Quantitative Study of Molecular Orientation in Hemicyanine Langmuir–Blodgett Films by Fourier Transform Infrared Spectroscopy and Second Harmonic Generation

W.-F. A. Su,[†] T. Kurata, H. Nobutoki, and H. Koezuka[*]

Materials & Electronic Devices Laboratory, Mitsubishi Electric Corporation, 1-1 Tsukaguchi-Honmachi 8-Chome, Amagasaki, Hyogo 661, Japan

The molecular orientation in amphiphilic hemicyanine Langmuir–Blodgett (LB) films has been studied quantitatively by Fourier transform infrared (FTIR) spectroscopy and second harmonic generation (SHG). From the analysis of transmission and reflection absorption (RA) spectra of FTIR, the tilt angles to the surface normal of the hydrocarbon chain axis and the chromophore of amphiphilic hemicyanine LB film were estimated to be 24° and 43°, respectively. The SHG measurements yielded a chromophore tilt angle of 44°. Both techniques have shown consistent results for the chromophore orientation in the hemicyanine LB film.

1. Introduction

The Langmuir–Blodgett (LB) technique has the ability to organize molecules into a highly ordered monolayer and to manipulate a multilayer film toward a desired architecture. By this technique specific physical and chemical properties of materials can be easily controlled, compared with other techniques such as vacuum evaporation. The LB technique has the potential for fabricating next generation novel devices operating at an extremely small scale for information processing, transmission, and storage.[1] The structure of assembled LB films has to be quantitatively evaluated in order to understand the relationship between the molecular orientation and the characteristics of a specific device. Among the various analytical methods applicable to thin organized films, such as LB films, Fourier transform infrared (FTIR) spectroscopy is the most convenient and useful. In particular, several attempts have been made to apply infrared reflection absorption (RA) spectroscopy to molecular orientation analysis.[2,3] Chollet et al. had quantitatively analyzed the structure of the thin films by comparing peak intensities of the RA spectra with those of the transmission spectra.[2] However, they had assumed that the enhancement factor for the RA spectra on a metal surface was independent of frequency. Recently this analytical method has been further improved by Takenaka et al.[4] They calculated infrared intensities and enhancement factors using the rather rigorous optical formalism for the multilayer films developed by Hansen.[5]

The detection of second harmonic generation (SHG) gives another powerful tool to investigate the molecular orientation in LB films. The SHG signals can be observed even from a single monolayer on a substrate.[6] A hemi-

cyanine dye has attracted much attention as an organic nonlinear material because of its large molecular hyperpolarizability. Girling et al. first reported that the hemicyanine dye LB film generated large SHG.[7,8] From analysis of SHG data, the tilt angle of the hemicyanine dye chromophore was determined, although that of the long alkyl chain could not be estimated.[7,9] Many studies using the SHG technique have been conducted for the hemicyanine dye LB films to determine the molecular orientation as described above.[7-11] On the other hand, little work using the FTIR method has been performed for the hemicyanine dye LB films. Stroeve et al. reported the chromophore orientation of hemicyanine by using FTIR.[12] Two types of samples were studied, Z-type multilayer hemicyanine LB films and alternate layers of hemicyanine and arachidic acid LB film. By comparing the peak intensities of transmission spectra with those of RA spectra quantitatively, they concluded that the orientation of the hemicyanine dye was closer to the normal when it was interleaved with arachidic acid.

In this paper, we have studied the quantitative evaluation of the molecular orientation of hemicyanine LB films by FTIR spectroscopy for the alkyl chain and the chromophore, individually. We have also shown that a SHG method is very useful in the investigation of molecular orientation.

2. Experimental Section

The chemical structure of amphiphilic hemicyanine consists of a long alkyl chain and chromophore as shown in Figure 1. Hemicyanine was purchased from Japan Research Institute for Photosensitizing Dyes Ltd., and purified by column chromatography using silica gel. Spectra grade chloroform was used as

† Permanent address: Westinghouse Electric Corp., Science and Technology Center, 1310 Beulah Rd., Pittsburgh, PA 15235.
(1) *Langmuir-Blodgett Films*; Roberts, G., Ed.; Plenum Press: New York, 1990.
(2) Chollet, P.-A.; Messier, J.; Rosilio, C. *J. Chem. Phys.* 1976, 64, 1042.
(3) Allara, D. L.; Nuzzo, R. G. *Langmuir* 1985, 1, 45, 52.
(4) Umemura, J.; Kamata, T.; Kawai, T.; Takenaka, T. *J. Phys. Chem.* 1990, 94, 62.
(5) Hansen, W. N. *J. Opt. Soc. Am.* 1968, 58, 380.
(6) Koezuka, H.; Kurata, T.; Tsumura, A.; Fuchigami, H. *Mater. Res. Soc. Symp. Proc.* 1989, 173, 691.

