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Nonlinear Absorption Spectroscopy of Porphyrin J-aggregates in Aqueous Solution: Evidence for Control of Degree of Association by Light-Induced Force

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Spectroscopic evidence was obtained for molecular aggregation states to be controlled by the irradiation of light, which is off-resonant below the peak absorption energies of both monomers and well-grown J-aggregates. In low (undersaturated)-concentration aqueous solutions of porphyrin molecules (tetraphenyl porphyrin tetrasulfonic acid; TPPS) where the monomer absorbance dominates, irradiation with a 532 nm laser induces a decrease in the monomer absorbance and an increase in the aggregate absorbance. The increase in the absorbance of J-aggregates occurs in a broad spectral range associated with the increase in the number of not only variously sized oligomer aggregates but also aggregates structurally different from well-grown stable J-aggregates. In high-concentration solutions where the J-aggregate absorbance dominates, a blue shift of the absorption peak of J-aggregates is induced at the same 532 nm irradiation, corresponding to a decrease in the aggregation number or in the association energy. By contrast, for spin-coated polymer films of monomers and J-aggregates where molecules are immobile, these features are not observed. It is remarkable that the gradient force potential is smaller by more than seven orders of magnitude than the kinetic energy of the thermal motion of the molecule at room temperature, but the absorption change in solution indicating the increase in the number of aggregates is as large as $\Delta A \sim 10^{-3}$ in magnitude.

I. INTRODUCTION

The photophysical control of the crystallization of organic molecules by nonresonant laser light irradiation has been pursued for the last two decades [1, 2]. In particular, from the demand of high-quality protein crystals for the X-ray diffraction analysis of the atomic structure of proteins, the laser-induced rapid formation of a nucleus for crystallization or the accelerated crystal growth of amino acids has been demonstrated [3–6]. Usually in these experiments, a supersaturated solution of solute molecules is initially prepared such that the thermodynamical equilibrium state is the solid phase. The laser light works as a trigger for nucleation or an accelerator (promoter) of crystal growth [7, 8].

For molecular J-aggregates [9, 10], too, similar experiments have been performed [11, 12]. There has been an increasing request for fabricating a molecular nanostructure or periodic structure on demand. The bottom-up answer to this request from nature is the self-assembly of molecules in solution by molecular stacking, i.e., molecular aggregates. The aggregation states are determined by externally controllable parameters, such as the concentration of molecules, electrolyte concentration, pH [13], temperature[14], and viscosity[15] of solvents. However,

the size and structure of fundamental molecular blocks (microaggregates) are difficult to control actively because they are the equilibrium states determined by the environmental conditions in such a way that they are spontaneously formed as a sudden change in the phase by first-order phase transition.[14, 16] The reaction intermediates or transition states in the phase transition between monomers and well-grown aggregates are difficult to observe because they are of short lifetimes. For example, once the condition for the aggregate growth is satisfied, TPPS J-aggregates tend to make well-developed microaggregates as a result of the equilibrium among aggregates, two kinds of monomers, and protons [13], although the density of microaggregates varies depending on the conditions.

The crystal growth of amino acids and proteins or the growth of molecular J-aggregates by light-induced force (gradient force) has been mostly observed through photoluminescence image, light scattering image, or photoluminescence spectra [11, 12]. However, it has been difficult to obtain detailed information on the aggregation states or the aggregation number from the luminescence because it reflects only the lowest excited state.

The most controversial experimental issue in this field is stated as follows: It has been observed in various experiments that the light-induced force works effectively on molecules [17, 18] at room temperature, but the optical trap potential of a 1-nm-size molecule due to the laser-light gradient force is by many orders of magnitude

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smaller than the kinetic energy of the thermal motion of the molecule at room temperature. For larger particles, there have been many experimental achievements to demonstrate light trapping forces on the particles. For dielectric nanoparticles and metallic nanoparticles, the range in which stable trap was observed is more than 10 nm in diameter [19, 20]. It was both theoretically and experimentally demonstrated that radiation pressure can be exerted on CuCl nanocrystals down to 10 nm in size under resonant conditions with sharp exciton resonance at cryogenic temperature[21, 22]. So far, the stable trap and manipulation of 1-nm-size molecules at room temperature by the light-induced force are challenges, although a manipulation method of single molecules with resonant laser irradiation has been theoretically proposed [23].

