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Photoisomerization-Induced Orientational Wave Generation in Two-Dimensional Liquid Crystals at the Air-Water Interface

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Certain class of amphiphilic derivatives of azobenzene form a stable monolayer analog of single-layer smectic-C (SmC) phase at the air-water interface. Due to the broken up-down symmetry, this two-dimensional liquid crystal shows intriguing static orientation structures such as the stripe and higher-order point defects in equilibrium. We found that weak excitation of isomerization reaction of azobenzene core results in a persistent generation of orientational waves and solitons propagating in the plane of the monolayer. This is the first example of purely light-driven nonequilibrium pattern formation. Analysis of the static structures has revealed the essential significance of the coupling between the orientational order and molecular density. Although no definite explanation as yet exists for the dynamic behavior, we believe the density-orientation coupling should play an important role.

Keywords: 2D smectic-C phase; photo-isomerization; Langmuir monolayer; nonequilibrium pattern; orientational wave

INTRODUCTION

Spatio-temporal pattern formation in condensed media is a generic phenomenon which occurs in a wide range of physical, chemical and biological systems impregnated with a proper form of positive feedback mechanism[1,2]. Static patterns such as stripes and bubbles in ferromagnets could result, when competing agents, one (eg. Domain wall) in favor of uniform states and the other (eg. Dipole-dipole

interaction) in favor of nonequilibrium states, are operative in equilibrium[3]. If a continued dissipation of energy and/or matter is furthermore allowed so as to let the system reach a state far from equilibrium, dynamic patterns could also emerge in the form of multiple stationary states, oscillations, and traveling and solitary waves as seen typically in Rayleigh-Benard convection[4-7], Belousov-Zhabotinsky reactions[8, 9], and the electrohydrodynamic instabilities in liquid crystals[10-13].

Since the pioneering theoretical work by Nitzan and Ross[14, 15], photochemical processes have also been regarded as a possible source of dissipation to generate dynamic patterns. Though some of the predictions based on the photothermal mechanism have indeed been confirmed experimentally[16], no purely light-induced dynamic pattern formation[1,9] had yet been recognized until our first discovery[17], except for the case of optical bistability in multicomponent photochemical systems due to the competitive light absorption[2, 18].

In this paper, the observation of light-driven spatio-temporal pattern formation in liquid-crystalline Langmuir monolayers consisting of photochromic azobenzene molecules is described. The observed patterns, ranging from steady-state asymmetric stripes to traveling and solitary waves, are molecular orientational in nature, and are driven by the orientational third-order optical nonlinearity[19] of the liquid crystal monolayer associated with the photoisomerization of constituent molecules. Moreover, the in-plane polarity existing in the Langmuir monolayers, which is expected to play an important role in the dynamic pattern formation coupling with the molecular density, is confirmed by Second Harmonic Generation (SHG) microscopy.

EXPERIMENTAL

We used 4-octyl-4'-(3-carboxytrimethylenoxy) azobenzene (8AZ3), which forms a two-dimensional (2D) SmC liquid crystalline monolayer at the air-water interface[20]. A chloroform solution of 8AZ3 is spread on a carefully cleaned water surface in a homemade trough with double movable barriers. All the observations reported here were performed at 25°C.

Figure 1 shows the experimental setup to observe the photo-induced dynamics in the Langmuir monolayers. The excitation light at 488nm

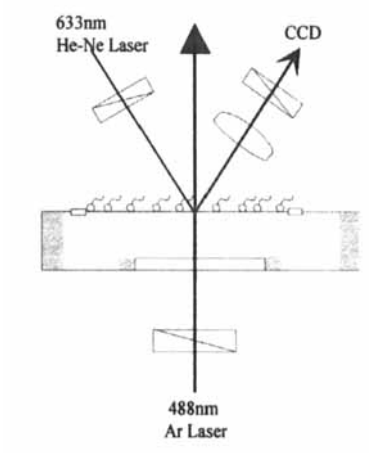

FIGURE 1. Experimental setup for observation of the photo-induced dynamic patterns. 488nm Ar-ion laser beam is used for the excitation with the power of $10\mu W/cm^2$ and 5mm diameter. DRLM is used for the observation; p-polarized He-Ne beam is incident at the angle of $20°$ and the s-polarized component of the reflection is imaged by the CCD camera.

