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SURFACE SYMMETRY IN ORGANIC THIN FILMS STUDIED BY OPTICAL SECOND-HARMONIC GENERATION

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Abstract The surface symmetry of hemicyanine monolayer and merocyanine monolayer is studied by surface second-harmonic generation. While the monolayer consisting of dye monomer has $C_{\infty v}$ symmetry with the rotation axis along the surface normal, the monolayer containing J-aggregated merocyanine has C_{2v} symmetry whose rotation axis lies in the surface plane. This anisotropy in the surface plane is diminished by heating due to the dissociation of the J-aggregates.

INTRODUCTION

In order to construct a highly controlled molecular system for a molecular electronics device, it is important to understand how the molecules distribute in the system such as a monolayer. Many surface probes have been tried to clarify the monolayer structure.[1-14] Among them, surface second-harmonic generation (SHG)[15-17] is one of the most sophisticated tool because it is very sensitive enough to determine how the symmetry of a monolayer is.[17-21] We have studied the compression processes of the molecular monolayer on water using surface SHG.[17] Here, we summarize the molecular structures in hemicyanine and merocyanine monolayers from view points of orientation and symmetry.

EXPERIMENTAL

The monolayer materials used were hemicyanine, merocyanine, whose chemical structures are illustrated in Fig.1, and arachidic acid. They were dissolved in chloroform and spread onto water. The deposition was accomplished by the conventional vertical deposition method.

We used a Nd:YAG laser (Spectra Physics DCR-11) running at its fundamental wavelength 1064nm. The fundamental beam of the incident angle 45° generates the

second-harmonic (SH) light in the monolayer. Filtered SH light from the fundamental light was detected by photomultiplier (Hamamatsu R955). Figure 1 shows the optical geometry in this experiment.

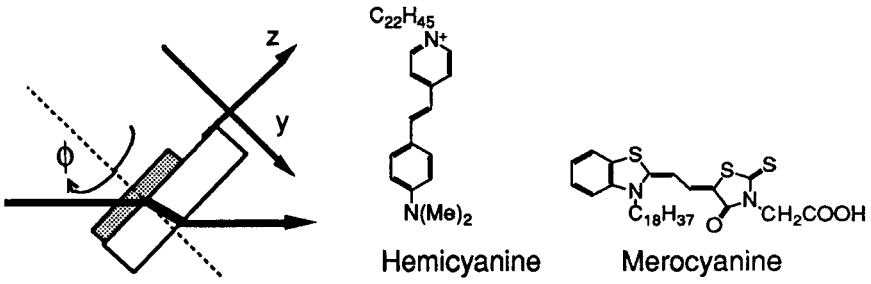

FIGURE 1 Optical geometry and the chemical structures.

RESULTS AND DISCUSSION

$C_{\infty v}$ monolayer

In order to determine the symmetry of the monolayer, j-polarized SH light intensity generated by i-polarized fundamental light, I(i,j), was measured as a function of a rotation angle ϕ of the monolayer around the surface normal. The results are shown in Fig.2, where the radial length between the center and the circle indicates the intensity at the corresponding rotation angle ϕ.

Figure 2(a) shows I(p,p) and I(s,p) from a mixed hemicyanine monolayer with arachidic acid of a molar ratio 1:2 (HEMI:AA), where no aggregation bands were observed in the absorption spectra.[22] The circular profiles in Fig.2(a) prove the monolayer of $C_{\infty v}$ symmetry. As for a monolayer of pure hemicyanine, however, I(p,p) in Fig.2(b) lacks circularness, suggesting inhomogeneity of the monolayer. Actually, the symmetry change by the formation of the H-aggregates, which was confirmed to exist in the pure hemicyanine monolayer by absorption spectra,[22] was already pointed out by detailed surface SHG measurements.[17] I(s,p) in the pure hemicyanine monolayer is very weak compared with I(p,p), suggesting that the H-aggregates well align along the surface normal. We also confirmed in both monolayers that I(p,s) and I(s,s) are negligibly weak due to at least nearly $C_{\infty v}$ symmetry.

From these results, the average molecular tilt angle with respect to the surface normal in the mixed hemicyanine monolayer is 50.7°. This value is a little smaller than the values (around 60°) of the monolayer on water.[17]

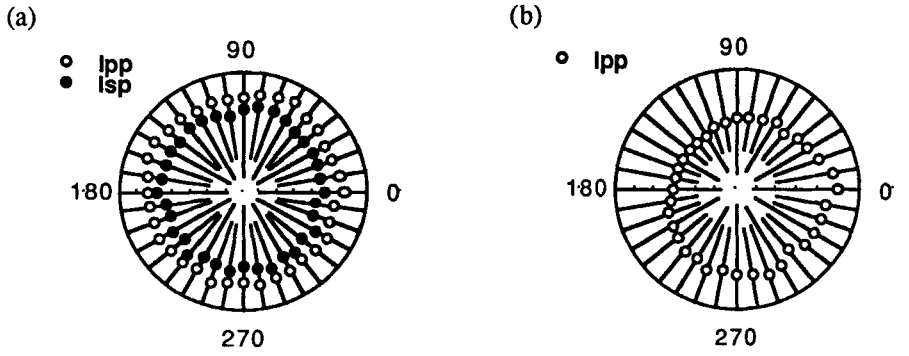

FIGURE 2 SH intensity profiles. (a) a mixed hemicyanine monolayer with arachidic acid (HEMI:AA=1:2) (b) a pure hemicyanine monolayer