In this study, a change in the molecular aggregation states induced by light-induced force is observed through the change in the absorption spectra for the first time to the best of our knowledge. Molecules are dissolved at undersaturated concentrations (less than the aggregation growth concentration), and the absorption spectra of unstable aggregates that are transiently generated only during the laser irradiation are measured, as opposed to the conventional experiments where crystal (aggregate) growth has been triggered by laser irradiation in solutions where solute molecules are dissolved at supersaturated concentrations.

II. EXPERIMENTAL METHODS

A. Absorption spectra of TPPS
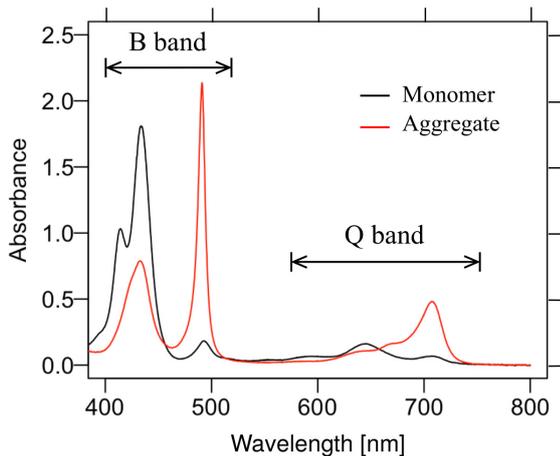
Fig. 1: Absorption spectra of TPPS aqueous solutions under monomer (black line) and aggregate (red line) dominated conditions.

TPPS has an absorption called Q band and B band in the near-infrared and visible regions, respectively. This is explained by Gouterman's four orbital model, where the energy level of the LUMO is split due to the asymmetry of the molecular structure [24, 25]. TPPS molecules form aggregates due to Coulomb attraction between the porphyrin nucleus and the sulfone group of the substituent. TPPS changes the association state depending on acidity or concentration in the solution such that one-dimensional aggregates are formed at a certain level of acidity or concentration. This is because the proton coordinates with the nitrogen of the porphyrin ring to strengthen Coulomb attraction between molecules [26]. In this state, a long-lived Frenkel exciton delocalized over constituent molecules is generated by the transition dipole Coulomb interaction of the molecule, so that the absorption peak is redshifted from that of the monomer by the formation of the aggregate. This is called a microaggregate or a coherent aggregate within which the exciton wave function preserves its coherence. Microaggregates are further assembled to make a higher-order structure called a macro-aggregate such as a sheet structure or a tube structure under aggregate formation conditions [27, 28]. Figure 1 shows the absorbance spectra of solution samples with different aggregation states in a 1-mm-thick quartz cell measured with a spectrophotometer (UV-3150, Shimadzu). In the B band, the absorption peak of the D-monomer, which is located at 433 nm, and that of the F-monomer, which is located at 414 nm, are sharpened and redshifted to be located at 490 nm due to the formation of the J-aggregates. In the Q band, too, the absorption band is redshifted.

B. Sample preparation

A sample of an aqueous solution with a concentration of 0.2 mmol/L in which TPPS (Tokyo Chemical Industry Co.) was dissolved in deionized water was prepared. 400 μL of this solution was measured out with a micropipette (Kartell) and diluted with 5 mL of deionized water to obtain a 16 μmol/L TPPS solution dominated by TPPS D monomers. In this solution, the B-band absorption of the D monomer in which the proton is coordinated to the porphyrin core appears at 433 nm, as shown in Fig. 1. By adding 0.4 mL of 1 mol/L hydrochloric acid to this TPPS aqueous solution, aggregates were formed to exhibit a sharp B-band absorption of the J-aggregates at 490 nm. On the other hand, when 0.2 mL of an aqueous solution of sodium hydroxide at a concentration of 0.1 mol/L is added, D monomers are converted into F monomers for the absorption peak to be blue-shifted to appear at 414 nm. In the pump-probe measurement for aqueous solutions, the solution was allowed to flow at a speed of 4 cm/s with a peristaltic pump (BIOInstrument ATTA SJ-1211) in a cell made with a spacer of 0.3 mm thickness sandwiched between glass slides in order to prevent photobleaching by the heat of a pump laser.

