. *J. Am. Chem. Soc.* **2025**, *147* (24), 20582-20589. DOI: 10.1021/jacs.5c03529.
- (54) Wang, Q. N.; Cai, Y. M.; Teng, P. C.; Zhang, S.; Wu, S. H.; Li, Y. H.; Zhang, F. L.; Wang, S. T. Strategies for Continuous Responsive Motion in a Constant Environment. *Adv. Mater.* **2025**, *in press*. DOI: 10.1002/adma.202502926.
- (55) Uchida, E.; Azumi, R.; Norikane, Y. Light-induced crawling of crystals on a glass surface. *Nat. Commun.* **2015**, *6* (1), 7310. DOI: 10.1038/ncomms8310.
- (56) Yamada, M.; Kondo, M.; Mamiya, J.; Yu, Y.; Kinoshita, M.; Barrett, C. J.; Ikeda, T. Photomobile polymer materials: towards light-driven plastic motors. *Angew. Chem. Int. Ed.* **2008**, *47* (27), 4986-4988. DOI: 10.1002/anie.200800760.

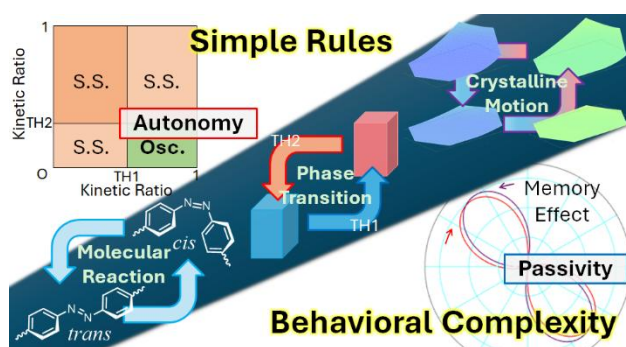
- (57) Nakano, H.; Suzuki, M. Photoinduced mass flow of photochromic molecular materials. *J. Mater. Chem.* **2012**, *22* (9), 3702-3704. DOI: 10.1039/C2JM16517A.
- (58) Tong, F.; Kitagawa, D.; Bushnak, I.; Al - Kaysi, R. O.; Bardeen, C. J. Light - Powered Autonomous Flagella - Like Motion of Molecular Crystal Microwires. *Angew. Chem. Int. Ed.* **2020**, *60* (5), 2414-2423. DOI: 10.1002/anie.202012417.
- (59) Kageyama, Y. Light-Powered Self-Sustainable Macroscopic Motion for the Active Locomotion of Materials. *ChemPhotoChem* **2019**, *3* (6), 327-336. DOI: 10.1002/cptc.201900013.
- (60) Yoshida, R.; Takahashi, T.; Yamaguchi, T.; Ichijo, H. Self-Oscillating Gel. *J. Am. Chem. Soc.* **1996**, *118* (21), 5134-5135. DOI: 10.1021/ja9602511.
- (61) Yoshida, R. Self-Oscillating Gels Driven by the Belousov-Zhabotinsky Reaction as Novel Smart Materials. *Adv. Mat.* **2010**, *22* (31), 3463-3483. DOI: 10.1002/adma.200904075.
- (62) Yamada, Y.; Ito, H.; Maeda, S. Artificial temperature-compensated biological clock using temperature-sensitive Belousov-Zhabotinsky gels. *Sci. Rep.* **2022**, *12* (1), 22436. DOI: 10.1038/s41598-022-27014-z.
- (63) Howlett, M. G.; Engwerda, A. H. J.; Scanes, R. J. H.; Fletcher, S. P. An autonomously oscillating supramolecular self-replicator. *Nat. Chem.* **2022**, *14* (7), 805-810. DOI: 10.1038/s41557-022-00949-6.
- (64) Leira-Iglesias, J.; Tassoni, A.; Adachi, T.; Stich, M.; Hermans, T. M. Oscillations, travelling fronts and patterns in a supramolecular system. *Nat. Nanotechnol.* **2018**, *13* (11), 1021-1027. DOI: 10.1038/s41565-018-0270-4.
- (65) Zhang, Z.; Howlett, M. G.; Silvester, E.; Kukura, P.; Fletcher, S. P. A Chemical Reaction Network Drives Complex Population Dynamics in Oscillating Self-Reproducing Vesicles. *J. Am. Chem. Soc.* **2024**, *146* (27), 18262-18269. DOI: 10.1021/jacs.4c00860.
