Determination of the Hyperpolarizability Components of Hemicyanine Dyes by Measuring the Anisotropic Fluorescence and Second Harmonic of the Dyes Uniformly Aligned within Zeolite Channels

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A unidirectional ensemble of hemicyanine molecules was prepared by inserting the molecules into the vertical channels of a uniformly oriented zeolite (silicalite-1) film grown on a glass substrate. Fluorescence from this sample excited with light polarized along the vertical channel was 50 times larger than that excited with light polarized orthogonal to the vertical channel direction. These vertically aligned hemicyanine dyes were used to determine the ratio of the molecular hyperpolarizability components β_{zxx}/β_{zzz} of hemicyanine.

1. Introduction

Organic molecules with π-conjugated electrons have been studied for decades due to their strong light absorption and emission in the visible range and the large nonlinear optical susceptibility.[1,2] As a popular example, the hemicyanine dye and its derivatives have a very high molecular hyperpolarizability,[3] and have been used as nonlinear optical probes for the molecular layers and biological samples.[4] They are also frequently used as fluorescent probes for detecting fast change in the electric field of the biological environment such as membrane voltage in neurons.[5,6] For many of these applications the orientation of the hemicyanine molecules in the monolayer or membrane is a critical factor, and polarized fluorescence, fluorescence dipole radiation analysis, and NMR have been used to find out the exact orientation of the dye molecules in the membrane.[4-7] As the analysis is straightforward, second-harmonic generation (SHG) with polarized beams also has been commonly used to determine the orientation of the dye molecules.

In all previous SHG analyses, however, it has been assumed that the molecular hyperpolarizability of hemicyanine dye is dominated by β_{zzz} (z is the coordinate along the long axis of the molecule) as compared to the off-diagonal component, such as β_{zxx}.[8-10] On the other hand, there have been several calculations carried out to find out the hyperpolarizability components in model nonlinear optical molecule of *p*-nitroaniline.[11-13] For example, Lalama and Garito calculated the frequency dependence of the hyperpolarizability components of *p*-nitroaniline, and they found out that β_{zzz} and β_{zxx} of hyperpolarizability components dominated near resonance, with $\beta_{zxx}/\beta_{zzz} \sim -0.3$.[11] This result implies the usual assumption of the single dominant hyperpolarizability component needs to be investigated more carefully because the determination of the molecular orientation is crucial for many applications. For this purpose, it would be ideal to have an ensemble of molecules aligned uniformly in a well-defined system. Such a system

would also be desirable for the utilization of its large optical nonlinearity for practical applications.

To have well-aligned uniform arrangement of molecules, corona-poling and Langmuir−Blodgett technique have been most commonly used for the practical purpose of realizing nonlinear optical devices, chemical sensors, and electrical devices.[14-16] However, molecular alignment in these systems assessed by measuring polarized luminescence or second-harmonic generation (SHG) was less than ideal.[17-20] Thus these systems were not suitable for accurate determination of the hyperpolarizability components.

Recently, as a possible means to achieve an ensemble of uniformly aligned molecules, attempts have been made to incorporate the molecules into zeolite crystals along the channel direction, and linear absorption and lasing action were studied.[21-25] However, even when very large zeolite crystals (3−4 μm in length) were used, the measurement and utilization of their optical properties were not easy. Light-emitting polymer molecules were incorporated into uniformly aligned channels of mesoporous silica to realize an artificial light-harvesting unit.[26,27] In that work with a rather large-sized pore (22 Å), the alignment of the polymer chains as inferred from polarization dependence of fluorescence was less than ideal as the main focus of the work was not the alignment of chromophores, but controlled energy migration. To characterize various optical properties as well as for practical applications such as lasers and nonlinear optical media, it would be highly desirable to have a matrix of macroscopic size where molecules can be embedded in a uniformly aligned way.