(7) Girling, I. R.; Cade, N. A.; Kolinsky, P. V.; Montgomery, C. M. *Electron. Lett.* 1985, 21, 169.
(8) Girling, I. R.; Cade, N. A.; Kolinsky, P. V.; Earls, J. D.; Cross, G. H.; Peterson, I. R. *Thin Solid Films* 1985, 132, 101.
(9) Girling, I. R.; Cade, N. A.; Kolinsky, P. V.; Jones, R. J.; Peterson, I. R.; Ahmad, M. M.; Neal, D. B.; Petty, M. C.; Roberts, G. G.; Feast, W. J. *J. Opt. Soc. Am.* 1987, B4, 950.
(10) Marowsky, G.; Chi, L. F.; Mobius, R.; Steinhoff, R. *Chem. Phys. Lett.* 1988, 147, 420.
(11) Kajikawa, K.; Shirota, K.; Takezoe, H.; Fukuda, A. *Jpn. J. Appl. Phys.* 1990, 29, 513.
(12) Stroeve, P.; Saperstein, D. D.; Rabolt, J. F. *Thin Solid Films* 1989, 179, 529.
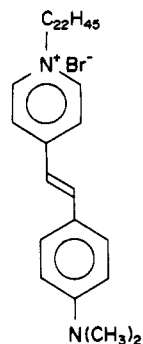
$C_{22}H_{45}$

N^+ Br^-

$N(CH_3)_2$

Figure 1. Structure of amphiphilic hemicyanine dye.
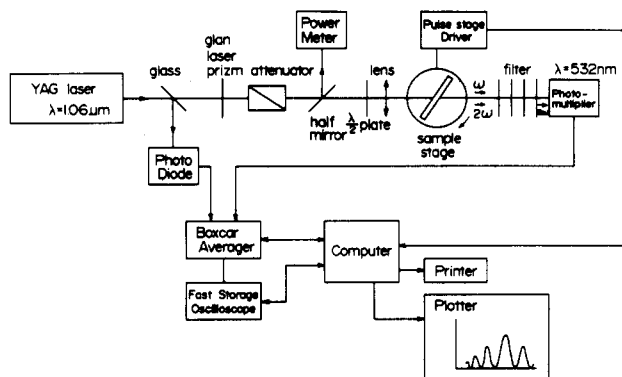
Figure 2. Experimental configuration for SHG measurement.

Figure 3. Infrared transmission and RA spectra of five-monolayer hemicyanine dye LB film.

a solvent without further purification. Silver-coated glass slides were used for infrared RA spectroscopy measurements. The glass slides were first ultrasonically cleaned with chloroform and ethanol and then covered with a vacuum-evaporated 60-nm-thick silver film. Calcium fluoride substrates were used for infrared transmission spectroscopy measurements. The CaF_2 crystals were thoroughly cleaned with neutral detergent and water. LB films were deposited on cleaned glass slides for all the SHG measurements. A Kyowa Kaimen Kagaku Model HBM-AP Langmuir trough was employed for LB film preparation. The trough was cleaned with chloroform, ethanol, deionized water, and distilled water in that sequence. Twice-distilled water was used for the subphase. A 100-μL hemicyanine chloroform solution (1.6 × 10^{-3} M) was spread on the water subphase containing cadmium chloride (3 × 10^{-4} M) and sodium bicarbonate (1 × 10^{-4} M). The pH of the subphase was 6. The temperature of the subphase was kept at 20 °C. The monolayer was formed by compressing the spread hemicyanine at a speed of 10 cm^2/min to the surface pressure of 22 dyn/cm. Then the monolayer on the subphase was transferred to the substrate at the speed of 5 mm/min by dipping the substrate to the subphase vertically. The multilayers were prepared by repeating the monolayer deposition. The drying time between each deposition was 30 min.