from Ar-ion laser passes through a polarizer and is incident normally on the monolayer from below through a quartz window. Orientational textures of the film are simultaneously observed with a depolarized reflected light microscope (DRLM)[21], where p-polarized light from a 10mW He-Ne laser is obliquely incident on the monolayer and the depolarized (s-polarized) component of the reflection is imaged with a CCD camera. The depolarized reflectivity from an optically uniaxial monolayer is generally given by[22]

$$I = |r_{sp}|^2 = h^2(\cos\alpha - f)^2 \sin^2\alpha, \qquad f = \frac{n_w^{\,2} \tan\vartheta_t}{n_m^{\,2} \tan\beta} \tag{1}$$

where α and β are the azimuthal angle and the tilt angle of the director defined in Figure 2, ϑ_t is the angle of refraction in water, n_w and n_m are the refractive indices of water and monolayer, respectively, and h is a Fresnel factor independent of α. On the basis of this formula, the director orientation of the liquid crystalline monolayer can be quantitatively inferred from DRLM images. The present monolayer is viewed at the incident angle of 20°, which gives f~0.25 with $\beta \sim \pi/4$ and n_m ~1.6.

For the SHG measurement, a mode-locked Ti:Sapphire laser system (Kapteyn Murnane Laboratories L.L.C., excited by Spectra Physics Millennia V) was used to produce 0.3 nJ infrared pulses at 800nm with about 100 fs pulsewidth at a repetition rate of 80 MHz. The linearly polarized beam was focused on the Langmuir monolayer with a diameter of about 20 μm at an incident angle of 45°. The reflected beam went through an analyzer and an interference filter, resulting in only the SHG component was directed to a PMT. The detected photon is counted by Hamamatsu Photon Counting System C2550. During the SHG experiment, the illuminated point by the femto-second laser beam was observed under the DRLM.

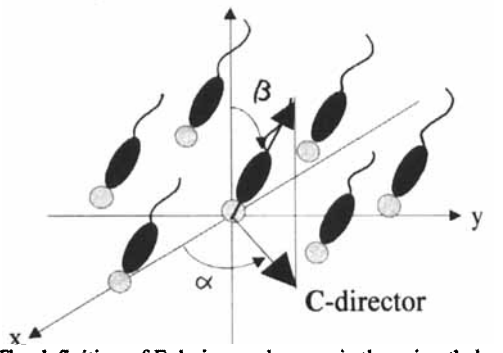

FIGURE 2. The definition of Eulerian angles. α is the azimuthal angle between the c-director (the unit vector parallel to the projection of the liquid crystal director onto the water surface (xy-plane)) and x-axis. β is the tilt angle between the director and z-axis (normal to the water surface).

RESULTS AND DISCUSSION

Figure 3 shows the surface pressure vs area-per-molecule isotherm of 8AZ3 Langmuir monolayer at 25°C. At low surface-pressure region of 0 ~ 11 mN/m, the monolayer forms the SmC phase with strong optical anisotropy and high fluidity[20]. When the film is compressed over the kink at 12mN/m, the SmC structure is replaced by the solid-like texture showing sharp domain boundaries without orientational flicker[20]. Interestingly, the photo-induced dynamic pattern is observed only in SmC phase but never in the solid-like phase. The following photo-induced dynamics were all observed in the SmC phase at about 5mN/m.