- (66) Hardy, M. D.; Yang, J.; Selimkhanov, J.; Cole, C. M.; Tsimring, L. S.; Devaraj, N. K. Self-reproducing catalyst drives repeated phospholipid synthesis and membrane growth. *Proc. Nat'l. Acad. Sci. USA* **2015**, *112* (27), 8187-8192. DOI: 10.1073/pnas.1506704112.
- (67) Takahashi, H.; Kageyama, Y.; Kurihara, K.; Takakura, K.; Murata, S.; Sugawara, T. Autocatalytic membrane-amplification on a pre-existing vesicular surface. *Chem. Commun.* **2010**, *46* (46), 8791-8793. DOI: 10.1039/C0CC02758H.
- (68) Ikegami, T.; Kageyama, Y.; Obara, K.; Takeda, S. Dissipative and Autonomous Square-Wave Self-Oscillation of a Macroscopic Hybrid Self-Assembly under Continuous Light Irradiation. *Angew. Chem. Int. Ed.* **2016**, *55* (29), 8239-8243. DOI: 10.1002/anie.201600218.
- (69) Kageyama, Y.; Ikegami, T.; Satonaga, S.; Obara, K.; Sato, H.; Takeda, S. Light-Driven Flipping of Azobenzene Assemblies-Sparse Crystal Structures and Responsive Behaviour to Polarised Light. *Chem. Eur. J.* **2020**, *26* (47), 10759-10768. DOI: 10.1002/chem.202000701.
- (70) Obara, K.; Kageyama, Y.; Takeda, S. Self-Propulsion of a Light-Powered Microscopic Crystalline Flapper in Water. *Small* **2022**, *18* (6), 2105302. DOI: 10.1002/smll.202105302.
- (71) Norikane, Y.; Tanaka, S.; Uchida, E. Azobenzene crystals swim on water surface triggered by light. *Cryst. Eng. Commun.* **2016**, *18* (38), 7225-7228. DOI: 10.1039/c6ce00738d.
- (72) Kaneko, S.; Asakura, K.; Banno, T. Phototactic behavior of self-propelled micrometer-sized oil droplets in a surfactant solution. *Chem. Commun.* **2017**, *53* (14), 2237-2240. DOI: 10.1039/C6CC09236E.
- (73) Xiong, J.; Li, X.; He, Z.; Shi, Y.; Pan, T.; Zhu, G.; Lu, D.; Xin, H. Light-controlled soft bio-microrobot. *Light: Sci. Appl.* **2024**, *13* (1), 55. DOI: 10.1038/s41377-024-01405-5.
- (74) Zarghami, S.; Xiao, Y.; Wagner, P.; Florea, L.; Diamond, D.; Officer, D. L.; Wagner, K. Dual Droplet Functionality: Phototaxis and Photopolymerization. *ACS Appl. Mater. Interfaces* **2019**, *11* (34), 31484-31489. DOI: 10.1021/acsami.9b08697.
- (75) Bunea, A. I.; Martella, D.; Nocentini, S.; Parmeggiani, C.; Taboryski, R.; Wiersma, D. S. Light - Powered Microrobots: Challenges and Opportunities for Hard and Soft Responsive Microswimmers. *Adv. Intell. Syst.* **2021**, *3* (4). DOI: 10.1002/aisy.202000256.
- (76) Kageyama, Y.; Tanigake, N.; Kurokome, Y.; Iwaki, S.; Takeda, S.; Suzuki, K.; Sugawara, T. Macroscopic motion of supramolecular assemblies actuated by photoisomerization of azobenzene derivatives. *Chem. Commun.* **2013**, *49* (82), 9386-9388. DOI: 10.1039/C3CC43488E.
- (77) Michl, J. Photophysics of Organic Molecules in Solution. *Handbook of Photochemistry*, 3rd ed.; Montalti, M., Credi, A., Prodi, L., Gandolfi, M. T. Eds.; CRC Press, 2006; pp 1-47.