In our experiment, silicalite-1 films were chosen as the hosts for organization of hemicyanine dyes in a uniform orientation. Silicalite-1 films are transparent in the ultraviolet and visible regions. As the channel diameter is ∼5.5 Å, hemicyanine molecules can hardly move or rotate once they enter the channels. As silicalite-1 is composed of pure silica, the host is chemically and thermally stable. On glass plates, they grow with the straight channels (*b*-axes) orienting normal to the glass substrates, and hemicyanine molecules enter into the straight channels.[28] Figure 1 shows (a) the chemical structure of the hemicyanine molecule, (b) a SEM image of a silicalite film

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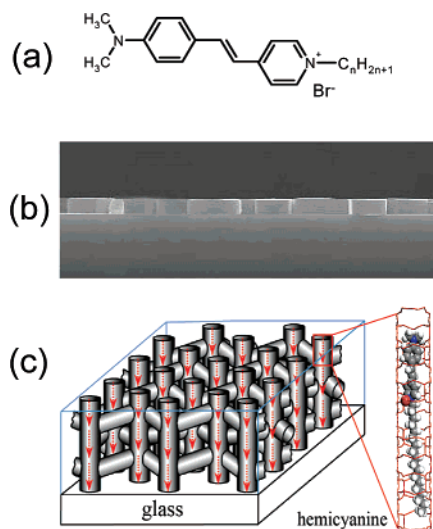*J. Phys. Chem. B, Vol. 110, No. 34, 2006* **16875**

Figure 1. (a) Chemical structure of hemicyanine. (b) Scanning electron microscope (SEM) image of a silicalite-1 film grown on a glass plate. (c) Schematic illustration of the directions of straight and sinusoidal channels of silicalite and the incorporated hemicyanine in the straight channels of silicalite-1 film.

Figure 2. HC-18 in silicate-1 plate seen (a) from an incidence angle of ~70° and (b) from the normal direction.

grown on a glass (SL/G) plate, and (c) the schematic illustration of the directions of straight channels and hemicyanine incorporation in the silicalite layer of a SL/G plate.

Polarized fluorescence measurements of the hemicyanine-incorporating films confirmed that the dye molecules were indeed oriented along the directions of straight channels (*b*-axes). The intensities of the second-harmonic signals were much stronger when the input beams were polarized parallel to the straight channel direction, which allowed us to determine the relative magnitudes of the nonlinear hyperpolarizability components β_{zxx}/β_{zzz}.

2. Experimental Section

Continuous zeolite (silicalite-1) films grown on glass (denoted as SL/G) plates were prepared according to the method described in previous reports.[28] The thicknesses of the obtained films were ~400 nm. The synthesis of hemicyanine dyes (4-[4-(dimethyl-amino)styryl]-1-*n*-alkylpyridinium bromide, hereafter denoted HC-n) was described in previous reports.[28] The hemicyanine dyes were incorporated into the channels of silicalite films by immersing SL/G plates into a vial containing a methanol solution of HC-n (10 mL, 1 mM), and the vial was kept at room temperature for a desired period of time. The immersion period of 4 h was enough to reach the maximum number densities of the dyes in SL/Gs. When the length of the alkyl chain was long, hemicyanine dyes enter the silcailte-1 channels unidirectionally with the alkyl chain side first, due to the hydrophobic nature of the walls of the silicalite channels. After equilibration, the hemicyanine-incorporating SL/G (HC-n/SL/G) plates were removed from the solution, washed with copious amounts of fresh methanol, and dried in the air.

The measurement of the steady-state fluorescence of HC-n/SL/G plates was carried out by using a spectrofluorometer system (Quantamaster, PTI-QM). The wavelength of the excitation light was 400 nm, and the polarization of the excitation light was adjusted with a Glan-Laser polarizer placed in front of the sample. A femtosecond Ti:sapphire laser (Tsunami, Spectra-physics) and time-correlated single photon counting (TCSPC, Becker & Hickl, SPC-730) were used for the measurement of the time-resolved fluorescence and the quantification of the fluorescence by the polarized-beam excitation. The second
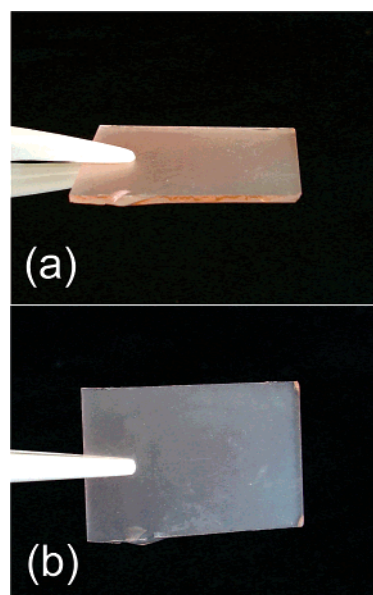
harmonic of 800 nm output was sent through a Glan-Laser polarizer and was incident from the edge of the film, using the confocal microscope (objective lens NA = 0.67) to excite HC-n/SL/G plates. The fluorescence collected with the same lens was sent to the monochromator and detected by a photomultiplier tube. With a fast photomultiplier tube (Becker & Hickl, PMH-100-4) the instrument response function was ~120 ps fwhm. All the spectra were measured at room temperature (22 °C).

