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Mechanism for Giant Electro-Optic Response of Porphyrin J-Aggregates in Polymer Film and Aqueous Solution

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We report the dependence of the polarizability difference $\Delta\alpha$ on the orientational distribution of porphyrin J-aggregates. For quasi-one-dimensionally oriented aggregates in a polymer film, the red shift in $\boldsymbol{Y} \perp \boldsymbol{F}$ configuration was about 2 to 3 times smaller than that in $\boldsymbol{Y} \parallel \boldsymbol{F}$ configuration, where $\boldsymbol{Y}$ is the orientational direction of the J-aggregates and $\boldsymbol{F}$ is the applied AC electric field vector. For an aqueous solution where J-aggregates were three-dimensionally oriented, the exciton band showed an electric-field-induced broadening. In addition, a red-shifted signal for two-dimensionally oriented aggregates in the polymer film was reduced by one order of magnitude at 77 K compared with that at room temperature. These results were explained reasonably well by the molecular rearrangement model, which was applied to a variety of orientational distributions.

Keywords: porphyrin, J-aggregate, static polarizability, Frenkel exciton, electroabsorption, electrooptic effect, Kerr effect, polymer film, aqueous solution, orientational distribution

1. Introduction

In recent years, self-assembled molecular J-aggregates attract much interest as potential materials for optical information technology, because of their large optical nonlinearity. Since the J-aggregates of tetraphenyl porphyrin tetrasulfonic acid (TPPS) especially have sharp absorbance and a large transition dipole moment owing to Frenkel excitons, it is a prominent candidate for nanosize materials.[1–12]

Previously,[1] we found by electroabsorption measurement that the difference in the static polarizability $\Delta\alpha$ in two-dimensionally oriented TPPS J-aggregates between the excited and the ground states is nearly 100 times larger than that in a monomer TPPS. Moreover, we proposed the 'molecular rearrangement model' to explain the giant electro-optic effect.[2] For example, the large $\Delta\alpha$ and the electric-field dependence were explained in terms of the change in angles between monomer molecular planes and the intermolecular bonding axis of J-aggregates when the electric field was applied.[2] However, the model has not yet been examined in the case where J-aggregates have a one- or three-dimensional distribution of orientation.

In the present work, we confirm the validity of the "molecular rearrangement model" in various cases of orientational distribution. First, we measure the electroabsorption spectra of TPPS J-aggregates with quasi-one-dimensional orientation in a polymer film prepared by vertical spin coating,[3] to find the difference in signal strength between the J-aggregate axes parallel and perpendicular to the applied electric field. Second, electroabsorption spectra of J-aggregates with isotropic distribution in an aqueous solution are investigated. Third, the temperature dependence of the electroabsorption signal for two-dimensionally oriented J-aggregates in a polymer film is studied. All the results are shown to be consistent with the model.

2. Experimental and Analysis Methods

For film samples, TPPS J-aggregates dispersed with quasi-one-dimensional orientation in poly(vinyl alcohol) (PVA) thin films on glass substrates were prepared by a vertical spin coating method.[3] Throughout this paper, the orientation axis generated by vertical spin coating in the film plane is denoted by the Y-axis. Prior to the preparation of sample films, an array of 8 and 14 interdigitated aluminum electrodes whose gaps were 0.5 and 0.4 mm, respectively, was deposited on a slide glass by vacuum evaporation. An AC electric field of $F_{\text{ext}} = F_0 \sin 2\pi ft$ with $F_0 = (3.00-3.13) \times 10^6$ V/m and $f = 221$ Hz was applied between the electrodes using a function generator (NF 1956 multifunction synthesizer) in combination with a high-voltage amplifier (Matsusada HEOPT-5B20). For the study of temperature dependence, PVA film samples where J-aggregates were two-dimensionally dispersed by normal spin coating were used. Samples were set in a vacuum room on a copper plate cooled by thermal conduction from a liquid nitrogen reservoir in a home-made metal cryostat. To avoid vacuum discharge at the electrode gap, an electric field of about one-sixth as low as that in air was applied.