- (78) Silmore, K. S.; Strano, M. S.; Swan, J. W. Buckling, crumpling, and tumbling of semiflexible sheets in simple shear flow. *Soft Matter* **2021**, *17* (18), 4707-4718. DOI: 10.1039/D0SM02184A.
- (79) Kobayashi, Y.; Yasugahira, Y.; Kitahata, H.; Watanabe, M.; Natsuga, K.; Nagayama, M. Interplay between epidermal stem cell dynamics and dermal deformation. *NPJ Comput. Mat.* **2018**, *4* (1), 45. DOI: 10.1038/s41524-018-0101-z.
- (80) Naumov, P.; Chizhik, S.; Panda, M. K.; Nath, N. K.; Boldyreva, E. Mechanically Responsive Molecular Crystals. *Chem. Rev.* **2015**, *115* (22), 12440-12490. DOI: 10.1021/acs.chemrev.5b00398.
- (81) The data is corresponding to Fig. 6a in the ref.68. Further examples are also shown in the reference.
- (82) Uchida, K.; Sukata, S.-i.; Matsuzawa, Y.; Akazawa, M.; de Jong, J. J. D.; Katsonis, N.; Kojima, Y.; Nakamura, S.; Areephong, J.; Meetsma, A.; et al. Photoresponsive rolling and bending of thin crystals of chiral diarylethenes. *Chem. Commun.* **2008**, (3), 326-328. DOI: 10.1039/B715251E.
- (83) Kitagawa, D.; Kawasaki, K.; Tanaka, R.; Kobatake, S. Mechanical Behavior of Molecular Crystals Induced by Combination of Photochromic Reaction and Reversible Single-Crystal-to-Single-Crystal Phase Transition. *Chem. Mater.* **2017**, *29* (17), 7524-7532. DOI: 10.1021/acs.chemmater.7b02558.
- (84) Taniguchi, T.; Sato, H.; Hagiwara, Y.; Asahi, T.; Koshima, H. Photo-triggered phase transition of a crystal. *Commun. Chem.* **2019**, *2* (1), 19. DOI: 10.1038/s42004-019-0121-8.
- (85) Fujimoto, A.; Fujinaga, N.; Nishimura, R.; Hatano, E.; Kono, L.; Nagai, A.; Sekine, A.; Hattori, Y.; Kojima, Y.; Yasuda, N.; et al. Photoinduced swing of a diarylethene thin broad sword shaped crystal: a study on the detailed mechanism. *Chem. Sci.* **2020**, *11* (45), 12307-12315. DOI: 10.1039/D0SC05388K.
- (86) Hagiwara, Y.; Takanabe, A.; Asahi, T.; Koshima, H. Photo-triggered Phase Transition of Crystals and Photoactuation. *Chem. Eur. J.* **2024**, *30* (40), e202401590. DOI: 10.1002/chem.202401590.

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Emergent Complexity in a Light-Driven Self-Oscillatory Crystal: A Molecular Perspective on Autonomous Behavior and Stimulus-Modulated Motion

Yoshiyuki Kageyama, Yasuaki Kobayashi, Makiko Matsuura, Toshiaki Shimizu, Tomonori Ikegami, Norio Tanada, and Daisuke Yazaki

TOC-Graphic



TOC- Synopsis

A theoretical and experimental study of a light-driven, self-oscillatory crystal whose behavior varies with spatial conditions and memory effects, with clarified conditions for its emergence.