The second-harmonic signal from the sample was measured with use of Maker's fringe method with 1064 nm picosecond pulse from the Nd:YAG laser. The input-beam polarization was changed between s- and p-polarization by a half-wave plate, and the p-polarized second-harmonic signal in the transmission direction was filtered and detected by a photomultiplier tube. To reduce the light scattering from SL/G plates, index matching fluid (dimethyl sulfoxide) was applied on the sample and topped with cover glasses on both sides of the plate.

3. Results and Discussion

The preferential alignment of the hemicyanine dyes normal to the surface was also obvious from visual inspection. Figure 2 shows the zeolite (silicalite-1) sample viewed from (a) an incidence angle of ~70° and (b) the normal direction. The appearance of intense color only from oblique incidence indicates at once that the dipole moments of the molecules are mainly aligned along the surface normal. As it is known that the silicalite-1 film grows with its vertical (and straight) channel normal to the surface,[28] it can be inferred that the hemicyanine molecules are adsorbed only into the vertical channel of the silicate film, as shown schematically in Figure 1c. The pores parallel to the surface are not straight, and presumably the size of the hemicyanine molecule is too big to fit into that channel.

The steady-state absorption and the fluorescence spectra of hemicyanine dyes in methanol and in SL/G plates are shown in Figure 3a. The absorption maximum of HC-n/SL/G plates appeared at 494 nm and the fluorescence peak appeared at 584 nm. As expected, varying the chain length HC-n at the pyridinium moiety did not change the steady-state absorption and emission spectra. The absorption maximum slightly red-shifted and the fluorescence peak blue-shifted from those of
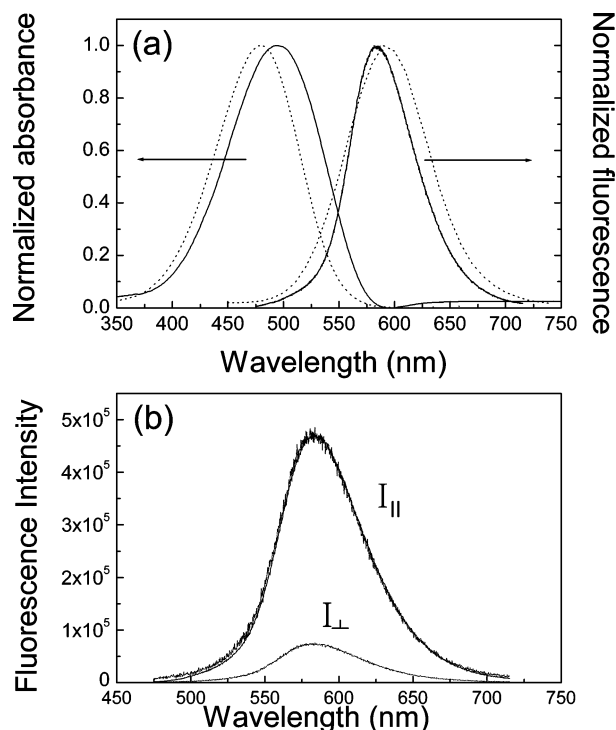
Figure 3. (a) Steady-state absorption and fluorescence spectra of hemicyanine in methanol (dotted lines) and in SL/G (solid lines). (b) Fluorescence spectra of the HC-18/SL/G measured with a fluorometer with a p-polarized excitation beam ($I_{\parallel}$), and an s-polarized excitation beam ($I_{\perp}$). $I_{\perp}$ is shown to overlap with $I_{\parallel}$ after multiplication by 6.4.

the hemicyanine in methanol, reflecting the differences in the polarity and the solvation properties of the host media. Since the aggregation of dye molecules or formation of molecular crystal change the spectral shape of a dye with respect to that in solution,[29−31] the similarities of the absorption and fluorescence spectra of hemicyanine in SL/G and methanol (except shifts) indicate that the dyes exist individually in the silicalite channels. Figure 3b was measured by adding the polarizer in front of the excitation beam path of the standard fluorometer, i.e., the polarized beam was used to excite HC-n/SL/G plates with 45° incidence angle, and the fluorescence was collected from the 45° direction. It is shown that the fluorescence is 6.4 times stronger for p-polarized beam excitation as compared to s-polarized beam excitation, indicating the molecules are aligned preferentially along the vertical channel. Except for the intensity, the spectral shapes of fluorescence were the same in both cases.