For solution samples, TPPS J-aggregates dispersed three-dimensionally in aqueous solution were prepared by dissolving specific amounts of TPPS (3.1 mg) and KCl (47.6 mg, 0.13 mol) in water of 5 ml. For aqueous solution, a pair of indium tin oxide (ITO) glasses whose gap was 0.1 mm was used as electrodes, and an electric field with $F_0 = 1.5 \times 10^4$ V/m at $f = 235$ Hz and $f = 21$ Hz was applied.

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In both experiments, field-induced absorption spectral changes were detected by a polychromater with a multi-channel lock-in amplifier.[13)] The white light from a xenon-lamp (Hamamatsu L2273) was collimated after being focused through a 0.4 mm pinhole and then loosely focused to be as large as 10 mm in diameter on the sample.

The absorbance changes detected at the modulation frequency f and its second harmonic $2f$ are due to the Pockels and Kerr effects, respectively. Here, we focused on the Kerr response, for which $\Delta\alpha$ was deduced from the red shift of the B band (Soret band) for J-aggregates. The method of data analysis was as described in refs. 1, 14, and 15. An absorption change can be written as

$$\begin{aligned}\Delta A = A_0 \frac{dA}{dE}\Delta\mu \cdot s \cdot F + \frac{1}{2} B_0 \frac{dA}{dE}\Delta\alpha \cdot (s \cdot F)^2 \\ + \frac{1}{2} C_0 \frac{d^2A}{dE^2}|\Delta\mu|^2 \cdot (s \cdot F)^2,\end{aligned} \tag{1}$$

where F is the applied electric field, A_0, B_0, and C_0 are constants depending on the degree of molecular orientation, and s is a local field factor. Equation (1) indicates that a difference in static polarizability ($\Delta\alpha$) and a difference in static dipole moment ($\Delta\mu$) between the excited and ground states can be evaluated by comparing the changes in absorbance with the first and second derivatives of the absorption spectrum, respectively. Since there is some uncertainties in the values for such constants as B_0 and s, the electro-optical parameters in the present study containing them are as follows:

$$s^2\,\mathrm{Tr}(\Delta\alpha)B_0 = C_1 \cdot \frac{hc}{{F_0}^2} \cdot \frac{10^{40}}{1.113} \tag{2}$$

$$s|\Delta\mu|C_0 = C_2^{\frac{1}{2}} \cdot \frac{hc}{F_0} \cdot \frac{10^{30}}{3.34}. \tag{3}$$

Here, h is the Planck constant, c is the speed of light, C_1 and C_2 are the fitting constants from the first and second derivatives of absorbance, respectively.

3. Results

Figure 1 shows the absorption spectra of a quasi-one-dimensionally oriented film prepared by vertical spin coating, measured for polarizations parallel (solid line) and perpendicular (dashed line) to the J-aggregate orientation axis (Y-axis). The film had a linear dichroism with 2 : 1 ratio for the J band peak at approximately 490 nm.

The absorption and electroabsorption spectra of quasi-one-dimensionally oriented films are shown in Fig. 2. The fitting curves (dashed line) are the first derivative of the absorption spectra.

Table 1 shows a list of $\Delta\alpha$ for quasi-one-dimensionally oriented films averaged for 8 data and for monomers. The table indicates that $\Delta\alpha$ for the Y-axis parallel to $\boldsymbol{F}$ is two or three times larger than that for the Y-axis perpendicular to $\boldsymbol{F}$.

Figure 3 shows the stationary absorption spectra and electroabsorption spectra of TPPS J-aggregates in aqueous solution, measured with the unpolarized probe light. In contrast to the results of J-aggregates in polymer films, a broadening signal was observed in aqueous solution. The fitting curve (dashed line) is the second derivative of the absorption spectra. The frequency dependence of signal magnitude is considered to be mainly due to the frequency-dependent impedance of the ITO electrode cell containing the solution.