All the infrared spectra were measured by a JOEL JIR-100 FTIR spectrometer equipped with a MCT (mercury cadmium telluride) detector. A JOEL IR-RSC110 reflection attachment was used for RA spectroscopy measurements. The resolution of the measured spectra was set to 4 cm^{-1}. The infrared beam was polarized by a JOEL PL-81 polarizer. For the RA spectroscopy, the incident angle of the infrared beam was 80° from the surface normal. Four hundred interferograms were collected for each measurement to yield the spectra with a high signal-to-noise ratio.

The experimental equipment for the SHG measurements is schematically shown in Figure 2.[13] A Q-switched Nd:YAG laser (Quantel YG-571, 1.06 μm, 10-Hz repetition, fwhm 10 ns) was utilized. The pulse energy was 5 mJ using an attenuator, and the polarization of the fundamental wave was horizontally polarized using a Glan laser prism. Polarization was controlled by rotating a half-wavelength plate. The laser beam was focused on a sample
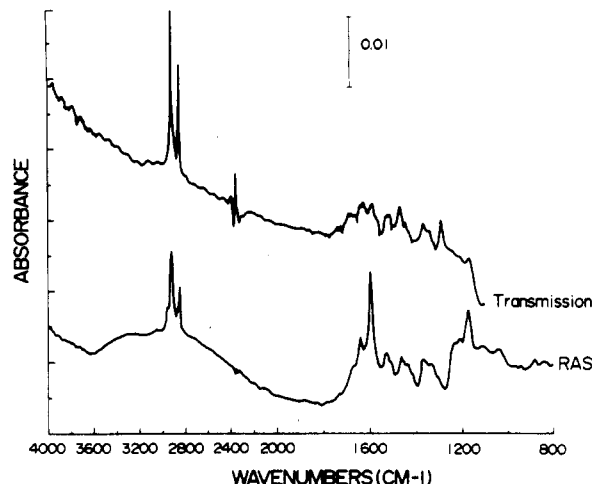
placed onto a rotating stage by a 50-cm-focal-length lens. Second harmonic radiation generated from the samples was detected by a photomultiplier (Hamamatsu Photonics, Model R928) after passing it through an IR-cut filter (Schott RG850), a short wavelength cut filter (Toshiba V-Y-42) and a band-pass filter (Toshiba KL-53). The signals from the photomultiplier were processed with a boxcar averager (Stanford Research Systems, Model SRS-250). All the measuring systems were controlled with the aid of a personal computer (Yokogawa-Hewlett-Packard, Model 340). A quartz single crystal (d_{11} = 1.1 × 10^{-9} esu) was used as a reference sample to obtain the nonlinear optical coefficient.

3. Results and Discussion

The results of FTIR and SHG are discussed separately as follows.

3.1. FTIR Measurement. In the transmission spectra of FTIR, the electric field vector is parallel to the film surface, so the infrared radiation probes only the vibrations having components of their transition moments in the plane of the film. On the other hand, the electric field vector perpendicular to the sample surface is enhanced in the RA spectroscopy, so that the infrared radiation selectively probes those vibrations that have components of their transition moments normal to the film. Therefore, the functional group orientation of the molecules in the films can be evaluated by comparing the transmission spectra to the RA spectra.[4,14,15]

A series of nonpolarized and polarized infrared transmission spectra of the LB films were measured. Those spectra had the same peak height which was independent of infrared beam polarizations; thus, the distribution of hemicyanine molecules is in-plane isotropic. Figure 3 shows polarized transmission and RA spectra of a multilayer film consisting of five hemicyanine monolayers. The assignments of the absorption bands are summarized in Table I. The transmission spectrum is different from the RA spectrum. In the transmission spectrum, both the symmetric (2850 cm^{-1}) and the antisymmetric CH$_2$ stretching band (2918 cm^{-1}) are stronger than those in the RA spectrum. The transition moments of the antisymmetric as well as the symmetric CH$_2$ stretching bands are perpendicular to the long alkyl chain axis. The alkyl chain axis is therefore considered to be approximately aligned along the surface normal.

(13) Kurata, T.; Tsumura, A.; Fuchigami, H.; Koezuka, H. *J. Phys. Chem.* **1991**, *95*, 8831.

(14) Cheung, J.; Rubner, M. F. *Polym. Prepr.* **1990**, *31* (1 (April)), 404.
(15) Kawai, T.; Umemura, J.; Takenaka, T. *Langmuir* **1990**, *6*, 672.