L1,2,4 f=100mm

L3 f=50mm
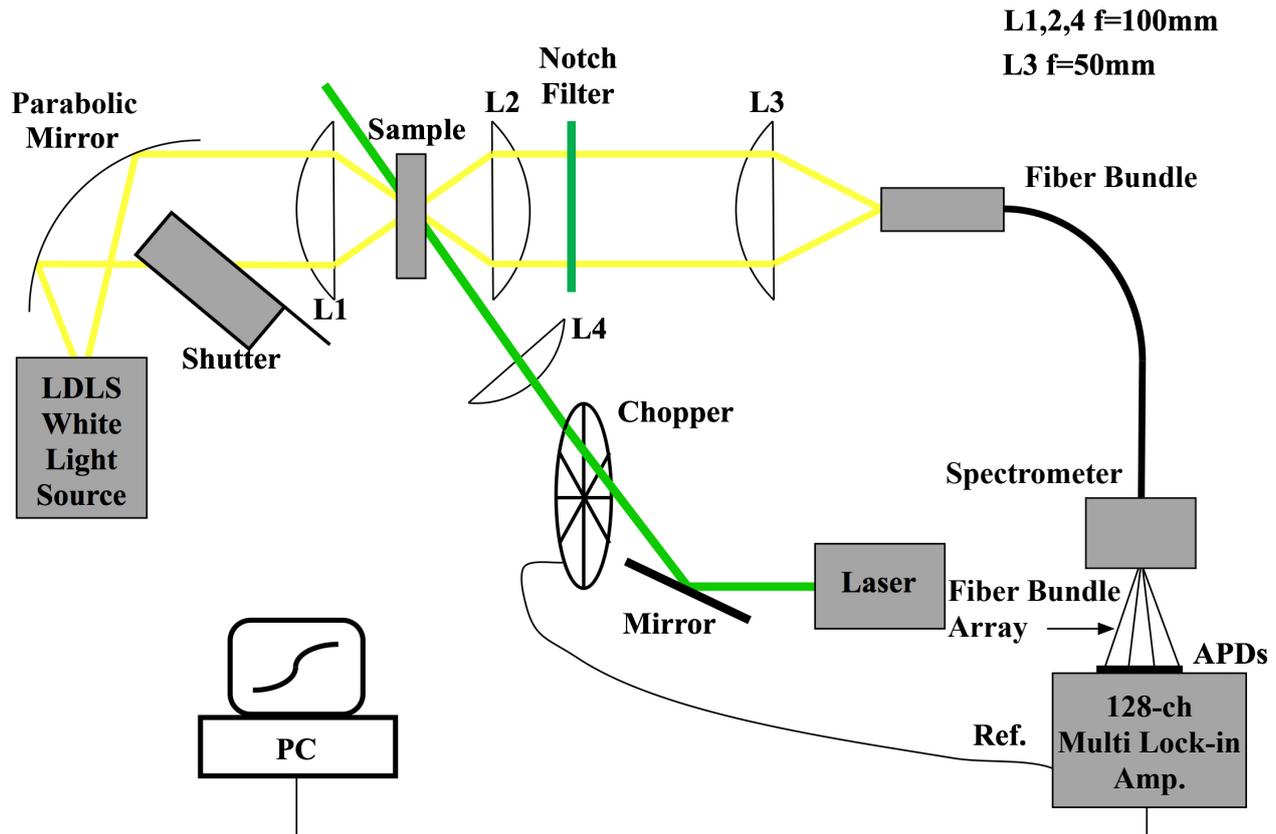
Fig. 2: Experiment setup for detecting the pump-induced change in the probe light spectra transmitted through a flowed sample with a 128-channel lock-in amplifier combined with a spectrometer. The scattered pump light was blocked with a super-notch filter. The shutter is used for subtracting the contribution of luminescence by tandem lock-in detection to modulate the probe light. L: achromatic lens, Ref.: reference signal, APDs: avalanche photodiodes.

For a comparative experiment, TPPS and polyvinyl alcohol (PVA) were dissolved in deionized water and spin-coated on a glass slide to prepare a polymer film sample. Since TPPS molecules are immobilized in the polymer, the effect of light-induced force is restricted.

The absorbance spectra were measured with a spectrophotometer (UV- 3150, Shimadzu). All the experiments were performed at room temperature (293 K).