Figure 4 shows the electroabsorption spectra of a two-dimensionally oriented film measured at 293 and 77 K. By decreasing temperature, the magnitude of the red-shifted signal was reduced to less than 1/10 of that at room temperature.

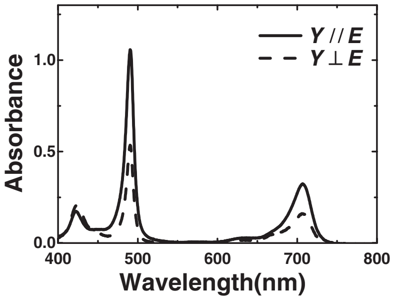

Fig. 1. Absorption spectra of quasi-one-dimensionally oriented films prepared by a vertical spin coating method at room temperature, measured for polarizations $\boldsymbol{E}$ parallel (solid line) and perpendicular (dashed line) to the orientation axis $\boldsymbol{Y}$ (Y-axis in Fig. 5). The film had linear dichroism with about 2 : 1 ratio for the J band peak at about 490 nm.

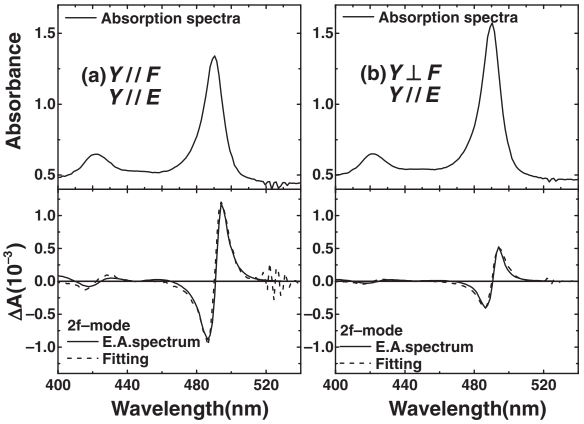

Fig. 2. Absorption and electroabsorption spectra of quasi-one-dimensionally oriented film at 293 K, (a) $\boldsymbol{Y} \parallel \boldsymbol{F}$ and (b) $\boldsymbol{Y} \perp \boldsymbol{F}$ with the applied electric field $F = 3 \times 10^6$ V/m. Fitting curves (dashed line) are the first derivatives of the absorption spectra. Both (a) and (b) show red shifts, but there is a significant reduction in the amount of red shift for $\boldsymbol{Y} \perp \boldsymbol{F}$.

Table 1. Difference in the static polarizability $\Delta\alpha$ of TPPS between the excited and ground states for the quasi-one-dimensionally oriented film.

	$\Delta\alpha$ (Å^3)
$\boldsymbol{Y} \parallel \boldsymbol{F}$	5000–10000
$\boldsymbol{Y} \perp \boldsymbol{F}$	3000–4000

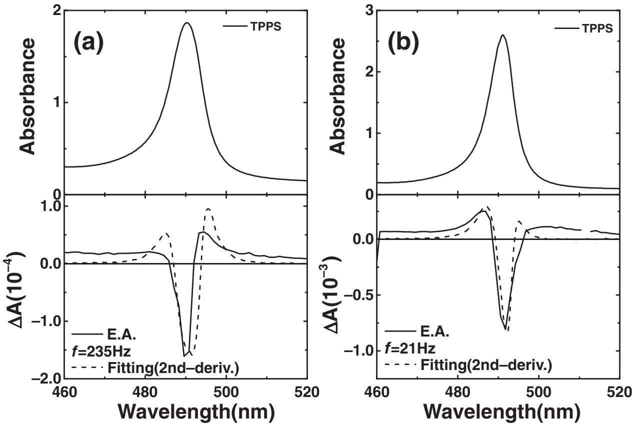

Fig. 3. Absorption and electroabsorption spectra of TPPS J-aggregates in aqueous solution with $F = 1.5 \times 10^4\,\mathrm{V/m}$ at 293 K with $f = 235\,\mathrm{Hz}$ (a) and $f = 21\,\mathrm{Hz}$ (b). The fitting curve (dashed line) is the second derivative of the absorption spectra. Note that F is about 1/200 of that applied to the film sample shown in Fig. 2.