The above setup of oblique incidence in the fluorometer, however, is not considered suitable to obtain quantitative information about the molecular orientation, as the following factors contribute to reduce the fluorescence contrast: (1) the difference in the Fresnel factors of the pump beams of s- and p-polarization, (2) the difference in the radiation patterns and Fresnel factors of fluorescence as collected by the lens, (3) depolarization due to scattering of the pump beam and the fluorescence from the uneven silicalite films in SL/Gs, and (4) possible existence of physisorbed hemicyanine dyes on the surfaces of SL/G plates. Among these, (1) and (2) would have little effect as the transmittance deduced from Fresnel factors for incoming and outgoing beams differ by only ∼8% between s- and p-polarization. To quantify the amount of physisorbed dyes on the surface, the HC/SL/G plate was put into methanol solvent up to 1 day. The sample did not show any change in absorbance after this treatment, nor did the methanol solvent show any measurable absorption from the dye. So it was
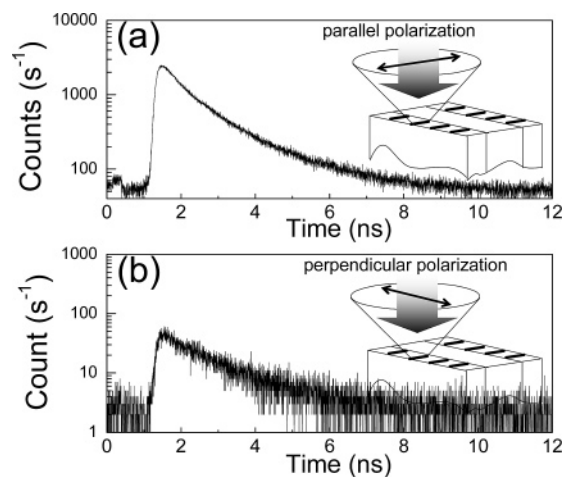

Figure 4. Fluorescence decay vs time: (a) pump beam polarized parallel to the vertical channel and (b) pump beam polarized perpendicular to the vertical channel direction. The insets show the experimental geometry for the corresponding data.

concluded that the physisorbed dye molecules on the surface as proposed in (4) would be very small, while the dyes incorporated in the channel are very robust and would not come out easily.

To quantitatively find out the orientational distribution of the dye molecules, the HC-n/SL/G plate was excited from the edge with the confocal microscope and the polarized beams, as in the insets of Figure 4a,b. Panels a and b of Figure 4 show the time-dependent fluorescence around the peak wavelength at 584 nm with the excitation beam polarized parallel and perpendicular to the vertical pore, respectively. The fluorescence intensity was 50 times stronger for the pump beam polarized parallel to the vertical pore direction. The difference between the fluorescence strengths in this case became much bigger than that in Figure 3b. However, as we move the focus down into the film by ∼100 μm, $I_{\parallel}$ decreased by $^1/_2$ and $I_{\perp}$ increased by ∼1.7 of the previous values such that the fluorescence intensity ratio became $I_{\parallel}/I_{\perp} \sim$ 15. As the fluorescence decay lifetimes did not change as we move the focus, it was believed the light scattering inside the silicate film caused the reduction in contrast as above. So the main cause of the difference between the polarization ratio as measured by fluorometer in oblique incidence (Figure 3b) and by the confocal setup (Figure 4) is considered to be from the light scattering, as suggested in (3) of the previous paragraph. As the excitation of the small confocal volume from the edge would work to reduce this scattering, it is believed that the fluorescence ratio in the confocal setup is well-suited for the quantitative analysis of the orientation of dye molecules.