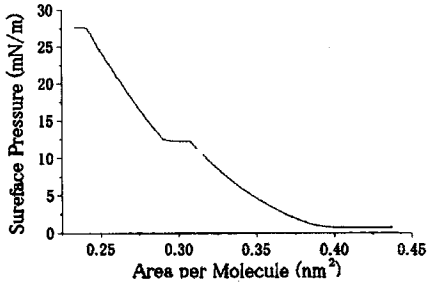

Figure 3. Surface pressure vs area-per-molecule isotherm of 8AZ3 Langmuir monolayer. At low surface pressure ranging from 0 mN/m to 11 mN/m, the film is in SmC phase. Through the first-order transition, it undergoes solid-like phase at the surface pressure higher than 12 mN/m.

Asymmetric Reorientation of Stripes

Even in the dark state, the monolayer spontaneously develops a static stripe pattern as shown in the top image of Figure 4 (a). Analyzing this stripe by using Eq.(1), we obtain the director field as in the top illustration of Figure 4 (b), where the c-director rotates continuously across the stripe. Such an orientational pattern is understood as resulting from competition between the Frank-Ossen curvature elasticity and the surface-induced flexoelectric polarization of the monolayer[23-25].

Illuminating the stripe structure in the SmC liquid crystalline monolayer with a linearly polarized light at a wavelength suitable for the weak trans-cis isomerization of azobenzene causes an asymmetric change in the director field. Depending on the polarization of the illumination, a certain quadrant of the 2π stripe expands, while all the other bands bunch up, forming almost a 2π wall. This transient reorientation terminates in a few seconds on illumination, which results in the anisotropic patterns shown in the middle and botttom images of Figure 4 (a). Although the photo-excitation should be locally nonpolar, the observed photoresponse shows a clear in-plane polarity. This result presents a striking contrast to the recent studies on light-induced reorientation of azobenzene derivatives bound on solid substrates[26] or polymer matrices[27], in all of which the molecules containing azobenzene moiety were found to exhibit a nonpolar angular distribution with a preferred orientation perpendicular to the plane of polarization. Undoubtedly, the polar liquid crystalline nature of the