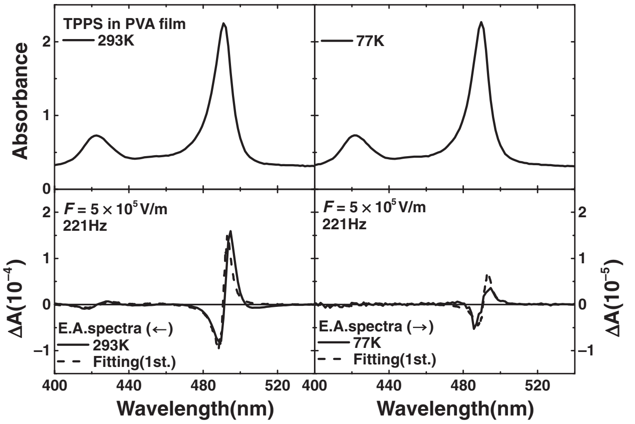

Fig. 4. Temperature dependence (at 293 and 77 K) of the electro-optic signal for two-dimensionally oriented film with $F = 5 \times 10^5\,\mathrm{V/m}$, which is 1/6 of F in Fig. 2.

4. Discussion

For J-aggregates, the excitation energy of Frenkel excitons depends on the aggregation number and molecular arrangement of the constituent monomers as

$$\begin{aligned} E_k &= E_0 + 2J\cos\left(\frac{k\pi}{N+1}\right) \\ &= E_0 + 2\,\frac{M^2}{4\pi\varepsilon_\mathrm{B} r^3}(1 - 3\cos^2\theta)\cdot\cos\left(\frac{k\pi}{N+1}\right), \end{aligned} \tag{4}$$

where E_0 is the excitation energy of monomer molecules, M is the transition dipole moment between the relevant electronic states in the molecule, r is the intermolecular distance, ε_B is the background permittivity, θ is the angle between the molecular transition dipole moment and the intermolecular bonding axis connecting the centers of the transition dipoles, i.e., J-axis, and N is the aggregation number, i.e., the number of molecules forming a coherent aggregate.[2,15)]

The molecular rearrangement model, which was introduced in ref. 2, can explain the energy shift of TPPS J-aggregates by the change in J, i.e., the interaction energy between monomer transition dipoles induced by the applied field. In this model, the observed energy shift in refs. 1 and 2 is caused by the change in θ as small as $\Delta\theta = 0.002$ deg. In the model, the direction of the J-axis and that of the $\boldsymbol{F}$ vector affect the change in excitation energy of J-aggregates.