Table I. Assignments of FTIR Main Peaks of Hemicyanine Five-Monolayer LB Film

wavenumber, cm⁻¹		
transmission	RA	assignment
2953	2956	antisym CH_3 stretching
2918	2922	antisym CH_2 stretching
2850	2852	sym CH_2 stretching
1628	1643	vinylic C=C stretching
1589	1599	aromatic ring C=C stretching
1470	1468	CH_2 scissoring
1173	1176	aliphatic (C—N) stretching

The splitting for the CH_2 scissoring band can be used as a criterion in distinguishing the lateral packing of the alkyl chains.[15] In our case the CH_2 scissoring band of the hemicyanine LB film appears as a singlet at 1470 cm⁻¹ in the transmission spectrum. Thus, the alkyl chains of the hemicyanine dye LB film are considered to be in a hexagonal subcell where each chain freely rotates around its alkyl long axis.[15] This conclusion means that the alkyl chain is in-plane isotropic, which is in an arrangement with the results of the polarized infrared beam study described above. An absorption band due to the in-plane aromatic ring (C=C) stretching appeared at 1589 cm⁻¹. The absorption was shown to be much stronger in the RA spectrum than that in the transmission spectrum, indicating that this transition moment is almost directed along the substrate normal. The chromophore, the core part of amphiphilic hemicyanine dye, has two aromatic rings, a benzene ring and pyridine ring. It is very difficult to assign this absorption band to be C=C stretching of either a benzene ring or pyridine ring or both (overlapping). Stroeve et al. had assigned this absorption band to the aromatic ring stretching.[12] Further discussion on the orientation of the core chromophore is given below.

The molecular orientation in the hemicyanine LB film is considered to be uniaxially distributed around the surface normal. Each functional group orientation of the hemicyanine in the LB films can be quantitatively evaluated according to Takenaka et al.[4,15] They suggested that the orientation of the transition moment of the specific vibration could be calculated by eq 1, assuming the uniaxial distribution of the transition moment around the surface normal z with the angle ψ.

$$\frac{A_T}{A_R} = \frac{\sin^2 \psi}{2m_z \cos^2 \psi + m_x \sin^2 \psi} \quad (1)$$

The film surface is defined as the xy-plane, and infrared beam incidence in the RA measurements is in the xz-plane. A_T and A_R are the absorbances of the specific band in the transmission and RA spectra, respectively. The m_z and m_x are the enhancement factors along the z and x axes of the RA intensity to the transmission intensity. The values of m_z and m_x can be estimated by comparing the calculated absorbances of transmission and RA spectra using Hansen's formulas.[5] Those values, whose calculation procedure was described in ref 4, depend on (1) the complex refractive indices of the film and the substrate, (2) the thickness of the film, (3) the infrared light incident angle in the RA measurements, and (4) the infrared wavelength. Our LB films can be regarded as a three-phase plane-bounded system for both the transmission and the RA measurements. For the transmission measurement where the incident angle is zero, the sample is an air/LB film/CaF_2 system. The known values n_1(air) = 1.00 and n_3-(CaF_2) = 1.415 were used as refractive indices for the first and the third phase, respectively. For the RA measurements, the system is air/LB film/silver; n_3*(Ag) = 0.62 +

Table II. Calculated Enhancement Factors and Tilt Angles for Specific Transition Moments of Hemicyanine LB Film

	wavenumber, cm⁻¹					
assignment	transmission	RA	A_T/A_R	m_x	m_z	ψ, deg
$\nu_a(CH_2)$	2918	2922	0.95	0.0595	4.79	72
$\nu_s(CH_2)$	2850	2852	1.47	0.057	4.82	75
$\nu(C=C)$	1589	1599	0.085	0.0185	5.06	43

25.1i was utilized as the complex refractive index of the third phase, a silver layer.[16] The refractive index of the second phase, a five-monolayer LB film, was assumed to be the same as that (1.50) of long stearic acid. The effect of the hemicyanine chromophore on the refractive index should be small in the infrared region because the characteristic absorption band of the chromophore appears in the visible region and is far from the infrared one. The determined thickness of the LB film by X-ray diffraction was 15.7 nm. The incident angle for our RA measurements was 80°. Since the calculated value of m_x is very small (see Table II), we neglected the m_x and used a simplified equation to calculate the tilt angle ψ as shown below.

$$\frac{A_T}{A_R} = \frac{\sin^2 \psi}{2m_z \cos^2 \psi} \quad (2)$$

Table II shows the tilt angles of each transition moment determined for three specific bands along with the calculated enhancement factor. The wavenumbers of the absorption bands in the RA spectra slightly varied from the corresponding wavenumbers in the transmission spectra due to anormalous dispersion in the real part of the refractive index originating from each absorption.