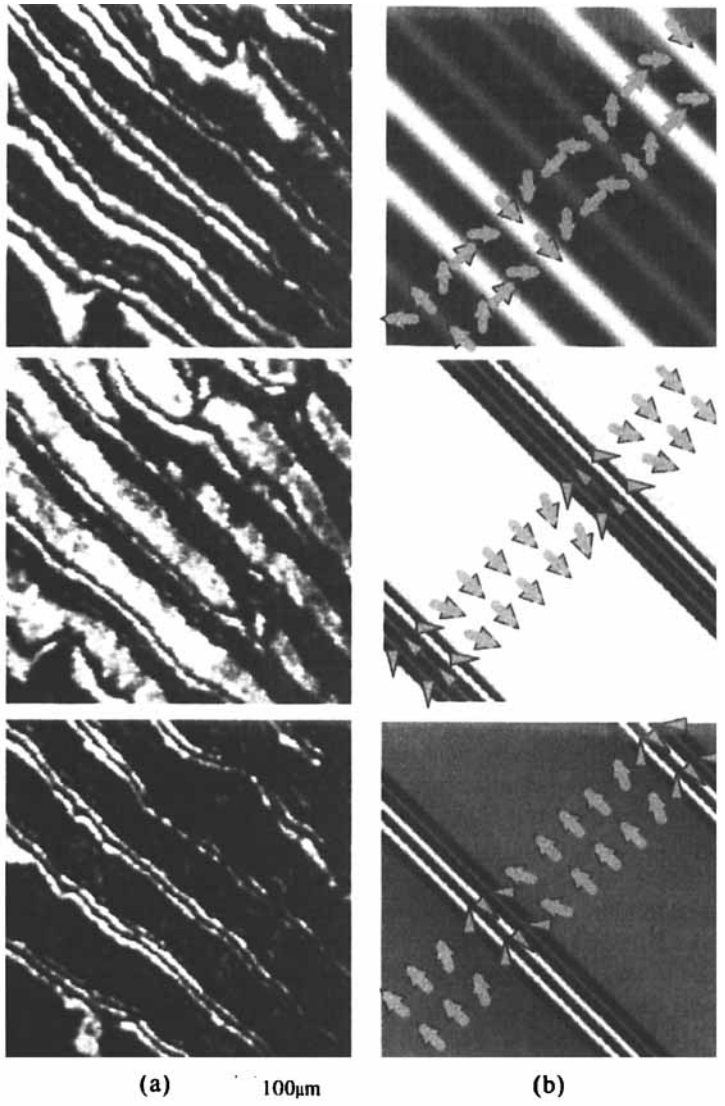

FIGURE 4. (a) Stripe patterns observed in the azobenzene Langmuir monolayer in the dark state (top), under the illumination of linearly polarized light, the polarization direction of which is parallel (middle) and perpendicular (bottom) to the stripe. (b) Numerically calculated steady states based on GL equation in each situation, where $W=10(2\pi K/L)$, $\lambda Q_1/\rho_0=2.5(2\pi K/L)$, $\lambda Q_0/\rho_0=0.5(2\pi K/L)$, $\beta=\pi/4$ with $L=50$ μm.

monolayer should be the origin of the asymmetric reorientation. The significance of the liquid crystalline ordering is also confirmed by the observation that the present photoresponse occurs at an extremely low incident power of 1-10 $\mu W/cm^2$ at 488 nm, which is least 2-orders of magnitude smaller than that in the previous reorientation studies[26,27]. When the incident power exceeds this level, the liquid crystalline structure breaks into a granular texture.

Traveling Orientational Waves

When the illumination is continued after the reorientation of stripes, a spontaneous generation of traveling orientational waves are observed. In the expanded and uniformly oriented region in the stripes, small dark domains spring up, grow and propagate in a certain direction, which seems to be determined by the boundary condition and the polarization direction of the illumination. The wave generation lasts as long as the excitation continues, except for the case that the boundary condition is unsuitably changed by a disturbing flow of the monolayer. In most cases, the wave is associated with a decrease in the tilt angle compared to the uniform background. As shown in Figure 5, the wave consists of elongated dark bands in which the tilt angle is nearly zero. The wave velocity is typically 50 μm/s, and is not considerably enhanced by increasing the power of illumination.

Occasionally, orientational solitary waves are also observed, in which the azimuthal angle is primarily changed as shown in Figure 6. The brightness is enhanced in the wave region from the surrounding with a bright fringe, which implies the wave does not involve only the tilt angle changes but associated with the azimuth change. In this solitary wave, the azimuthal angle of the center of the domain is estimated to rotate about 20° from the background. The typical size and the velocity are almost the same as those for the train waves.

In both traveling waves and solitary waves, the striking observation is that the propagation direction is perfectly reversed when the illumination polarization is switched by $\pi/2$. This indicates a close connection of the wave generation with the asymmetric transient photo-response.

SHG Microscopy

In the photo-induced orientational pattern formations described above, both out-of-plane and in-plane polar structures of the monolayer are