4.1 J-aggregates for quasi 1D orientation

Firstly, we show that the anisotropic electooptic signals in Fig. 2 is not in contradiction with the model. As shown in Fig. 6 in ref. 2, the red shift of the excitation energy is expected for the Y-axis parallel to $\boldsymbol{F}$ because the angle between the monomer transition dipoles and the J-axis decreases, while the signal with the blue shift is predicted for the Y-axis perpendicular to $\boldsymbol{F}$ since the angle increases. Thus, the model can be applied to the large red shift observed for the Y-axis parallel to $\boldsymbol{F}$ in Fig. 2(a). In the present experiment, however, the red shift was also observed for the Y-axis perpendicular to $\boldsymbol{F}$, as shown in Fig. 2(b). This shift is probably produced by an incomplete one-dimensional orientation, i.e., the red shift occurs because there are some TPPS J-aggregates whose J-axis has components parallel to $\boldsymbol{F}$. Indeed, an incomplete one-dimensional orientation order is indicated by the ratio for dichroism, which is as small as 2 : 1, as shown in Fig. 1. Then, a significant reduction in the red shift of $\Delta\alpha$ for $\boldsymbol{Y}$ perpendicular to $\boldsymbol{F}$ shown in Fig. 2(b) compared with the red shift shown in Fig. 2(a) is not in contradiction with the model. For two-dimensionally oriented films prepared by conventional spin coating, the amount of such aggregates showing the red shift is twice as large as that showing the blue shift as shown in Fig. 6 of ref. 2, leading to the red-shifted spectra as a whole.[1,2)] Similarly, we can explain the overall red shift for $\boldsymbol{Y}$ perpendicular to $\boldsymbol{F}$, considering orientation distribution as follows.

Figure 5 shows a model of a quasi-one-dimensionally oriented polymer film in the experiment. The arrow $\boldsymbol{J}$ represents the orientation distribution of J-aggregates in the film. Its angle θ from the Y-axis is defined by

$$\theta = \int_0^{\pi/2} \theta' f(\theta')\,d\theta', \tag{5}$$

where $f(\theta)$ is the orientational distribution function of J-aggregates in the vertically spin-coated film. The ratio of the amount of J-aggregates oriented in the X-axis to that in the Y-axis in the film plane is assumed to be x/y $(y > x)$. The Y-axis is the direction of the J-axis in the case of a complete one-dimensional orientation. If $\boldsymbol{F} \parallel Y$ and $\boldsymbol{E} \parallel Y$ (condition A in Fig. 5), where $\boldsymbol{E}$ is the electric field of the linearly polarized light, the component of the applied electric field $\boldsymbol{F}$ parallel to the $\boldsymbol{J}$-axis (F_J) and that perpendicular to it (F_H) are $F_J = (y/r)F$ (red shift) and $F_\mathrm{H} = (x/r)F$ (blue shift), respectively, where $r = \sqrt{x^2 + y^2}$. On the other hand, if $\boldsymbol{F} \perp Y$ and $\boldsymbol{E} \parallel Y$ (condition B in Fig. 5), they are $F_J = (x/r)F$ and $F_\mathrm{H} = (y/r)F$, respectively. The Kerr signals, i.e., the red and blue shifts induced by $\boldsymbol{F}^2$,

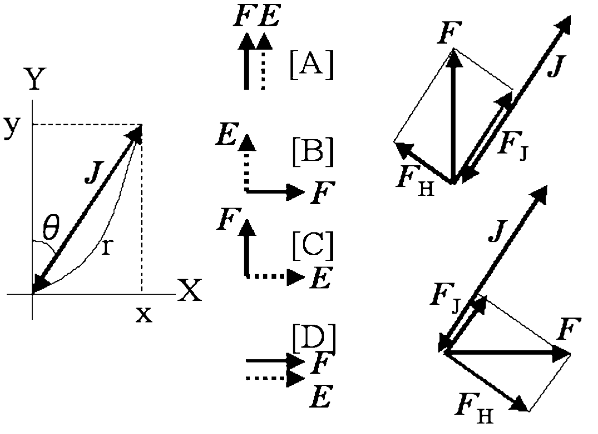

Fig. 5. Model of transition dipole moment for a J-aggregate in a quasi-one dimensionally oriented film. The arrow ***J*** indicates averaged orientational direction of J-aggregates. The *Y*-axis is the direction of J-axis in the case of complete one-dimensional orientation. In the experiment, we measured electroabsorption spectra with four configurations A, B, C, and D between the electric field ***F*** (solid arrow) and the optical polarization ***E*** (dashed arrow).