C.   Measurement Method

The pump-probe experimental setup is shown in Fig. 2. The stationary white light from a laser-driven light source (EQ-99, ENERGETIQ) as the probe was collimated with a parabolic mirror and focused on a sample with an achromatic lens, and the transmitted light was observed through a spectrometer (SpectraPro 300i, Acton) with a 128-channel lock-in detector. The laser light as the pump, which was chopper-modulated at 224 Hz, was irradiated to the focal point of the probe light on the sample, and the pump-induced change in the transmitted probe light spectrum was observed mainly in the wavelength range of the B band. Since the change in the transmitted light intensity synchronized with the pump modulation frequency includes photoluminescence from the sample, the probe light is also modulated using a shutter to detect the change correlated with both pump and probe modulations by tandem lock-in detection. This procedure avoids the contribution from the photoluminescence in the detected signal. A detailed description of the tandem multichannel lock-in detection method is given for example in Refs.[29, 30]. The excitation laser light sources were a diode-laser-pumped solid-state laser

(Changchun New Industries Optoelectronics Tech) at 532 nm. The excitation laser power was 120 mW to be focused into 240 μm beam diameter with an achromatic lens (f = 100 mm) to obtain the excitation intensity of 265 W/cm^2 for the experiment described in Fig. 3. For the experiments for Figs. 4 and 5, the excitation conditions are given in the figure captions.

III. RESULTS

The absorption change upon excitation with the 532 nm laser of aqueous solutions of F monomers at different concentrations is shown in Figs. 3(a) and 3(b). No absorption peak of the aggregates was observed in the samples used in this experiment. In the B-band region for both Figs. 3(a) and 3(b), a sharp absorption decrease at the F-monomer peak and a broad absorption increase in the redshifted wavelength region including the wavelength (490 nm) of the well-developed J-aggregate peak were observed. This result suggests that various types of aggregates with different association numbers were transiently formed when the excitation laser was irradiated, which were converted from monomers as demonstrated by the decrease in the monomer absorption.

Next, pump-probe experiments were performed on samples dominated by D monomers and by J-aggregates for both aqueous solution and polymer film samples. Here, solutions were flowed in the 0.3-mm-thick flow cell.

Firstly, the results for the D-monomer dominated samples were compared between the solution and the polymer samples in Figs. 4(a) and 4(b). In the absorbance spectra of both solution and polymer samples, the major absorbance structure is due to D monomers but a small amount of J-aggregates are also observed. For the solution, in both B and Q bands, a broad-band increase in the absorption in the wavelength region redshifted from the monomer band was observed as well as a decrease in the monomer-band absorption. For the polymer film, by sharp contrast, a similar absorption decrease in the monomer band was observed but no increase in the redshifted region was observed.

For the polymer sample, since the positions of molecules are fixed in the polymer matrix, although a small position or orientation rearrangement of molecules is allowed, the observed absorbance change should be mainly caused by the real excitation of the molecular electronic state. That is, the result for the polymer sample should be caused by the absorption saturation due to the ground-state depletion, since there is a finite absorbance at 532 nm, although it is small, to allow for the real excitation of the electronic state. For the solution sample, the broad absorption increase, which was not observed in the polymer samples, suggests that various aggregation states with different aggregation numbers are transiently formed by the laser irradiation, converted from monomers as demonstrated by the decrease in the monomer absorption. Real excitation should also
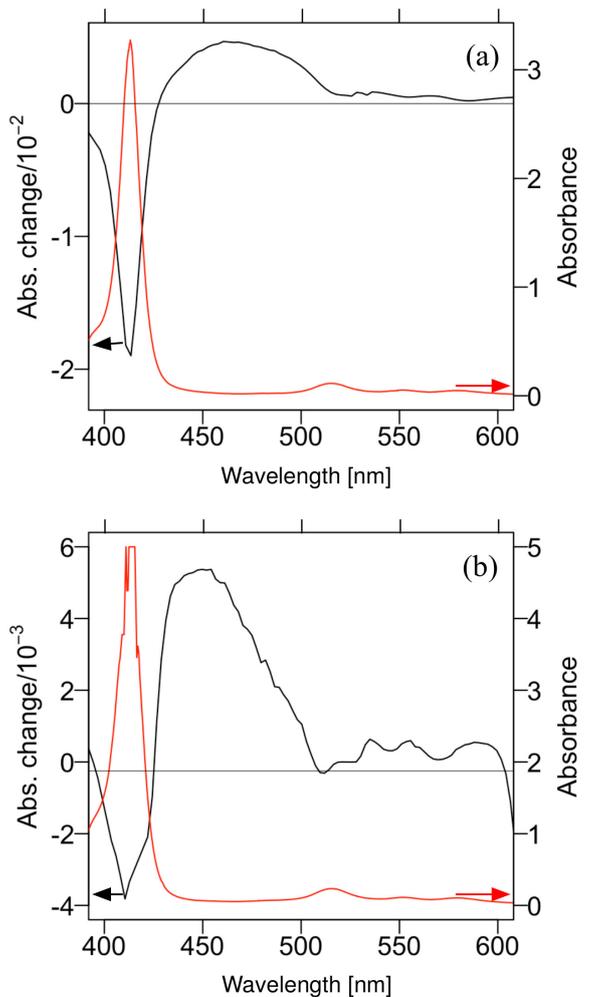
Fig. 3: Absorbance change on the excited spot of TPPS F-monomer aqueous solution in a 1 mm cell (not flowed) by 532 nm laser excitation. (a) and (b) are the results for samples of different F-monomer concentrations. For (b), the F-monomer peak absorbance is extremely high above the sensitivity limit of the spectrophotometer (about 4), so that the absorbance change at the F-monomer peak is not quantitatively reliable. In both experiments, the pump laser was focused on the sample with an achromatic lens (f=100 mm) such that the excitation intensity of the pump laser on the sample is 265 W/cm^2.