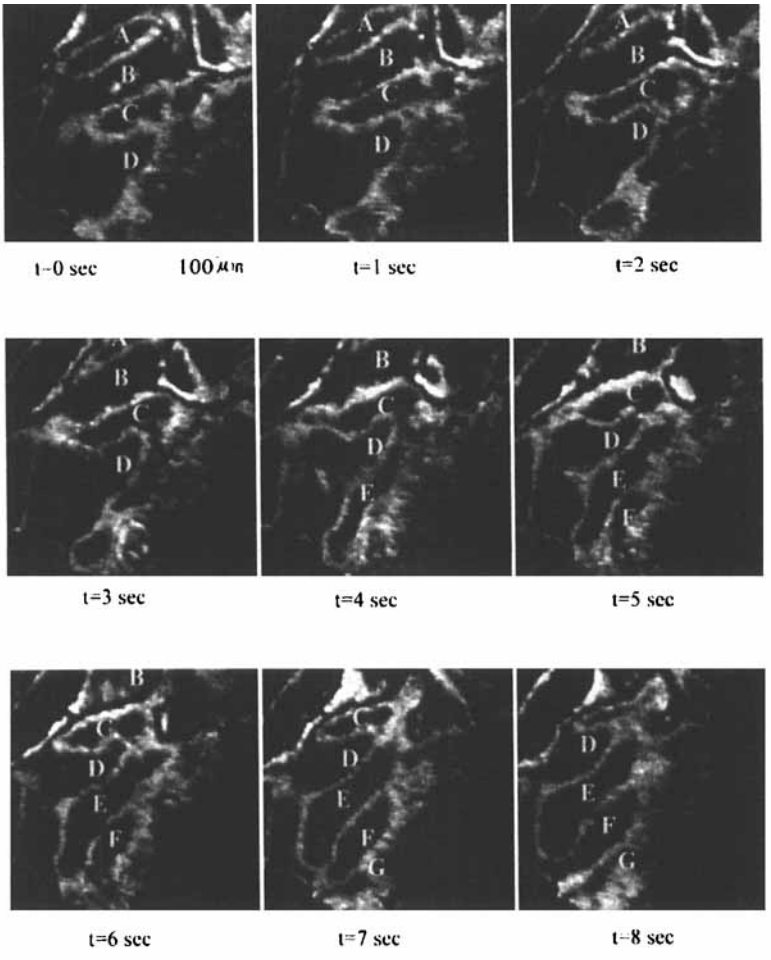

FIGURE5. Generation and propagation of the orientational waves in the azobenzene Langmuir monolayer excited by continued illumination of linearly polarized light. The dark domains denoted by A~G are generated in the uniformly oriented region and propagate in the left-up direction. The power of excitation light is about 5!W/cm2 and the entire area in the image is uniformly illuminated. The polarization direction of the excitation is parallel to the lateral axis.