C_{2v} monolayer

We found that the merocyanine monolayer containing J-aggregates has the anisotropic structure within the monolayer.[21] In contrast to $C_{\infty v}$ monolayer, strong SH light generated by normal incidence fundamental light are observed. The SH intensity profiles for 45° incidence, I(p,p), I(s,p), I(s,s) and I(p,s), have anisotropic fashion as shown in Fig.3. The direction of the anisotropy is maintained within the magnitude of several millimeters.[21]

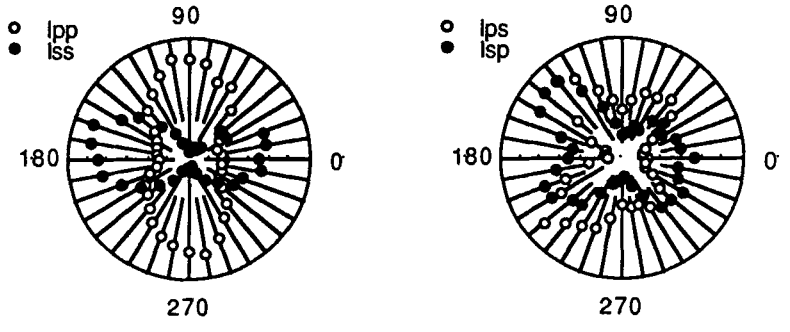

FIGURE 3 SH intensity profiles of a pure merocyanine monolayer.

We also confirmed that no anisotropic SH profile was observed in the merocyanine monolayer containing no J-aggregates such as the monolayer thermally treated, a

mixed merocyanine monolayer with fatty acid (low dye fraction). Figure 4 shows the example, an SH intensity profile of the thermally treated merocyanine monolayer (90°C, 30min).

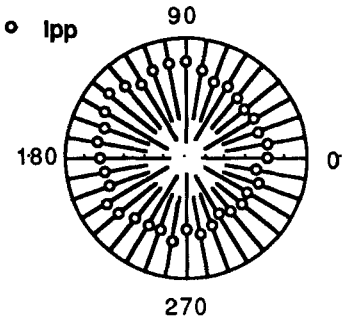

FIGURE 4 SH intensity profile of a thermally treated pure merocyanine monolayer.

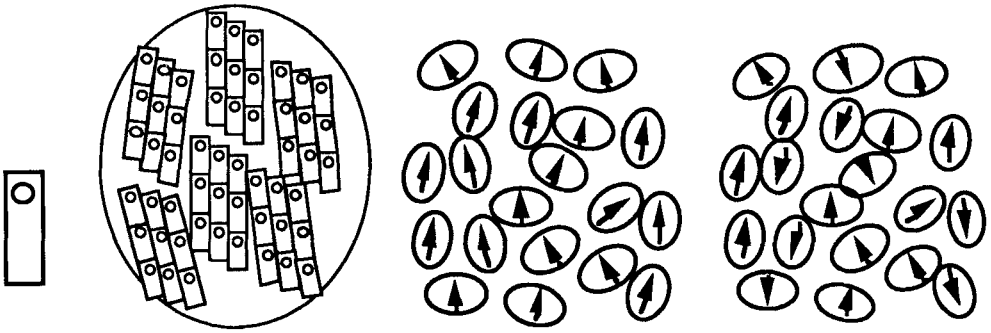

FIGURE 5 The top view of model orientational structure of the merocyanine monolayer. This picture is proposed based on the present results. (a) denotes the molecule, the circle corresponds to the alkyl chain in the merocyanine molecule. The anisotropic domain (b) is formed by the molecules. Notice that it is noncentrosymmetric. The noncentrosymmetric domains gather and construct the monolayer as shown in (c) same polar direction or (d) opposite polar direction. The arrow indicates the direction of noncentrosymmetry.

Nakahara et al. estimated that the number of molecules contained in one aggregate is nine or ten.[5] The aggregates were found to form a anisotropic domain of several

micron's by polarizing microscope observation.[1,2] The domain should be maintained noncentrosymmetric structure for the strong SHG reported above. The possible picture of the J-aggregated merocyanine monolayer is illustrated in Fig.5. The SH active domain, which is noncentrosymmetric, distributes in the monolayer. We propose a couple of possible pictures, the domains have the same polar direction Fig.5(c) or the opposite direction Fig.5(d).

CONCLUSION

Surface SHG measurements revealed the structures of hemicyanine and merocyanine monolayers. While the monolayer consisting of non-aggregated molecules, i.e. monomer molecules, has $C_{\infty v}$ symmetry, the J-aggregated merocyanine monolayer has C_{2v} symmetry. This anisotropy is diminished due to the dissociation by heating. Experiments to answer how the anisotropy takes place are in process and will be reported elsewhere.

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