occur in the solution sample, so that the decrease in the monomer band in the solution is composed of both absorption saturation and conversion from monomers to aggregates.

Secondly, the results for the J-aggregate-dominated samples were compared between the solution and the polymer samples in Figs. 5(a) and 5(b). In the absorbance spectra for both solution and polymer, the major absorbance structure is due to well-developed J-aggregates at 490 nm, which are accompanied by H-aggregates peaked at 424 nm. For the aqueous solution, a blue shift in the absorption peak of the J-aggregates
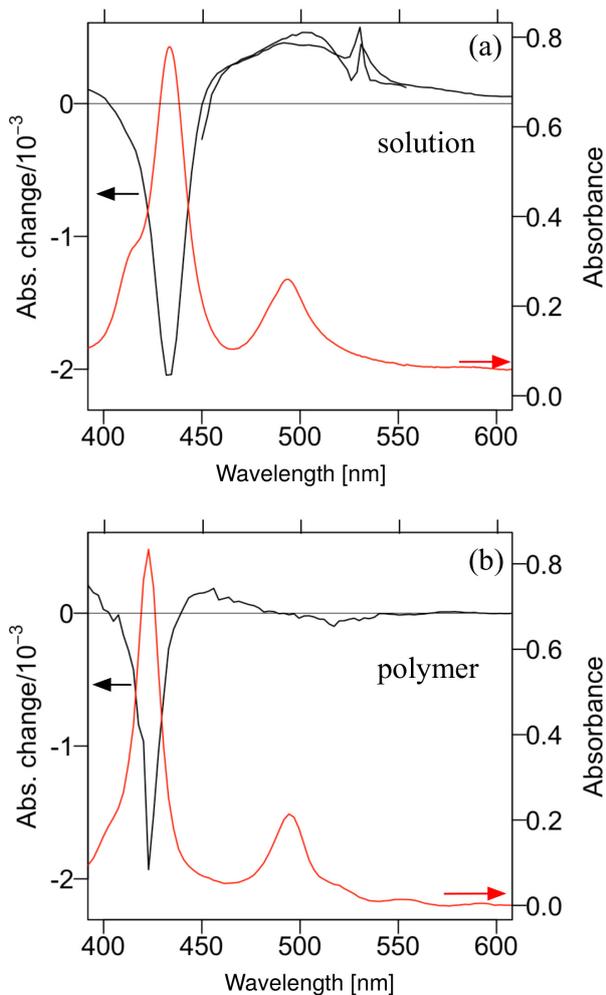
Fig. 4: Absorbance change upon 532 nm excitation in an aqueous solution in a flow cell (a) and in a PVA film (b) both dominated by TPPS D monomers. The excitation power was 46.6 mW, the focal radius was 120 μm, and the excitation intensity was 103 W/cm^2. In the polymer, the D-monomer band is shifted to appear at almost the same wavelength as the H-aggregate band. Since the wavelength span of multichannel detection is limited to about 325 nm with a grating of 150 grooves/mm in the 30-cm-focal-length monochromator, the ΔT signal was measured separately in the B- and Q-band regions (224 to 554 nm and 450 to 772 nm, respectively) and combined in (a), while the signal was measured nearly in the whole visible wavelength range (377 to 701 nm) in (b).