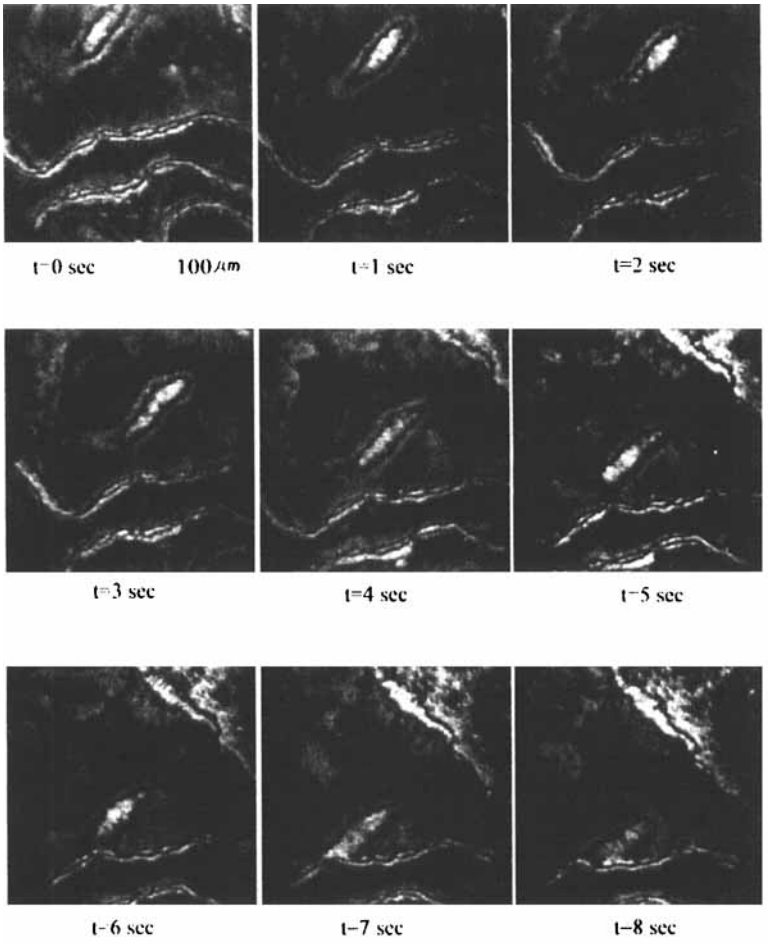

FIGURE 6. Snapshot of a solitary orientational wave in the azobenzene Langmuir monolayer under the illumination. The polarization direction of the excitation light is parallel to the lateral direction.
The rotation of the azimuthal angle of the center of the wave is about 130 from the surroundings.

considered to play an important role. To detect the polar structure of the monolayer at the air-water interface, SHG microscopy should be an effective tool[28].

Figure 7 shows the typical temporal traces of SH signal for the SmC at 5 mN/m and the solid-like phase at 15 mN/m, for the orientational textures shown at the top. The SH signals under the geometry in which both the incident and reflected light are p-polarized (P_{in}-P_{out}) are shown in the middle two figures. For the P_{in}-P_{out} geometry, the detected SH signal gives a measure of the out-of plane polarity which should exist in all Langmuir monolayers because of the trivial symmetry of the water surface[28]. As intuitively clear, the molecular tilt from the surface normal as large as 45° in the SmC monolayer leads to a strong dependence of SH intensity on the azimuthal angle of incidence relative to the molecular axis. Since the monolayer flows rather rapidly in the SmC phase, the molecular azimuth at the illuminated region by the femto-second beam also varies in time. This flow effect accounts for the large irregular variation of SH intensity in Figure 7. Despite the clear first order transition separating the SmC and the solid-like phase shown in the isotherm (see Figure 3), the SH intensities from these two phases are approximately the same, but slightly small in the solid-like phase.

When either the incident or the reflected light is s-polarized, the resultant SH signal should be generated only when the polar structure exists in the layer plane. In the bottom two figures of Figure 7 presenting the SHG under P_{in}-S_{out} geometry, we see the strong SH signals, providing clear evidence for the in-plane polar structure. As far as the SH intensity is concerned, the in-plane polarity is almost of the same magnitude as the out-of-plane polarity, which indicates that the molecular azimuth is preferentially ordered as tightly as that for the upright orientation of molecules.

Discussion

To explain the observed photo-induced response, we start with a Landau free energy for 2D tilted smectics given as[23-25]

$$F = \int d^2r[\frac{K_1}{2}\sin^2\beta(\nabla\cdot\mathbf{c})^2 + \frac{K_3}{2}\sin^2\beta(\nabla\times\mathbf{c})^2 + \frac{W}{2}(\cos\beta-\cos\beta_0)^2 + (\mu+\lambda\Psi)\sin\beta(\nabla\cdot\mathbf{c}) + \frac{1}{2\kappa}\Psi^2 + \frac{u}{2}(\nabla\Psi)^2] \quad (2)$$