The fluorescence intensity began to drop after 4−5 s of exposure even with ∼18 μW of average pump power (2.3 kW/cm²), presumably due to photodegradation of the dye molecules in the focal volume. However, TCSPC could measure the fluorescence decay profile shown in Figure 4 in a very short time, and the average fluorescence decay lifetime deduced from the fitting of the data in Figure 4 was 0.77 ns for the parallel excitation and 0.79 ns for the perpendicular excitation. So, the fluorescence decay characteristics are very similar between the two cases within experimental uncertainties. Although the fluorescence spectrum could not be measured reliably with the confocal setup due to photodegradation of the sample, it is inferred from Figure 3b that the spectral shape is also similar between the excitations with different polarizations. Thus the molecules excited by pump beams perpendicular to the vertical channel direction had very similar photophysical characteristics
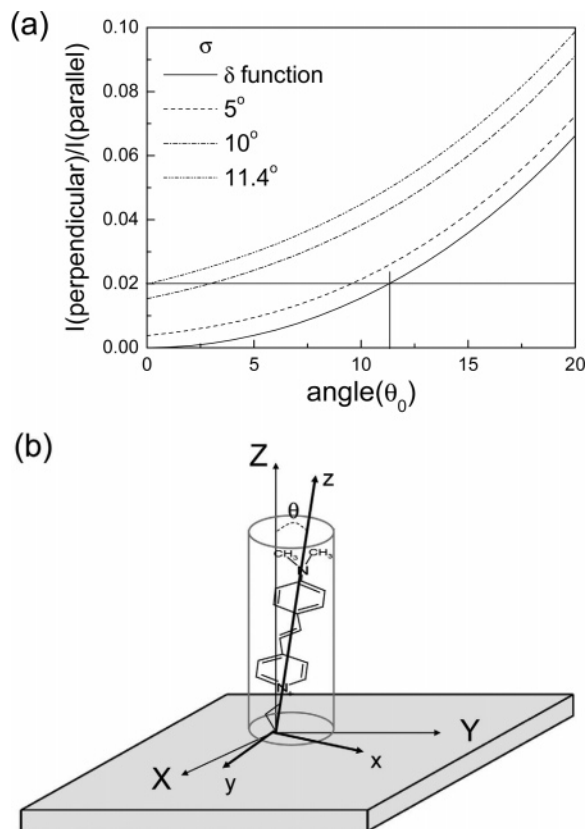
Figure 5. (a) Calculated values of the relative fluorescence intensities with use of the orientational distribution in eq 1. The horizontal line in the graph is the experimental value. (b) Coordinate system used for hemicyanine in silicalite-1. θ is the angle between the molecular long axis (z) and the surface normal (Z-axis).

as those excited in the parallel direction, and the relative fluorescence intensities would reflect only the angular distribution of the dye molecules. To have a quantitative idea about the angular distribution, we assumed the following distribution function of embedded dye molecules:

$$f(\theta) \approx \exp[-(\theta - \theta_0)^2/\sigma^2] \qquad (1)$$

where θ is the angle between the surface normal and the dipole moment of the molecule, and θ_0 and σ are the peak angle and the width of the polar distribution of the molecules, respectively. With the distribution above, the calculation of fluorescence ratio for parallel and perpendicular excitation is straightforward. We set the coordinates such that the X- and Y-axes lie on the sample surface and the Z-axis is along the surface normal, as shown in Figure 5b. Then the molecule shown in Figure 5b has dipole vector components as ($\cos\phi \sin\theta$, $\sin\phi \sin\theta$, $\cos\theta$). When electric fields of polarizations of $E_{parallel} = (0, 0, E)$ and $E_{perp} = (0, E,$

0) are applied to the edge of the HC-n/SL/G plate (insets in Figure 4a,b), the fluorescence intensity is given by

$$I_{\parallel}(\theta) \propto \int \cos^2\theta \, f(\theta) \, \sin\theta \, d\theta \, d\phi$$

$$I_{\perp}(\theta) \propto \int \sin^2\theta \, \sin^2\phi \, f(\theta) \, \sin\theta \, d\theta \, d\phi \qquad (2)$$