are proportional to ${F_\mathrm{J}}^2$ and ${F_\mathrm{H}}^2$, respectively. Since the red shift is two times larger than the blue shift, as explained in Fig. 6 of ref. 2, and the signal is detected with the linearly polarized light as $\boldsymbol{E} \parallel Y$ for both cases,

$$\Delta A \propto (2{F_\mathrm{J}}^2 - {F_\mathrm{H}}^2)\frac{y}{r}. \tag{6}$$

If $\boldsymbol{F} \parallel Y$ and $\boldsymbol{E} \parallel Y$,

$$\Delta A_{Y\parallel F} \propto \left(2\frac{y^2}{r^2} - \frac{x^2}{r^2}\right)\frac{y}{r}F^2. \tag{7}$$

If $\boldsymbol{F} \perp Y$ and $\boldsymbol{E} \parallel Y$,

$$\Delta A_{Y\perp F} \propto \left(2\frac{x^2}{r^2} - \frac{y^2}{r^2}\right)\frac{y}{r}F^2. \tag{8}$$

Consequently, the signal ratio of $Y \parallel \boldsymbol{F}$ to $Y \perp \boldsymbol{F}$ is given by

$$\frac{\Delta A_{Y\parallel F}}{\Delta A_{Y\perp F}} = \frac{2y^2 - x^2}{2x^2 - y^2}. \tag{9}$$

If $\boldsymbol{E} \parallel X$ (conditions C and D in Fig. 5), its result is also equal to that in eq. (9). In the present study, the ratio of $\Delta\alpha$ for $Y \parallel \boldsymbol{F}$ to that for $Y \perp \boldsymbol{F}$ is 2–3, so we obtain

$$\frac{\sqrt{5}}{2}(\approx 1.1) < \frac{y}{x} < \frac{\sqrt{7}}{\sqrt{5}}(\approx 1.2). \tag{10}$$

From linear dichroism of the quasi-one-dimensionally oriented film in Fig. 1, we obtain $y/x = 1.3$–1.7, in rough agreement with the value shown in eq. (10). The anisotropy in the electro-optic signal, however, could be explained by the purely electronic origin even without referring to the rearrangement model.

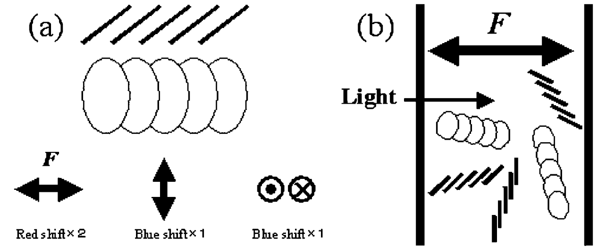

Fig. 6. (a) Six possible directional arrangements of TPPS J-aggregates in aqueous solution. Any arrangement of the aggregates is expressed by the combination of these six arrangement. The broadening effect is dominant when the electric field is applied because red and blue shifts take place evenly. (b) Isotropic orientation of TPPS J-aggregates between ITO glasses.

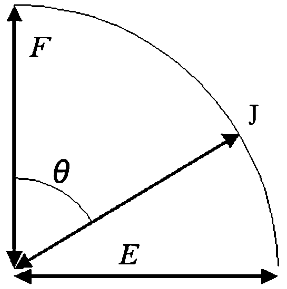

Fig. 7. Model for the aqueous solution, where the applied electric field ***F*** is perpendicular to the optical electric field ***E***. The bonding axis ***J*** of the TPPS J-aggregate is distributed in between. Actually, ***J*** was distributed three-dimensionally, but it can be reduced to the two-dimensional distribution, as shown here. This is because ***E*** pointed in all the directions within the plane perpendicular to ***F*** since the unpolarized probe light was used.