However, these differences of the wavenumber were not large so that we used the wavenumber of the absorption band in the transmission spectra to calculate the tilt angles.

The tilt angles of the transition moments of the antisymmetric and symmetric CH_2 stretching bands have been determined to be 72° and 75°, respectively, using eq 2 (see Table II). Let them to be α and β, respectively. The directions of the transition moments of both the antisymmetric and the symmetric CH_2 stretching bands and the long alkyl chain axis are perpendicular to each other. The tilt angle of the alkyl chain axis from the surface normal, γ, can be evaluated by the following orthogonal relationship among α, β, and γ.

$$\cos^2 \alpha + \cos^2 \beta + \cos^2 \gamma = 1 \quad (3)$$

When $\alpha = 72°$ and $\beta = 75°$ were substituted into eq 3, the tilt angle of the alkyl chain axis was calculated as 24°.

The tilt angle of the transition moment of the aromatic ring was also calculated to be 43° using eq 2. To confirm the chromophore tilt angle of the hemicyanine dye, the relationship between the transition moment and the hemicyanine molecular axis should be made clear. Thus, the vibrational analysis has been carried out for this alkyl chain substituted hemicyanine dye molecule. At first, the molecular structure of hemicyanine was optimized by using a semiempirical molecular orbital method, MNDO in MOPAC.[17] This optimization was carried out by using a supercomputer, CRAY-1, because this molecule included 100 atoms and the calculation needed a huge amount of time. The optimized molecular structure confirmed that the benzene ring and the pyridine ring of the hemicyanine chromophore were on the same plane. The vibrational

(16) Ordal, M. A.; Long, L. L.; Bell, R. J.; Bell, S. E.; Bell, R. R.; Alexander, R. W., Jr.; Ward, C. A. *Appl. Opt.* 1983, 22, 1099.
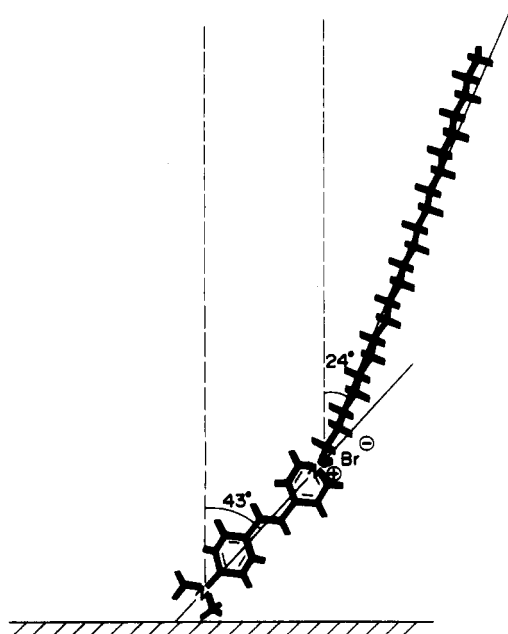(17) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* 1977, 99, 4899.

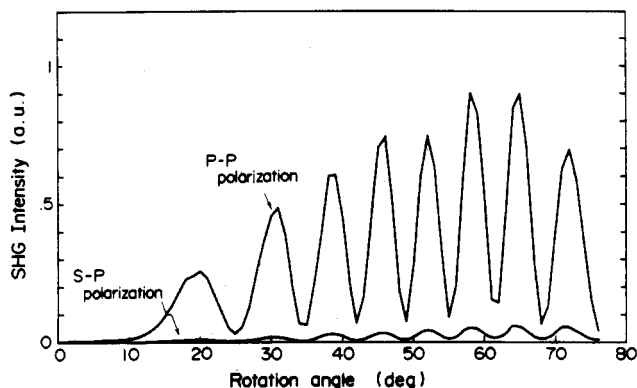**Figure 4.** Molecular configuration of amphiphilic hemicyanine dye.

Figure 5. Typical SHG characteristics of hemicyanine dye monolayer.

analysis for this optimized molecular structure was carried out. The analysis has shown that there were four absorption bands around 1600 cm^{-1} due to the aromatic rings having large transition dipole moments. Two absorptions are due to the pyridine ring; the other two bands come from the benzene ring. It was difficult to assign the measured absorption band of 1589 cm^{-1} to either the benzene ring or pyridine ring vibration or both. However, the angle between each transition dipole moment and the direction vector from the nitrogen atom of the pyridine ring to the nitrogen atom of the amine was less than 10°. Therefore, the transition moment of the measured absorption band of 1589 cm^{-1} should be almost parallel to the molecular axis.