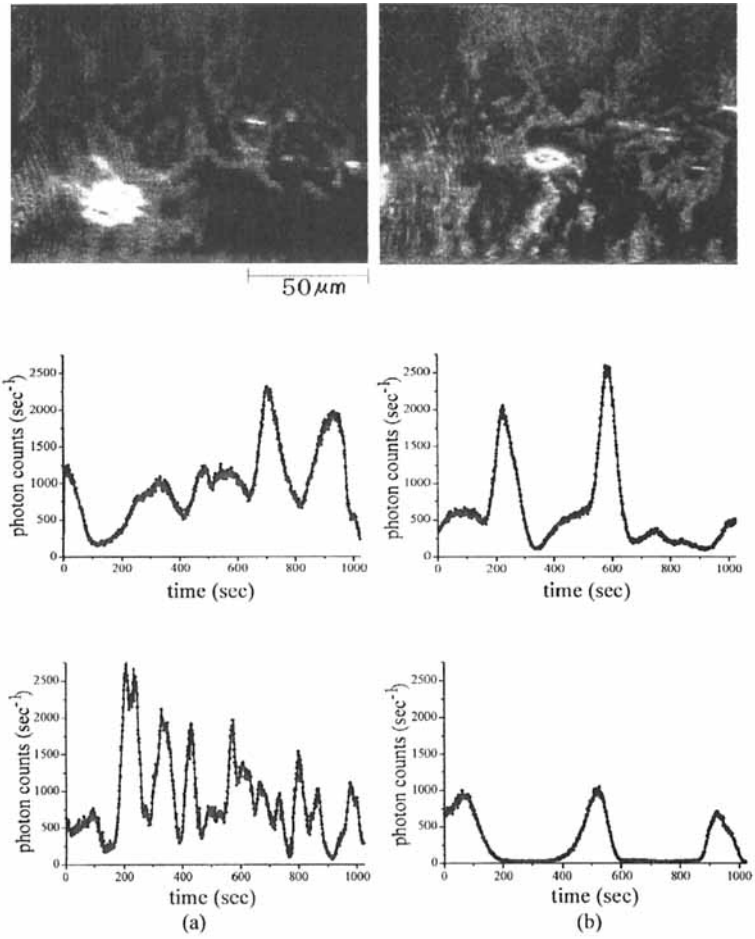

FIGURE 7. Top:Textures of 8AZ3 monolayer observed under DRLM during the SHG experiment (a) in SmC phase and (b) in the solid-like phase, where the bright spot indicates the illuminated region by the infrared beam for SHG.
Middle: P-polarized SH signal from (a) SmC phase and (b) solid-like phase vs time. The incident beam was p-polarized.
Bottom: S-polarized SH signal from (a) SmC phase and (b) solid-like phase vs time for the p-polarized incident light.

where the first three terms present the elastic energy with the Frank elastic constants of K_1, K_3 and anchoring energy efficient W. The next term indicates the linear term of director distortion and its coupling to the density variation Ψ, which is given by $\Psi \approx (\rho - \rho_0)/\rho_0$ with the molecular density ρ, followed by the Landau expansion of Ψ. Our previous microscopy work has proved $\mu \cong 0$ and has succeeded in reproducing the stripe texture as a thermal equilibrium state using Eq. (2)[29]. The essential origin of the static modulation has been found to be the competition between the linear coupling term of the *c*-director distortion to the molecular density variation and the elastic energies for the director distortion[23-25, 29].

Irradiation of the monolayer with a low-power polarized light induces an anisotropic yet nonpolar local increase in the cis-isomer fraction[27]. Because of the shape, only the rod-like trans-isomer can form liquid crystalline phase, which means that the anisotropic increase of cis-isomer should cause the anisotropic decrease of molecular density of ρ. Since the cis-isomer generation is less than 10 percent, the change of molecular density may be regarded as a small perturbation of Ψ as

$$\Psi \rightarrow \Psi_0 - \frac{Q_1 \sin^2 \beta (\mathbf{c} \cdot \mathbf{E})^2 + Q_0}{\rho_0} \tag{3}$$

where Ψ_0 is the density variation in the dark state, and the second term is the perturbation coming from the anisotropic cis generation. Here, Q_1 and Q_0 are the constants connected with orientational order parameter, and $\mathbf{E}$ is the electric field of the excitation light. The resultant description of dynamical behaviors of director results in a reaction-diffusion type Ginzburg-Landau equation for the tilt and the azimuthal angles. Figure 4 (b) shows the initial and the steady-state orientational patterns obtained by numerically equilibrating the director profile based on the GL equation, showing a good agreement with the experimental results. The traveling waves, however, has not yet been successfully reproduced within this formalism due to the highly nonlinear character of the GL equation. Nevertheless, we consider

that the coupling between 2D liquid crystallinity and molecular density variation, which makes the asymmetric reorientation possible, should play a key role.

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