Fig. 5: Absorbance change upon 532 nm excitation in an aqueous solution in a flow cell (a) and in a PVA film (b) both dominated by TPPS J-aggregates. The excitation power was 103 mW, the focal radius was 190 μm, and the excitation intensity was 91 W/cm^2.

E_0 constituting the aggregate in a medium of the permittivity ϵ to be expressed by

$$E_k = E_0 + 2J \cos(\frac{k\pi}{N+1}) \tag{1}$$

$$J = \frac{M^2}{4\pi\epsilon r^3}(1 - 3\cos^2\theta_0) \tag{2}$$

with the aggregation number N, the aggregation distance r, and the aggregation angle θ_0 [31]. For J-aggregates, $J < 0$, and the lowest k state ($k = 1$) is optically allowed to be observed as absorption. In Fig. 4(a), the absorption spectral peak of D monomers is at 433 nm, 2.86 eV in photon energy. If this value is taken as E_0, the value

was observed [Fig. 5(a)], while a redshift was observed for the polymer [Fig. 5(b)].

IV. DISCUSSION

The energy of the coherent aggregate E_k is obtained by Coulomb interaction between the transition dipole moments M of TPPS molecules with the excitation energy

for J is estimated to be $J = -0.16$ eV using Eq. (1), from the well-developed J-aggregates located at 490 nm, 2.54 eV in energy, which can be regarded as $N \to \infty$ with a large association number. From Eq. (1), the energy of the J-dimer, J-trimer, and J-tetramer is estimated as $N = 2$, 3, and 4 for $k = 1$, respectively, to be 2.70 eV (459 nm), 2.63 eV (471 nm), and 2.60 eV (477 nm). In fact, these N-mers were previously observed in aqueous solution with the application of an AC electric field [13]. In the present observation, the spectra of absorption increase in Figs. 3(a), 3(b), and 4(a) cover a wide range of wavelength regions where these N-mers appear. The spectrally structureless (without sharp peaks) and smooth absorbance increase in Figs. 3(a) and 3(b) suggests that N-mers with the continuous number of N are generated. Normally, the energy of the absorption peak of J-aggregates converges to the value for $E_0 + 2J$ as the association number N increases, so that the absorption peak of aggregates never appears at the wavelength longer than 490 nm. In addition, as long as the value of J is the same, the absorption of the J-aggregate will not appear on the wavelength side shorter than 459 nm where the dimer appears. However, it deserves the highest attention that in Figs. 3(a), 3(b), and 4(a), the absorption increase extends over the wavelength side shorter than 459 nm and the wavelength side longer than 490 nm, i.e., 500 nm or more. In other words, it strongly suggests that unstable aggregation states are transiently generated, which have J values with the aggregation angle θ_0 or the aggregation distance r different from those for the stable, well-developed J-aggregates. With respect to the absorption increase on the wavelength side shorter than 459 nm, there is also a possibility that the dipole transition is more partially allowed for the state of $k > 1$ to be optically observed owing to the broken symmetry of transient aggregation states [32].

In the experiment described in Fig. 3, the laser was focused into the spot size of 120 μm radius with an achromatic lens such that the excitation intensity was 265 W/cm^2 and the optical field strength was $F = 4.46 \times 10^4$ V/m. The polarizability volume (1450 Å^3) and the polarizability α (1.61×10^{-37} Cm^2/V) of the molecule are estimated from the van der Waals radius of the constituent atoms. Thus, the trap potential $\alpha F^2/2$ of the light-induced gradient force exerted on the molecule is estimated to be 1.00×10^{-9} eV. This energy is by seven orders of magnitude smaller than the thermal energy (kinetic energy) of the molecule, $k_B T = 2.52 \times 10^{-2}$ eV. The absorbance change expected from this estimation should be on the order of 10^{-7}, but we observed the absorbance increase as large as 10^{-3}. It is therefore difficult to explain this absorption change only by the light-induced force.

