



# Visualizing polarization structure of lipid Langmuir monolayer by surface second-harmonic generation technique

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## ABSTRACT

By using optical second harmonic generation (SHG) technique, we visualized lipid Langmuir monolayers comprised of molecules with an SH active moiety, 1,2-dipalmitoyl-sn-glycero-phosphoethanolamine-N-(7-nitro-2-1,3-benzoxadiazol-4-yl) (NBD-PE), on focussing the shape and polarization structure of the domains. The domain shape visualized by the SHG was the same as that by the Brewster angle microscopy (BAM), while polar structure was identified at the cusps of dendritic domains. These results were found well supported by our theoretical prediction in our previous study.

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## 1. Introduction

The physicochemical properties of amphiphile monolayers at the air–water interface have attracted much attention since the discovery of so-called Langmuir monolayer. Those properties are governed by the structure of monolayers and change in accordance with the monolayer compression. One of the significant parameters to describe the state of monolayer is orientational order of the constituent molecules. For quantitative evaluation of the molecular orientation, a set of orientational order parameters is introduced from a statistical viewpoint [1]. Hence, the physicochemical properties of monolayer depend on these orientational order parameters [2].

Monolayers form domain structures, i.e., islands of condensely-packed molecules, in the two-phase coexistent states. The shape of domain drastically changes during monolayer compression, and is determined by the competition among the inner and the outer surface tensions of the domain, the line tension at the domain boundary, and the Maxwell's stress due to the electrostatic interaction inside the domain [3]. In other words, the equilibrium domain shapes are given by minimizing the free energy  $F$  of monolayer domain [4]. Shape equation describing the domain shape is given as a function of curvature radius of a domain  $\kappa(s)$  in a form as,

$$\delta P - \lambda_0 \kappa(s) - P_{0\perp} E_{\perp}(\mathbf{r}(s)) - \mathbf{P}_{0\parallel}(\mathbf{r}(s)) \cdot \mathbf{E}_{\parallel}(\mathbf{r}(s)) = 0 \quad (1)$$

Here,  $\delta P$  is the difference in the surface pressure between the inside and the outside of domain,  $\lambda_0$  is the line tension at domain boundary. The last two terms express the Maxwell's stress acting inside the domain. The symbols  $\perp$  and  $\parallel$  represent the direction of the vector with respect to the water surface, i.e., perpendicular and parallel to the water surface, respectively.

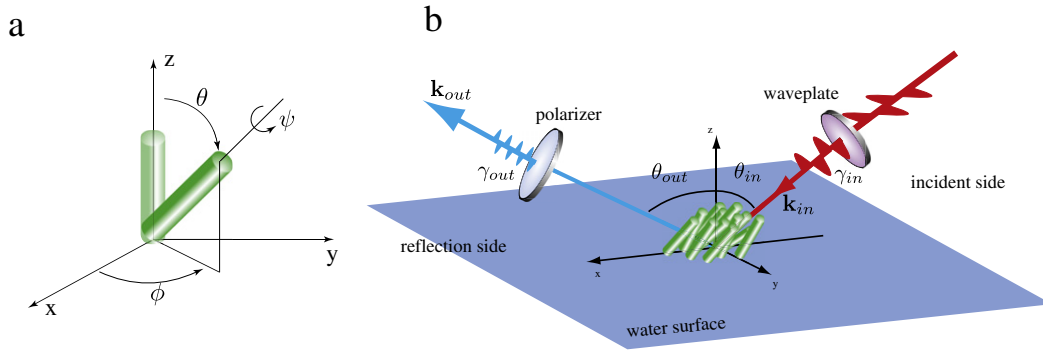
Since monolayers on a water surface form a noncentrosymmetric orientational structure, spontaneous polarization of the molecules is the origin of the electrostatic interaction. Therefore, to reveal the effect of the polarization structure on the domain shape is of great importance. Fluorescent microscopes (FM) and Brewster angle microscopes (BAM) are often used to observe the shape of domain [5–10]. These microscopes are quite powerful to directly visualize the shape of domains. However, these are not suitable to observe the polar structure of the monolayer, because both microscope techniques are based on the linear optical response of the molecules. In other words, BAM and FM signals provide the second-order orientational order parameter,  $S_2$  [11], which dominates the linear optical response, whereas the polar structure strongly connected to the first- and third-order orientational order parameters,  $S_1$  and  $S_3$  [12]. The optical second harmonic generation (SHG) signal is negligible when it is generated from the materials with inversion symmetry such as liquid under the electric dipole approximation [13], because of  $S_1 = S_3 = 0$ . On the other hand, SHG measurement provides us the surface or interface selective observation, on account of the broken symmetry at the air–water interface [14,15], where  $S_1$  and  $S_3$  are non-zero. In this paper, using lipid molecules with an SH active moiety (NBD-derivative), the polarization structure inside the lipid domains is directly visualized by using the optical SHG microscope. Then the SHG signal is analyzed in terms of the orientation of the molecule to reveal the polar structure inside the domains.