where $f(\theta)$ is the distribution function in eq 1. The calculated values of the relative fluorescence intensities for various values of θ_0 and σ in the above equation are plotted in Figure 5. The experimental value of $I_{\perp}/I_{\parallel} \approx 0.020$ would mean the angular spread of the dye molecules could be about $\sigma \approx 11.4°$ with maximum along the surface normal (i.e. $\theta_0 = 0$), or alternatively, δ-function-like distribution with $\theta_0 \approx 11.3°$ of tilt. Any distribution between these two heuristic distributions (Gaussian with $\sigma \approx 11.4°$ about surface normal, and δ-function with $\theta_0 \approx 11.3°$) is compatible with the experimental result, as the ratio value alone is not enough to further determine the shape of the orientational distribution. All of these are narrow distributions about the surface normal and this outcome were naturally expected as the size of the vertical channel (diameter 5.5 Å) compared with the lateral size of the hemicyanine molecule would not allow too much tilt of the molecules from the pore direction. Previous SHG experiment found the alignment of the dyes is not only uniform, but also quite unidirectional when the alkyl chain at one end of the molecule becomes long enough.[28]

With the very unidirectional angular distribution as well as the molecules in isolation with minimal interaction with the host matrix,[26,27] our sample is a very good system for studying various optical properties. We utilized it to determine the hyperpolarizability components of the embedded hemicyanine molecules. The second-harmonic signal measured from this sample with Maker's fringe method is shown in Figure 6a,b for S_{in}-P_{out} and P_{in}-P_{out} polarization combinations, respectively. As the silicalite-1 film is grown on both sides of the glass plate in a SL/G plate and hence the dye molecules are also incorporated on both silicalite films, the SHG signals from the front side and the back side interfere with each other as in Figure 6.[32,33] Maker's fringe signal from HC-18 in zeolite with p-polarized input beam was 2.1×10^3 times as large as that from s-polarized input beam. It should be remembered that in the popular case of a Langmuir–Blodgett film of nonlinear optical molecules $I(2\omega)_{p-p}/I(2\omega)_{s-p} \approx 10$ at best, and $I(2\omega)_{p-p}/I(2\omega)_{s-p} \approx 3$ for poled polymer films.[34-36] Thus it is again obvious that the dye molecules are very well aligned along the surface normal. In fact, this SHG result with the orientational distribution obtained from the polarized fluorescence measurement could be used to determine the ratio of diagonal to off-diagonal hyperpolarizability component, using $\chi^{(2)}_{ZXX}/\chi^{(2)}_{ZZZ} = 0.0097$ deduced from Maker's fringe analysis.[37]

The hemicyanine molecules have seven nonvanishing hyperpolarizability components of β_{zzz}, β_{zxx}, β_{zyy}, β_{xzx}, β_{yzy}, β_{xxz}, and
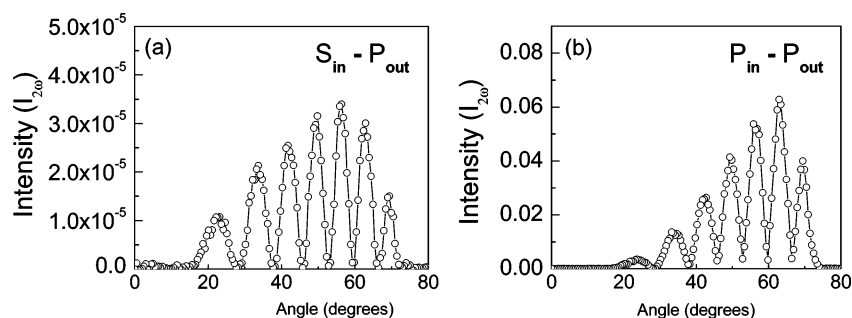
Figure 6. Maker's fringe data: (a) S_{in}-P_{out} and (b) P_{in}-P_{out} polarization combinations.

β_{yyz}, with $\beta_{xxz} = \beta_{xzx}$ and $\beta_{yyz} = \beta_{yzy}$ for second-harmonic generation.[38] We can use the analogy of the calculated hyperpolarizability components of *p*-nitroaniline to simplify our analysis.[11] As the π-electrons in hemicyanine core can move much more easily in the aromatic ring plane ($x-z$ plane) than normal to the plane (y-direction in Figure 5b), we can assume $\beta_{zxx} \gg \beta_{zyy}$ and $\beta_{xxz} \gg \beta_{yyz}$, as found from the calculations for *p*-nitroaniline. In the case of *p*-nitroanline, $\beta_{zxx} \approx 1.7\beta_{xxz}$ away from the second-harmonic resonance and $\beta_{zxx} \approx 15\beta_{xxz}$ as the second-harmonic approaches the resonance of the molecule.[11] So we also assumed $\beta_{zxx} \gg \beta_{xxz}$ as the second harmonic is in the absorption band of the hemicyanine molecule in our experiment. As a result, the distinct nonzero components reduce to just β_{zzz} and β_{zxx}, and $\chi^{(2)}_{ZXX}$ and $\chi^{(2)}_{ZZZ}$ can be expressed as follows.