Let us make a quantitative estimation about the real excitation of the electronic state. The absorption decrease of the F monomer may be related to absorption saturation due to real excitation. The sample absorbance at the excitation wavelength of 532 nm is 0.045 in Fig. 3(a). The absorbed photon flux density was 1.2 mol/(m^2 s). The concentration per area is estimated to be 1.6×10^{-5} mol/m^2 from the cell thickness of 1 mm and the concentration of 16 μmol/L. Assuming that the transition to the S$_1$ state of the TPPS monomer (corresponding to the Q-band absorption) occurs due to all the absorbed photons, the excitation rate is $\Gamma_p = 7.2 \times 10^4$ s^{-1}. This depletes partially the population of the ground-state molecule. The lifetime of the singlet excited state (S$_1$) of TPPS D monomers in aqueous solution was measured to be 3.5 ns as a fluorescence decay time [33, 34]. The fluorescence lifetime is the excited-state lifetime but not equivalent to the ground-state recovery time, which gives a major contribution to the stationary absorption saturation presently observed. Since TPPS does not contain a heavy central metal ion, the singlet to triplet conversion rate (intersystem crossing) via spin-orbit interaction is negligibly small, so that the long-lifetime triplet state as a bottleneck to the ground-state recovery is safely neglected. Therefore, we adopt 3.5 ns as the ground-state recovery time. Then, the recovery rate of the ground state is $\Gamma_r = 2.9 \times 10^8$ s^{-1}. Using the pumping rate of Γ_p and the recovery rate Γ_r to solve the rate equation of the two levels on the steady-state condition, the ratio of the excited molecules to the ground-state molecules is estimated to be 2.5×10^{-4}. This result corresponds to the absorbance decrease of 8.3×10^{-4} with respect to the absorbance of 3.3 at the absorption peak. The observed decrease in the absorbance of D monomers in Fig. 3(a) is more than one order of magnitude larger than the estimated contribution of real excitation. This supports the fact that the absorption decrease for D monomers observed in solution is mainly caused by the conversion of monomers to aggregates by light-induced force.

The redshift of the absorption peak (associated with the transition from the ground state to the lowest excited state) generally occurs as the quadratic Stark shift when an electric field is applied to atoms and molecules [31]. In fact, there have been many reports on the electroabsorption spectroscopy of molecular systems including J-aggregates [35–38]. For both TPPS monomers and aggregates, too, the electric-field-induced redshift is usually observed. For example, an enhanced redshift in TPPS J-aggregates by more than two orders of magnitude compared with TPPS monomers has been reported [39–41]. On the other hand, there are only a few reports on the electric-field-induced blue shift [31]. Concerning photoexcitation or pump-probe experiment, it is not usual to observe a spectral shift in the resonance peak, except for a blue shift in the exciton resonance due to one-exciton to two-exciton transition for J-aggregates [42] as well as due to the optical Stark effect [43] in ultrafast, femtosecond spectroscopy. Under the present stationary weak excitation condition, these mechanisms for the blue shift are ruled out. For example, the blue-shift-like shape in the Frenkel exciton resonance appears as an absorption decrease due to stimulated emission from the one-exciton state combined with absorption increase due to the tran-

sition from the one-exciton to the two-exciton state. This is observed only during the exciton lifetime, but the lifetime of the S_2 exciton in the B band is reported to be 300 fs [44] such that the absorbance change due to real excitation in the present excitation condition should be as small as 10^{-8}. This is in contradiction with the observed absorbance change of 10^{-3} in Fig. 5. Moreover, the excitation energy of 2.33 eV (532 nm) is far below the S_2 exciton energy of 2.53 eV (490 nm), so that only the S_1 excitons are generated for the transition from the one S_2 exciton to the two S_2 exciton state to be impossible.

Hence, there should be another mechanism for the blue shift. In order to explain the field-induced enhanced redshift in TPPS J-aggregates, the molecular rearrangement model was proposed[40, 41]. This model gives a more plausible mechanism as follows. From this model, the blue shift of the absorption peak is caused by the increase in the association angle θ_0 or in the association distance r, or the decrease in the association number N or in the transition dipole moment M for the molecule. Since it is unlikely for the molecular transition dipole moment to change, the blue shift suggests that the well-developed aggregates tend to be dissociated due to light-induced force. The magnitude of the energy differential of the absorption peak in Fig. 5(a) is 211 eV^{-1}, and the amount of the observed blue shift is 3.22 $\times 10^{-3}$, yielding the blue-shifted energy of 1.52 $\times 10^{-5}$ eV. If the association angle and association distance are assumed to be 23° and 9.3 Å[28], the observed blue shift is realized if the association angle or the association distance is changed only by $+3.3 \times 10^{-5}$ rad or $+1.4 \times 10^{-5}$ nm, respectively, for $J = -0.16$ eV. On the other hand, the redshift observed for polymer samples could be explained by the increase in the sample temperature.

