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Optical second harmonic generation (SHG) spectra and SHG images were investigated on merocyanine dye (MD)/arachidic acid mixed monolayer at the air-water interface. A sharp peak of the SHG spectrum was observed at the J-band of 620nm. In the low wavelength region below 400nm, a sharp increase of the SHG spectrum was also observed. Careful comparisons of SHG images taken at several wavelengths revealed that the whole spectrum originates from the J-aggregate states of MD.

Keywords: J-aggregate; merocyanine dye; second harmonic generation spectrum; second harmonic generation microscope

INTRODUCTION

Dye molecules align its chromophore group in certain conditions along a specific direction. The dye assembly is excited by light to form J-aggregate (JA), which is characterized by a red-shifted sharp absorption band and Stokes-shift-free fluorescence [1]. Using the second harmonic generation (SHG)/fluorescence (FL) microscope, we have recently found that the merocyanine dye (MD) forms mesoscopic JA domains which are SHG-active in the MD/arachidic acid (AA) mixed monolayer at the air-water interface [2,3]. In these studies, we investigated the mesoscopic structure of the MD/AA system with one wavelength of 1064nm. It would be much more interesting to study the system with wide range of wavelength including the resonant spectra and to compare the SHG

images taken at several wavelengths. This would enable us to clarify the active site which produces the characteristic nonlinear optical properties. With this motivation of the study, we measured the SHG spectrum and examined SHG images of MD/AA mixed monolayer at the air-water interface.

EXPERIMENTAL

Sample containing large SHG-active JA domains were prepared with aqueous ammonia (<0.03 wt.%, >pH10) as a subphase [3]. A laboratory dish was used as a trough. A mixture of MD and AA with molar ratio MD/AA of 2:3 was studied at the air-water interface. AA was mixed to stabilize the MD monolayer. The mixture compound was solved in chloroform (1mmol/l) and the solution was gradually spread on the subphase. Surface pressure was less than 14.7mN/m.

The optical parametric oscillator (OPO) was used for changing fundamental wavelength from 750nm to 1269nm. The OPO was pumped by the third harmonic wave (355nm) of YAG laser. The average power of the out put wave from OPO is 2~23mW and the repetition frequency is 20Hz. To increase the incident power density, a lens was set under the trough. SHG spectrum was detected by a polychromator equipped with semiconducter detector array. The exposure time was 4 seconds. Reflection spectrum was also detected by the polychromator. SHG image was taken by ICCD (Integrated charge coupled device) with gating image intensifier synchronized with the laser oscillation [4]. The exposure time is 20~30 seconds.

Prior to observation, we checked SHG, FL and two photon FL signals from subphase, AA and monomer of MD. There was no signal from them.

RESULTS AND DISCUSSIONS

SHG and reflection spectra of MD/AA mixed monolayer at the air-water interface are shown in Fig.1. A sharp band at 620nm in reflection spectrum corresponds to the J-band [3]. A sharp peak is also observed in the SHG spectrum at 620nm, which is resonant with the J-band. Below 400nm, another increase of SHG spectrum is observed. This may be the edge of a new resonant spectrum which is unique to the SHG spectrum, as no remarkable band is observed in the absorption spectrum[#]. Plausible

[#] For the absorption spectrum at short wavelength, see Ref.[5].

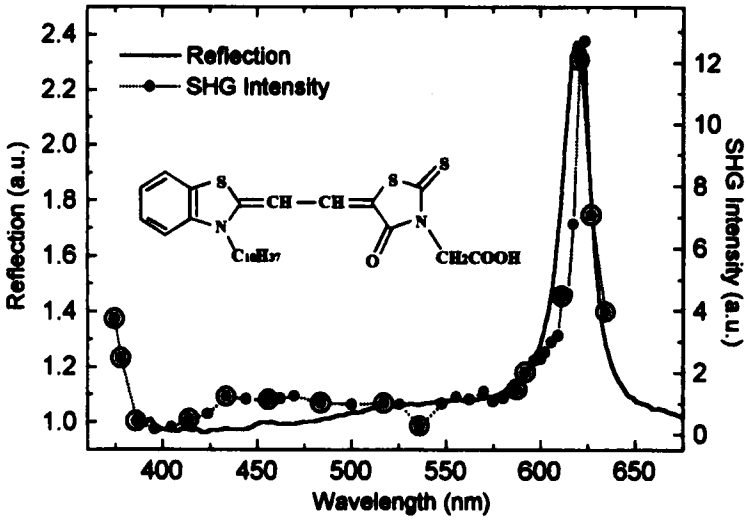

FIGURE 1 SHG spectrum of MD/AA mixed monolayer at the air-water interface. Double circles indicate the wavelength where SHG image was taken. Molecular form of merocyanine dye is also indicated.

origin would be due to the resonance with excitonic 2-strings, which is the bound state of two Frenkel excitons [6], but precise examination is necessary.

Double circles in Fig.1 indicate the wavelengths where SHG images of the MD/AA system were taken. During the observation, the optical geometry should have been rearranged when the wavelength is shorter than 867.4nm (shorter than 433.7nm for SHG) and we had to prepare a new sample under same condition. Thus we choose the SHG image taken at 433.7nm as the reference to compare the image for all spectrum range. In Fig.2, SHG images taken at several wavelengths are shown. Here the white parts indicate the SHG-active regions. The fluorescence observation of the same sample revealed that cigar-shaped JA domains coincide with the SHG-active domain [2,3]. In whole wavelength rage, no significant change in the image was observed. Thus we can safely conclude that SHG spectrum in Fig.1, even the spectrum near 370nm, is generated from JA forming MD domain. The future investigation with higher spatial resolution will be promising to elucidate the molecular origin of the spectrum.

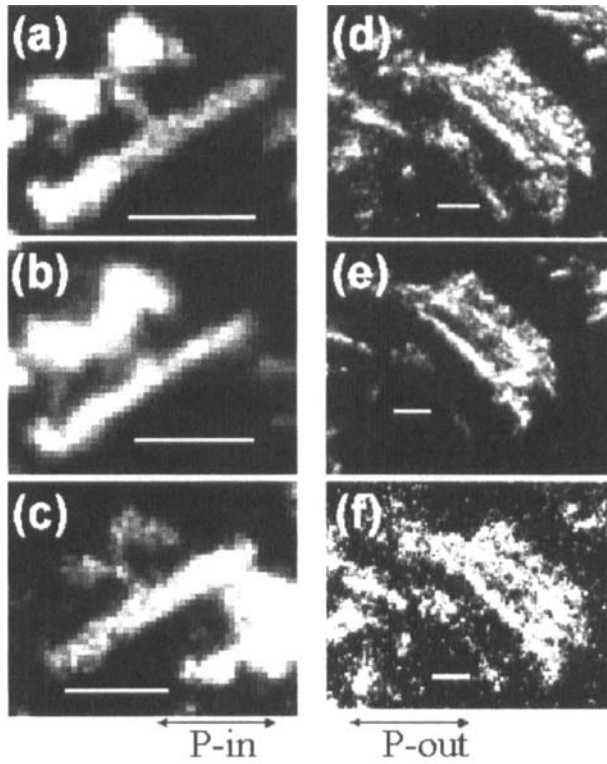

FIGURE 2 **SHG images of MD/AA mixed monolayer at the air-water interface. Wavelength of SHG is (a) 620.85nm, (b) 592.2nm, (c) and (d) 433.7nm, (e) 413.35m and (f) 378nm. Arrows indicate the polarization directions of fundamental and SH waves. White bar scale indicates 30μm.**

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