$$\chi^{(2)}_{ZXX} =$$

$$f_z(\omega_3)f_x(\omega_1)f_x(\omega_2)\left[\frac{1}{4}\beta_{zxx}(\langle\cos^3\theta\rangle + \langle\cos\theta\rangle) + \frac{1}{2}\beta_{zzz}\langle\cos\theta\sin^2\theta\rangle\right]$$

$$\chi^{(2)}_{ZZZ} = f_z(\omega_3)f_z(\omega_1)f_z(\omega_2)\left[\frac{1}{2}\beta_{zxx}\langle\cos\theta\sin^2\theta\rangle + \beta_{zzz}\langle\cos^3\theta\rangle\right] \quad (3)$$

Our result of $I(2\omega)_{p-p}/I(2\omega)_{s-p} \approx 2.1 \times 10^3$ together with the δ-function distribution (chosen among possible orientational distributions for the sake of simplicity) of $\theta_0 \approx 11.3°$ from the polarized-fluorescence measurement yields $\beta_{zxx}/\beta_{zzz} \approx -0.020$. Thus the hyperpolarizability of the hemicyanine is found to be dominated by its long-axis diagonal component β_{zzz}. This ratio value is much smaller than the ratio of the calculated values for *p*-nitroaniline, where $\beta_{zxx}/\beta_{zzz} \approx -0.15$ away from the resonance and $\beta_{zxx}/\beta_{zzz} \approx -0.3$ at the second-harmonic resonance.[11] The above difference between hemicyanine and *p*-nitroaniline is quite reasonable as our hemicyanine molecule is much more elongated along the z-axis than *p*-nitroaniline. Finally, the negative value of β_{zxx}/β_{zzz} implies the π-electron motion (main contribution to nonlinear polarization) with input fields in z- and x-direction is anticorrelated for both hemicyanine and *p*-nitroaniline molecules.

4. Conclusions

Hemicyanine dye molecules were inserted into the vertically aligned subnano ($\sim$0.55 nm) channels of silicalite-1 films grown on glass plates. By comparing the fluorescence intensities by using pump beams of different polarizations, we found that the molecules are uniformly oriented along the surface normal with the narrow distribution width of $\sim$11°. This orientational distribution together with the second harmonic measured by Marker's fringe method was used to determine the ratio of the molecular hyperpolarizability components β_{zxx}/β_{zzz}.

References and Notes

(1) For example, see: Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991.

(2) Sutherland, R. L. *Handbook of Nonlinear Optics*; Marcel Dekker: New York, 1996.

(3) Schildkraut, J. S.; Penner, T. L.; Willand, C. S.; Ulman, A. *Opt. lett.* **1988**, *13*, 134.

(4) Huang, J. Y.; Lewis, A.; Loew, L. *Biophys. J.* **1988**, 53, 665.

(5) Rohr, S.; Salzberg, B. M. *Biophys. J.* **1994**, *67*, 1301.

(6) Dombeck, D. A.; Blanchard-Desce, M.; Webb, W. W. *J. Neurosci.* **2004**, *24*, 999.

(7) Lambacher, A.; Promherz, P. *J. Phys. Chem. B* **2001**, *105*, 343.

(8) Marowsky, G.; Lüpke, G.; Steinhoff, R.; Chi, L. F.; Möbius, D. *Phys. Rev. B* **1990**, *41*, 4480.

(9) Duan, X. M.; Konami, H.; Okada, S.; Matusda, H.; Nakanishi, H. *J. Phys. Chem.* **1996**, *100*, 17780.

(10) Lu, X.; Han, K.; Ma, S.; Zhang, Z. *J. Phys. D*: *Appl. Phys.* **1996**, *29*, 1576.

(11) Lalama, S. J.; Garito, A. F. *Phys. Rev. A* **1979**, *20*, 1179.

(12) Sim, F.; Chin, S.; Dupuis, M.; Rice, J. *J. Phys. Chem.* **1993**, *97*, 1158.