4.2 *J-aggregates in aqueous solution*

Secondly, therefore, we show that the results for aqueous solution in Fig. 3 provide further support to the model. In the aqueous solution, the signal broadening was observed as shown in Figs. 3(a) and 3(b). A broadening signal usually reflects the orientation distribution of the static dipole moment. By contrast, the origin of this signal can be attributed to the orientation distribution of the ***J***-axis with respect to the applied electric field ***F***, as explained below. In this case, the model predicts that red (***J*** parallel to ***F***) and blue (***J*** perpendicular to ***F***) shifts evenly occur, because there are equivalent contributions of these shifts. This is exactly observed as shown in Fig. 6(a). More precisely, it is necessary to consider the fact that the applied electric field ***F*** is perpendicular to the optical electric field ***E***, as shown in Fig. 6(b). Figure 7 shows a model of J-aggregates in aqueous solution under the applied AC electric field. Since $\boldsymbol{E} \perp \boldsymbol{F}$ in the experiment, the components of the applied electric field parallel and perpendicular to the ***J***-axis are $F_J = F_0 \cos\theta$ and $F_\mathrm{H} = F_0 \sin\theta$, respectively. The signal is proportional to $\boldsymbol{F}^2$, the amount of red shift is twice as large as that of blue shift, and the optical electric-field component parallel to ***J*** is $E \sin\theta$. Therefore, the applied electric field induces the red and blue shifts as given by the following:

$$\int_0^{\pi/2} d\theta[(F_0 \cos\theta)^2 \times 2 \times \sin\theta] = \frac{2}{3} \quad \text{for red shift,} \tag{11}$$

$$\int_0^{\pi/2} d\theta[(F_0 \sin\theta)^2 \times \sin\theta] = \frac{2}{3} \quad \text{for blue shift.} \tag{12}$$

Thus, both shifts are expected to have the same size on the basis of the model. Therefore, the model is in good agreement with the broadening spectrum, which exhibited both blue and red shifts in the J-band.

The broadening signal usually reflects the difference in the static dipole moment $|\Delta\mu|^2$ in the third term in eq. (1), where

$$|\Delta\mu| = \sqrt{\sum_{i=1}^{n} \frac{|\Delta\mu_i|^2}{n}} \tag{13}$$

with n being the number of J-aggregates if it is more precisely expressed.[1)] This signal could appear when each J-aggregate (macro aggregate) has a static dipole moment with a random orientation. Without perturbation from the surroundings, the TPPS J-aggregate should have no static dipole moment because of its centrosymmetry originating from the symmetry of the monomer molecule. Perturbation from the surroundings, however, breaks the centrosymmetry resulting in a finite static dipole moment in both excited and ground states. This effect can induce broadening of the signal, but it should be noted that ΔA of TPPS in aqueous solution is unusually large. Perturbation-induced $\Delta\mu$ usually causes much smaller electro-optic signals than intrinsic $\Delta\alpha$, as observed for film samples in refs. 1 and 2. The signal in the present condition is about 10000 times larger in $\Delta A/F^2$ than in the polymer film. This is explained by the rearrangement model in such a way that J-aggregates are more readily realigned in liquid water than in a solid polymer. For J-aggregates, signal strength is given by[2)]

$$J \propto -2\,\frac{kF^2}{(\Omega^2 + 3kF^2)}\,{\theta_0}^2 \cos 2\omega t, \tag{14}$$

where Ω is the resonance frequency of rotation of the monomer molecule depending on the surroundings, k is the constant, θ_0 is the equilibrium angle between the molecular transition dipole moment and the aggregation axis, and ω is the modulation frequency of the applied electric field. A much higher signal intensity in the aqueous solution is considered to be due to a smaller Ω than in the polymer film because J-aggregates in the solution are more loosely bound in liquid water than those in the polymer matrix. If $\Omega^2 \gg kF^2$ in eq. (14), $J \propto kF^2/\Omega^2$. Using this equation, the observed magnitude of $\Delta\alpha$ is explained if $\Omega = 2\pi\nu \doteqdot 5 \times 10^{10}$ Hz, or $\nu \doteqdot 10$ GHz in the polymer film in Fig. 2(a) of ref. 2 and $\Omega = 2\pi\nu \doteqdot 5 \times 10^{8}$ Hz, or $\nu \doteqdot 100$ MHz in solution.