Finally, let us estimate the influence of local temperature rise due to irradiation of the laser light on molecular aggregation. It is assumed that all the light power $W = 120 \times (1 - 10^{-A})$ [mW] absorbed at the absorbance $A = 0.045$ becomes the spherical heat source of a uniform power density $w = W/(4/3\pi a^3)$ [mW/μm^3] with the focused radius $a = 120$ μm to diffuse in water with a thermal conductivity $\lambda = 0.592$ W / (m $\times$ K). For the three-dimensional steady-state temperature distribution $u(r)$, the Poisson equation in the spherical coordinate with r as the distance from the center of the source:

$$\frac{1}{r}\frac{\partial^2}{\partial r^2}(ru(r)) = \begin{cases} -\frac{w}{\lambda} & (r < a) \\ 0 & (r > a) \end{cases} \quad (3)$$

should be satisfied. For simplicity, we assumed an isotropic temperature distribution and the solution (water) extends over the infinite volume.

By solving Eq. (3), it is estimated that the temperature rise is 20 K at the origin of the distance $r = 0$ (center of the laser focal spot) and the temperature rise is 0.016 K at $r = 1$ mm. Correspondingly, the largest local viscosity change of about -0.41 mPa $\cdot$ s is expected to occur owing to this temperature rise. Since it is known that the

size of porphyrin aggregates increases in a solvent with a smaller viscosity [15], such a photothermal effect [45] as the change in the viscosity of the solvent may contribute to the observed change in the aggregation state. If the pump laser modulation is considered, the average temperature rise is about half of the values deduced above. Since the detected absorbance change is not due to the average temperature rise but due to the temperature-modulated component at 224 Hz, the contributed part of the viscosity change should be even smaller.

V. CONCLUSIONS

On the irradiation of a non-resonant cw laser (lower energy than B band, higher energy than Q band) for TPPS monomer molecules dissolved in aqueous solution below the saturation concentration (aggregate formation concentration), mainly in the B-band region, a decrease in the monomer absorption peak and a broad increase in the aggregate absorption were observed.

This characteristic absorption change was observed in both F and D monomers. The broad absorption increase in the aggregate extends from the wavelength region shorter than the J-dimer at 459 nm to the region longer than the peak wavelength of the J-aggregate at 490 nm. This fact suggests that unstable aggregation states such as aggregates of a small aggregation number (= J-oligomers) and aggregates of a different value for J (= different aggregation structure) are generated only during the laser light irradiation, which should appear transiently before well-developed, stable aggregates are formed.

Since the increase in the absorbance of the aggregate did not appear in the polymer film samples, it is confirmed that the formation of aggregates by light-induced force occurs only in the aqueous solution where monomer molecules are movable. In addition, the decrease in the absorbance of monomers in the aqueous solution was by more than one order of magnitude larger than estimated from the absorption saturation by real excitation, supporting the fact that the decrease in the monomer absorption is mainly caused by the conversion of monomers to aggregates.

On the other hand, in the solution dominated by aggregates, the blue shift of the aggregate absorption peak was observed under the similar excitation condition. This result suggests that the molecular rearrangement occurs in such a way that well-developed aggregates tend to be dissociated by light-induced force.

The trap potential energy of the excitation laser in this experiment is 7 orders of magnitude smaller than the thermal kinetic energy of molecules at room temperature. Despite this fact, we observed the absorption change by 10,000 times larger than expected from the light-induced gradient force. Therefore, the experimental results cannot be explained only by the direct effect of the light-induced force. To elucidate the mechanism,

it is necessary to consider the effect of light-induced temperature rise (photothermal effect), such as the influence of the decrease in the viscosity of the solvent due to local temperature rise on molecular aggregation.

Although the mechanism is yet to be resolved, the present results will open a new possibility to actively control molecular assembled states by light-induced force: The laser light does not work as a mere trigger to initiate crystallization nor a promoter to accelerate crystal growth toward the thermodynamical equilibrium, but works as an active controller of the aggregation states that do not exist in the equilibrium.

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