(13) Bella, S. D.; Lanza, G.; Fragala, I.; Yizehaik, S.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1997**, *119*, 3003.

(14) Kajzar, F.; Swalen, J. D. *Organic Thin Films for Waveguiding Nonlinear Optics*; Overseas Publishers Association: Amsterdam, The Netherlands, 1996.

(15) Ulman, A. *An Introduction to Ultrathin Organic Films*; *From Langmuir-Blodgett to Self-Assembly*; Academic Press: New York, 1991.

(16) Winkelhahn, H. J.; Winter, H. H.; Neher, D. *Appl. Phys. Lett.* **1994**, *64*, 1347.

(17) LeGrange, J. D.; Riegler, H. E.; Zurawsky, W. P.; Scarlata, S. F. *J. Chem. Phys.* **1989**, *90*, 3838.

(18) Pachence, J. M.; Amador, S.; Maniara, G.; Vanderkooi, J.; Dutton, P. L.; Blasie, J. K. *Biophys. J.* **1990**, *58*, 379.

(19) Guyot-Sionnest, P.; Shen, Y. R.; Heinz, T. F. *Appl. Phys. B* **1987**, *42*, 237.

(20) Higgins, D. A.; Byerly, S. K.; Abrams, M. B.; Corn, R. M. *J. Phys. Chem.* **1991**, *95*, 6984.

(21) Li, I. L.; Tang, Z. K.; Xiao, X. D.; Yang, C. L.; Ge, W. K. *Appl. Phys. Lett.* **2003**, *83*, 2438.

(22) Forrest, S. R. *Nature* **1999**, *397*, 294.

(23) Vietze, U.; Krauss, O.; Laeri, F.; Ihlein, G.; Schüth, F.; Limburg B.; Abraham, M. *Phys. Rev. Lett.* **1998**, *81*, 4628.

(24) Marlow, F.; Caro, J.; Werner, L.; Kornatowski, J.; Dahne, S. *J. Phys. Chem.* **1993**, *97*, 11286.

(25) Werner, L.; Caro, J.; Finger, G.; Kornatowski, J. *Zeolites* **1992**, *12*, 658.

(26) Wu, J.; Gross, A. F.; Tolbert, S. *J. Phys. Chem. B* **1999**, *103*, 2374.

(27) Nguyen, T. Q.; Wu, J.; Doan, V.; Schwartz, B.; Tolbert, S. *Science* **2000**, *288*, 652.

(28) Kim, H. S.; Lee, S.; Ha, K.; Jung, C.; Lee, Y.; Chun, Y.; Kim, D.; Rhee, B. K.; Yoon, K. B. *J. Am. Chem. Soc.* **2004**, *126*, 673.

(29) Huang, Y.; Cheng, T.; Li, F.; Luo, C.; Huang, C. H.; Cai, Z.; Zeng, X.; Zhou, J. *J. Phys. Chem. B* **2002**, *106*, 10031.

(30) Evans, C. E.; Song, Q.; Bohn, P. W. *J. Phys. Chem.* **1993**, *97*, 12302.

(31) Evans, C. E.; Bohn, P. W. *J. Am. Chem. Soc.* **1993**, *115*, 3306.

(32) Wiljekoon, W. M. K. P.; Wijava, S. K.; Bhawalkar, J. D.; Prasad, P. N.; Penner, T. L.; Amstrong, N. J.; Ezenyilmba, M. C.; Williams, D. J. *J. Am. Chem. Soc.* **1996**, *118*, 4480.

(33) Qiu, M.; Vilaseca, R.; Botey, M.; Sellares, J. *Appl. Phys. Lett.* **2000**, *76*, 3346.

(34) Marowsky, G.; Pinnow, M.; Sieverdes, F.; Heinemann, E. *Mol. Eng.* **1991**, *1*, 179.

(35) Tao, X. T.; Watanabe, T.; Zou, D. C.; Shimoda, S.; Sato, H.; Miyata, S. *Macromolecules* **1995**, *28*, 2637.

(36) Lee, S. H.; Kim, Y. K.; Won, Y. H. *Macromolecules* **1999**, *32*, 342.

(37) Herman, W. N.; Hayden, L. M. *J. Opt. Soc. Am. B* **1995**, *12*, 416.

(38) Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley: New York, 1984.