From the estimated tilt angles (Table II), the molecular configuration of the hemicyanine LB film is illustrated in Figure 4.

3.2. SHG Measurement. Figure 5 shows the typical SHG characteristics of the hemicyanine monolayer deposited on both sides of a glass substrate. The appearance of the fringe pattern is attributed to the interference between the second harmonic radiation derived from the monolayer on opposite sides of the glass substrate. For all the SHG measurements, only the p-polarized harmonic radiation was observed for p (P-P) and s (S-P) polarizations of the fundamental wave. The SHG intensity

increased with the incident angle, which was defined as the angle from the surface normal. In addition, the SHG signals were independent of the rotation in the sample plane. These observations indicate that the nonlinear optical polarization has no components in the film plane and is in-plane isotropic. This result is consistent with the fact that the absorption band intensities in the FTIR transmission spectra were isotropic in the sample plane. The LB films, therefore, have only two independent tensor components of nonlinear optical coefficient, that is, d_{33} and $d_{31}(=d_{32} = d_{24} = d_{15})$, assuming the Kleinman symmetry.[18,19] The effective nonlinear optical coefficient is expressed by the product of nonlinear optical coefficient d and projection factor $p(\theta)$ as shown in the following eqs (eqs 4 and 5), for P-P and S-P polarizations, respectively, neglecting the local field factor where θ is the incident

$$d\,p(\theta) = d_{33}\sin^3\theta + 3d_{31}\cos^2\theta\sin\theta\ \text{(P-P polarization)} \tag{4}$$

$$d\,p(\theta) = d_{31}\sin\theta\ \text{(S-P polarization)} \tag{5}$$

angle of the fundamental wave.

Coefficients d_{33} and d_{31} can be calculated from the above equations using quartz glass as a reference. In order to evaluate the chromophore tilt angle, ψ, and the molecular hyperpolarizability, β, a simple distribution model was applied.[9,20] The model carries the following assumptions:
(1) the molecule has one main component of β and the molecular axis is parallel to the direction of the main component of β and (2) the molecular axis is inclined at an average angle ψ to the surface normal with a random distribution of the azimuthal angle. These assumptions are rational for our systems which have only two independent nonlinear optical coefficients and are in-plane isotropic. In this model the nonlinear optical coefficients are expressed as the following equations. where N is the

$$d_{33}(=^1/_2\chi_{zzz}) = {}^1/_2N\beta\cos^3\psi \tag{6}$$

$$d_{31}(=^1/_2\chi_{xxx}) = {}^1/_4N\beta\sin^2\psi\cos\psi \tag{7}$$

number of molecular density, which was calculated from the monolayer thickness (31.3 Å) and monolayer molecular area (33.1 Å²). Using the above equations, the estimated molecular hyperpolarizability, β, was 63×10^{-30} esu and the molecular tilt angle, ψ, was 44°. The estimation of molecular hyperpolarizability, β, included unreliable factors such as the local field factor, which was neglected in this study. Thus, it is rather difficult to compare our calculated value with those obtained in other experiments. However, the tilt angle value is reliable, because its evaluation can be performed independent of the local field factor. The determined tilt angle, 44°, is consistent with the tilt angle of the hemicyanine chromophore, which is estimated to be 43° from FTIR measurements.

4. Conclusion

The molecular orientation in the hemicyanine LB films was studied quantitatively by FTIR spectroscopy. The

(18) Kleinman, D. A. *Phys. Rev.* **1962**, *126*, 1977.

(19) Williams, D. J. In *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic: New York, 1987; Vol. 1, p 405.

(20) Heintz, T. F.; Chen, C. K.; Ricard, D.; Shen, Y. R. *Phys. Rev. Lett.* **1982**, *48*, 478.

tilt angles of the alkyl chain and the chromophore were found to be 24° and 43°, respectively. The SHG measurement is very sensitive and can probe the molecular orientation of one monolayer. The tilt angle of molecular hyperpolarizability, that is, the chromophore axis, was estimated to be 44° using a simple distribution model analysis. The SHG result supports the FTIR evaluation. By using two methods, the molecular orientation in a LB film can be measured with precision and accuracy.

Registry No. Amphiphilic hemicyanine dye, 108050-43-7.