## 2. Theory

The origin of nonlinear polarization in a molecule is the electron displacement induced by the electric field of light, i.e. electronic polarization. Nonlinear molecular polarization  $\mathbf{p}(2\omega)$  is expressed as,

$$\mathbf{p}(2\omega) = \beta : \mathbf{E}(\omega)\mathbf{E}(\omega) \quad (2)$$

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**Fig. 1.** (a) Transformation of coordinate setting from molecular frame to the laboratory frame by applying Euler rotation matrix. (b) Coordinate setting of the laboratory flame and optical polarization.

where  $\mathbf{E}(\omega)$  is a local electric field vibrating at the frequency of  $\omega$  on a molecule, and the  $\beta$  is the second order molecular hyperpolarizability, which characterizes the nonlinear optical response of the molecule. Although the nonlinear polarization is very weak compared with a linear polarization, it is dramatically enhanced if the resonant condition is satisfied, and it gives strong SHG signals. To address the SHG signal from the molecular aggregate such as thin-film, we have to take an ensemble average of  $\beta$  of each molecule. Hence, the nonlinear optical susceptibility,  $\chi^{(2)}$ , is expressed as  $\chi_{ijk}^{(2)} = \sum_{i'j'k'} N_s \langle R_{ii'} R_{jj'} R_{kk'} \rangle \beta_{i'j'k'}$ .  $N_s$  is molecular density per unit surface, and  $R$  represents Euler rotation matrix for the coordinate transformation between the molecular system and the laboratory frame. It should be noted that SHG signal is the function of the order parameters  $S_1$  and  $S_3$ . For the simplicity, we here assume that the molecular hyperpolarizability component  $\beta_{zzz}$  is dominant, and the tilt and azimuthal angles of all molecule are respectively fixed. The macroscopic second-order polarization  $\mathbf{P}(2\omega)$  is expressed as the function of the tilt angle  $\theta$  and the azimuthal angle  $\phi$  of the molecule (see Fig. 1(a)) as,

$$\mathbf{P}(2\omega) = \chi^{(2)}(\theta, \phi) : \mathbf{E}(\omega)\mathbf{E}(\omega) \quad (3)$$

Here, we neglect the twist angle  $\psi$  of the molecules, because the NBD-PE has a rod-like shape. Accordingly, molecular orientation on a water surface can be evaluated from the surface SHG signal.

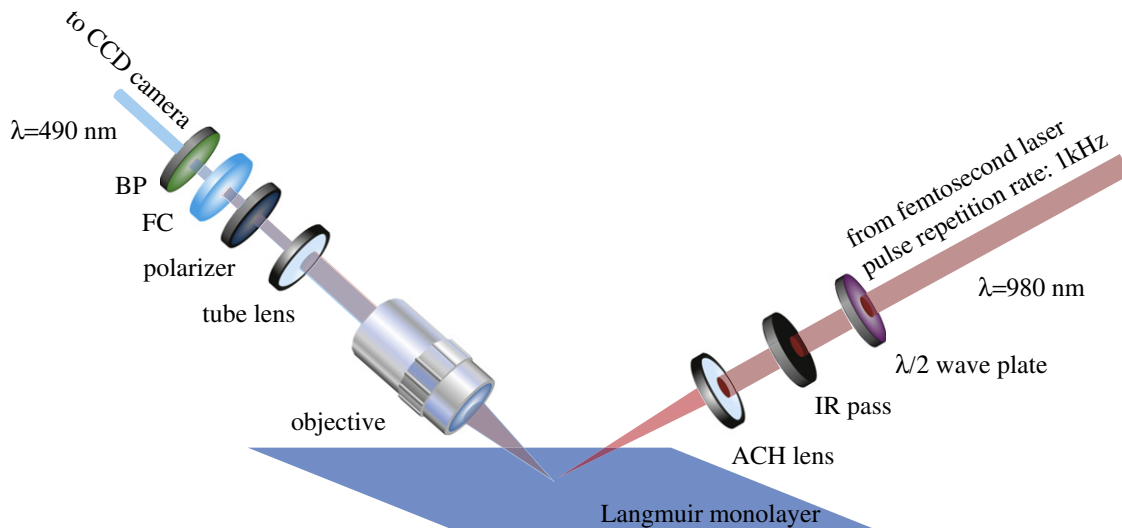
The surface SH intensity is expressed as [15]

$$I(2\omega) \propto \left| \mathbf{e}_{\gamma_{out}}^{2\omega} \cdot \chi^{(2)} : \mathbf{e}_{\gamma_{in}}^{\omega} \mathbf{e}_{\gamma_{in}}^{\omega} \right|^2 I^2(\omega). \quad (4)$$

Here,  $\mathbf{e}^{\omega}$  and  $\mathbf{e}^{2\omega}$  are the unit vectors of electric fields of incident and reflected light, respectively.  $\gamma_{in}$  and  $\gamma_{out}$  indicate the polarizations of incident light and reflected light (see Fig. 1(b)).  $I(\omega)$  is the intensity of the incident laser. In the experiment, we can observe the polar order of the molecules by changing the optical polarization conditions of the incident and reflected light, i.e. by changing  $\gamma_{in}$  and  $\gamma_{out}$  shown in Fig. 1(b).

### 3. Experimental details

Derivative of dipalmitoyl-phosphatidylcholine (DPPC) lipid molecule, 1,2-dipalmitoyl-sn-glycero-phosphoethanolamine-N-(7-nitro-2,3-benzoxadiazol-4-yl) (NBD-PE) was used in the experiment. The sample was purchased from Avanti Polar Lipid, Inc., and was used without further purification. The Langmuir monolayer was formed on a water surface of the Langmuir trough (Filgen. co., Japan). Subphase was ultra pure water with an electrical resistivity of 18.2 M $\Omega$  cm, and the temperature of the subphase was within  $\pm 3$  °C of a room temperature. Chloroform solution of NBD-PE with a concentration of 0.241 mM was spread on a water surface to form a monolayer. The molecular compression speed was 0.068  $\text{\AA}^2/\text{molecule}\cdot\text{sec}$ .



**Fig. 2.** Schematic diagram of the second harmonic generation microscopy technique for lipid Langmuir monolayer.

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