The local field factor, represented by the parameter s in eq. (2), is another possible origin for the larger electro-optic signal in aqueous solution than in polymer film. Since the static dielectric constant for liquid water is 80 while that for PVA is 5.9, the Lorentz local field for the aqueous solution sample is 9 times as high as that for the polymer sample. In eq. (2), s^2 is 81 times larger for the solution than for the film, thus yielding about a 100-fold difference. There remains, however, still a 100-fold difference, requiring consideration on the rearrangement model as stated above. The local field effect could explain partly the larger difference in signal magnitude, but there are questions whether the Lorentz field is most appropriate and whether the local field consideration is valid for relatively large macro aggregates. To answer part of these questions, the signal magnitude for the monomer in aqueous solution should be experimentally evaluated. At present, however, it is not clear because the signal magnitude for the monomer is much smaller than that for aggregates and it appears in the close vicinity of the H-band (due to H-aggregates coexisting with J-aggregates) to be mixed with the signal due to H-aggregates.

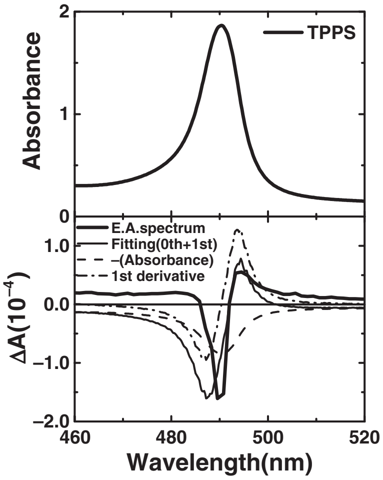

Fig. 8. Experimental results in Fig. 3(a) fit with the 0th and 1st derivatives of the absorption spectrum.

Note that the broadening signal is not precisely fit by the second derivative of the absorption spectrum. However, the fitting with the combination of the zeroth and first derivative components is worse than that with the second derivative component, as shown in Figs. 3 and 8. Therefore spectral broadening due to red and blue shifts induced by molecular rearrangement should be the main mechanism for the signal in aqueous solution.

4.3 Temperature dependence of electroabsorption signal

Finally, we present more solid evidence for the model with the temperature dependence of the electro-optic signal in Fig. 4. The more than 10-fold decrease in signal magnitude as the temperature was decreased from 293 to 77 K, observed for the two-dimensionally oriented polymer film, cannot be explained by the purely electronic origin. It requires the molecular orientational contribution as the origin to explain the result. Temperature dependence of electroabsorption spectra was studied, for example, using photosynthetic proteins and quinoline derivatives embedded in polymer films to obtain useful information.[16,17)] In ref. 16, quadrature phase components in electroabsorption signals are shown to be reduced with decreasing temperature. In ref. 17, it is shown that molecules are immobilized below 100 K because molecular orientational motion is strongly restricted in a polymer environment. Similarly, our observation is also explained by the restriction of the orientational motion of the constituent monomer molecules at this low temperature, supporting the validity of the molecular rearrangement model.

5. Conclusion

We found new evidence that the rearrangement model is appropriate for explaining the large increase in $\Delta\alpha$ owing to the formation of TPPS J-aggregates. First, $\Delta\alpha$ for the Y-axis parallel to $\boldsymbol{F}$ was two or three times larger than that for the Y-axis perpendicular to $\boldsymbol{F}$ in the electroabsorption spectra. Second, the unusually large broadening signal was measured in aqueous solution. Third, the more than 10-fold decrease in the signal magnitude with decreasing temperature from 77 to 293 K was observed for the two-dimensionally oriented polymer film. All the results are reasonably explained by the rearrangement model.

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